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Poster Abstract Book

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Pluronic F127 as a sol-gel matrix for drug delivery carriers

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The block copolymers have been highlighted as reliable agents for targeted drug delivery and gene therapy for several years. [1-4] In particular, pluronic block copolymers, with a triblock poly(ethylene oxide)_x-poly(propylene oxide)_y-poly(ethylene oxide)_x structure have emerged for controlled drug delivery. The pluronic F127 (x=100, y=70) is one of the most interesting due to the tunable and thermo-reversible sol-gel transition that can provide a stable gel phase at the body temperature. [5, 6] The F127 sol-to-gel transition is due to a disorder-to-order transition occurring at concentrations equal to or higher than 15 wt.% as a function of temperature. In particular, from an isotropic micellar phase to a body-centered cubic packing of the spherical micelles (up to 25 wt.%) take place with increasing temperature. The transition temperature can be appreciated by oscillatory rheological measurements (Figure 1 shows the crossover between the storage and loss moduli) while structural features are revealed by small X-ray scattering and dynamic light scattering.

Here, the focus is on the F127 as a matrix to entrap carrier agents such as nonionic vesicles (niosomes) or 2-hydroxypropyl- β -cyclodextrin (HP- β -CD). Diclofenac and celecoxib are loaded in niosomes and HP- β -CD carriers respectively. Diclofenac and celecoxib are anti-inflammatory active agents with a hydrophobic nature and a low solubility in water. The Hp- β -CD/CB was loaded in a matrix of PF127 and chitosan (to increase the mucoadhesive characteristic of the intravesical formulation). [7] Stationary and dynamic rheological experiments allow evaluating the effect of the entrapped active agents on the reversible micellar-to-cubic transition. At the same time, dynamic light scattering and microscopy allow determining the fate of the active agent carrier after thermogelation. The effect of carriers on the micellar phase and on the cubic phase can be appreciate by combining rheology with scattering techniques. Finally, the efficiency in drug release is estimated as a function of time at several polymer concentration.

Keywords: sol-gel transition, rheology, drug carriers, pluronic, hydroxypropyl- β -cyclodextrin

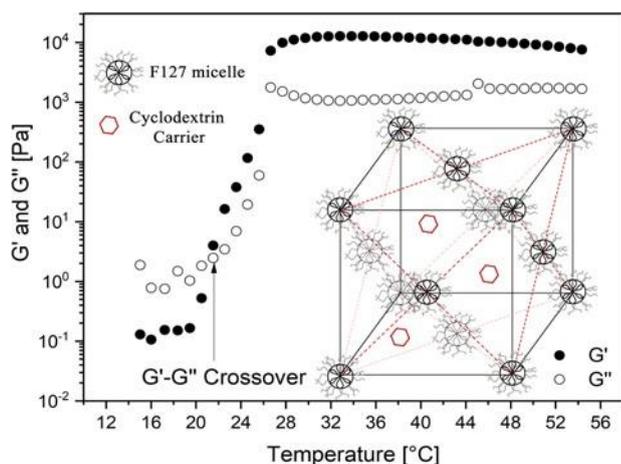


Figure 1. Temperature sweep performed at 0.1% strain and at a frequency of 10 rad/s. The storage modulus (G') and the loss one have a crossover at 21.5 °C at F127 concentration of 16 wt.%. The concentration of the carrier was around 2 wt.%.

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Nematic Lyotropic Liquid Crystal Gels

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Thermotropic liquid crystal gels and elastomers (LCEs) are currently the workhorses in the rapidly emerging fields of soft robotics and biomimetic actuation [1]. However, their lyotropic counterparts, lyotropic liquid crystal gels (LLC gels), may offer advantages over LCEs [2,3]. They are cheap in fabrication, compatible to aqueous media and might respond to a different range of chemical and biological stimuli. LLC gels might be particularly interesting for biomedical applications such as transdermal drug delivery. The gel-like consistency allows for easy application, while the LLC can solubilize water-insoluble drugs [4,5]. Other potential LLC gel applications are new water-based stimuli-responsive materials for sensors and actuators.

For LLC gels to work as stimuli responsive actuators, the gelled sample must be macroscopically aligned in its LLC state. The nematic phase should be the easiest to align due to its comparatively low viscosity, and was thus selected as the LLC basis for LLC gels.

The ternary system $C_{14}TAB/n$ -decanol/ H_2O , which contains two nematic phases (columnar N_C and discotic N_D) [6], was chosen as LLC. The ternary phase diagram of this system was recorded at 20°C with a focus on the nematic N_C phase. Furthermore, a pseudo-binary phase diagram as a function of the temperature and the total surfactant concentration was measured to determine the temperature dependency of the nematic (N_C) phase.

The nematic phase was gelled with the organogelator BHPB-6 [7]. Using polarized optical microscopy, SAXS, and FFEM the effect of the gelator on the nematic phase was studied. The viscoelastic properties of the LLC gel were studied via rheology. To macroscopically align the gelled samples both mechanical techniques such as shear and flow alignment as well as magnetic field alignment will be considered. In the final steps the swelling and thermal response of the LLC gel will be studied.

Keywords: Gels, Liquid Crystals, Self-Assembly

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Design of asymmetric microgels with liquid crystalline domains via precipitation polymerization

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Microgels exhibit unique properties and therefore gain rising attention due to their versatile fields of applications [1]. Microgels demonstrate huge potential in drug delivery and catalysis processes, or as surface coatings. However, the fabrication of asymmetric microgels that are anisotropic in shape and surface chemistry using conventional polymerization techniques is challenging [2].

In our work, we present an alternative approach towards the design of asymmetric microgels by making use of liquid crystalline monomers. Liquid crystals have the ability to self-organize depending on external stimuli such as temperature. They have been used to design polymer films and particles that exhibit shape-shifting behavior [3].

Our approach is to implement liquid crystalline domains into microgels to introduce permanent or reversible shapes. Therefore, we used a semi-batch precipitation polymerization approach to synthesize N-vinylcaprolactam (VCL) based microgels with 4-Methoxybenzoic acid 4-(6-acryloyloxy-hexyloxy)phenyl ester as liquid crystalline *co*-monomer (LCM), crosslinked with N,N-Methylenebis(acrylamide) (BIS). Depending on the reaction temperature, the time at which the LCM is added or the VCL:LCM ratio, the morphology of the microgels was tuned to versatile shapes such as multilobe-, dumbbell- or raspberry-like shapes (Figure 1). The microgel morphologies were characterized by transmission and scanning electron microscopy while the incorporation of the LCM into the microgel structure was determined via ¹H-NMR and Raman spectroscopy. We believe that this method can increase the accessibility of asymmetric microgels and has the potential of introducing shape-shifting behavior within microgels.

Keywords: asymmetric particles, liquid crystals, microgels

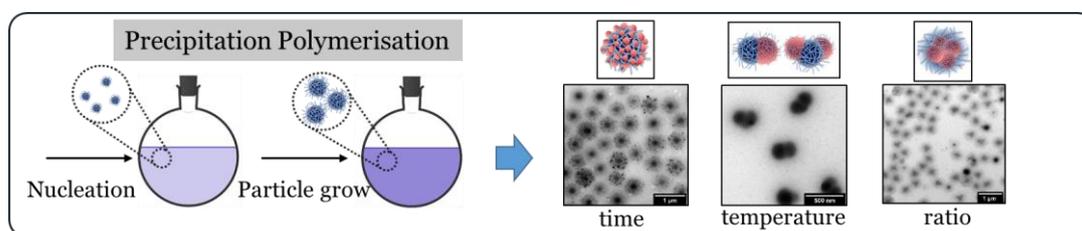


Figure 1. Precipitation polymerization of *p*(VCL-*co*-LC) microgels with different morphologies.

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Thermoreversible engineered emulsions enabled by branched copolymer surfactants

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“Engineered emulsions” transition between liquid and gel states in response to a stimulus. Whilst there are several reports of pH-responsive engineered emulsions (Weaver, Rannard and Cooper, 2009), thermoresponsive materials of this type are uncommon. These materials could transition from liquid to gel at body temperature, enabling *in situ* gelation and thus enhanced retention and therapeutic effect of drugs (Cook *et al.*, 2021).

This study investigates the use of polymeric surfactants to enable thermoresponsive emulsions. Thermoresponsive branched copolymer surfactants (BCSs) with varying cross-linker ratio and molecular weight were synthesised by free radical polymerization aiming to generate thermoresponsive engineered emulsions. These thermoresponsive BCSs were then characterised by Nuclear Magnetic Resonance (NMR), Gel Permeation Chromatography (GPC) and Small Angle Neutron Scattering (SANS).

Oil-in-water emulsions stabilised by the thermoresponsive BCSs demonstrated the formation of thermoresponsive engineered emulsions. The dispersed-to-aggregated phase transition in surface-functional emulsions was tracked by oscillatory shear rheology. It was found that cross-linker concentration, molecular weight, and polymer concentration are able to tune the temperature at which the thermoresponsive emulsions transition to a gel. Reversible thermoresponse was observed resulting in a dispersed conventional emulsion fluid upon cooling. Moreover, increasing the molecular weight and polymer concentration enhanced the thermogelation activity. SANS investigation of the BCS showed that the polymers formed elliptical nanostructures in solution which appear to aggregate and increase in dimensions upon heating. It is believed that the growth of these nanostructures leads to droplet-droplet bridging and the formation of the gel phase.

Overall, this study has demonstrated the ability of BCSs to generate thermoresponsive engineered emulsions and identified several design principles for these highly functional materials. These systems have the potential to be optimised further to gel at body temperature and generate thermoresponsive engineered emulsions for drug delivery and wider biomedical applications.

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Benzoxaborole-derived drug delivery by amphiphilic block copolymers with vicinal diols

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Amphiphilic block copolymers self-assemble into clinically efficacious nanostructures, whose size, stability, and surface chemistry can be easily adjusted to each purpose. This versatility has prompted the vast scope of their biomedical applications, especially in the field of drug delivery. In particular, polyester-based nanoparticles have been used in gene, nucleic acid, therapeutic protein and drug delivery for their *in vivo* biocompatibility and biodegradability. However, most studies have only focused on amphiphilic copolymers with short hydrophobic segments, with no modification and with a single preparation pathway. Here, we report the synthesis of poly(ethylene oxide)-*b*-poly(caprolactone) copolymers containing propargyl groups using two parallel approaches, a copolymerization with modified monomer and a post-polymerization modification. A subsequent thiol-yne click reaction with 1-thioglycerol yielded copolymers with vicinal diols capable of reversibly binding to a fluorescent benzoxaborole-derived model drug, thus facilitating drug release profiling and nanoparticle internalization analysis by fluorescence spectroscopy and microscopy and by flow cytometry. Both synthetic pathways were evaluated based on macromolecular characteristics afforded by nuclear magnetic resonance spectroscopy and by size exclusion chromatography. Furthermore, we conducted a comprehensive study of the self-assembly behavior by static and dynamic light scattering and by cryogenic transmission electron microscopy and assessed nanoparticles biocompatibility by performing MTT assays. Ultimately, these findings will enable the reproducible preparation of amphiphilic block copolymers capable of pH-induced binding to benzoxaborole- and boronic acid-based anticancer agents, thereby fostering further studies on their biomedical applications as nanocarriers in targeted drug delivery [1–2].

Keywords: Block copolymers, Nanoparticles, Drug delivery

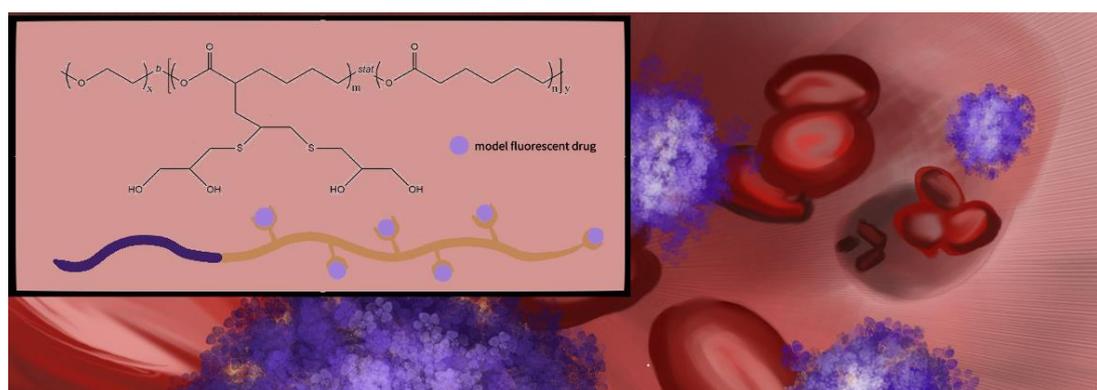


Figure 1. Poly(ethylene oxide)-*b*-poly(caprolactone) copolymers modified by propargylation and thiol-yne click

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Acid/base ionization of oligolysines in presence of oppositely charged polyelectrolytes

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Weak ampholytes, polybases or polyacids are interesting responsive pH systems, which may adsorb on oppositely charged polyelectrolytes. Theoretical understanding of acid-base ionization in such systems is still lacking. The aim of this study was to simulate the specific case of oligolysine ionization in presence of polymethacrylic acid (PMAA). To achieve this, we used a coarse-grained model and the constant-pH ensemble method implemented in the ESPResSo simulation software [1]. The simulated system comprised a solution of a weak oligobase with $pK_a = 10.53$, representing the oligolysine, and a strong polyacid, representing the PMAA which is fully ionized at $pH > 7$. Using this model we investigated how the interaction between the lysines and PMAA is affected by the pH and by the chain length of oligolysine. Simulation results suggest that oligolysine interacts with negatively charged PMAA not only at $pH < pK_a$, when the oligolysine is positively charged, but also at $pH > pK_a$, when the oligolysine should be uncharged.

By comparing the ionization of oligolysine in solution with and without PMAA, we observed that the ionization of lysine in the presence of PMAA is shifted to higher pH values, beyond $pH > pK_a$. This effect is stronger for longer oligolysine chains. These observations explain the experimental results on the interaction of PMAA with oligolysine, obtained in our group [2]. Furthermore, it can be generalized to conclude that the ionization of weak oligobases is strongly enhanced by the presence of an oppositely charged polyelectrolyte.

Keywords: Acid/base ionization, coarse-grained simulation, weak ampholytes, polyelectrolytes

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Influence of an anchoring layer on the properties of chitosan-carboxymethylcellulose multilayers

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The use of an anchoring layer for polyelectrolyte multilayer formation [1] is a known practice for tuning multilayer properties, mainly to improve surface coverage, roughness, and thickness. For this, poly(ethyleneimine), PEI, has been used as an anchoring layer for different combinations of polyelectrolytes. [2] One of such combinations is chitosan, CS, and carboxymethylcellulose, CMC. [3] These polyelectrolytes have gained much attention in recent years due to their antibacterial and antifungal properties while being biocompatible and non-toxic to humans. Due to these properties, CS/CMC multilayers have the potential to be used in agriculture, food processing and biotechnology as protective coatings. PEI proved to be a great anchoring layer to improve CS/CMC multilayer properties, but, unfortunately, the toxicity of PEI is still a matter of debate. [4,5] This fact makes it a questionable anchoring layer for a non-toxic combination of polyelectrolytes.

In this study, we prepared CS/CMC multilayers using dipping technique on Si-SiO₂ wafers with different anchoring layers and addition of NaCl at constant pH. Ellipsometry was used for monitoring film growth, while surface properties were determined using atomic force microscopy.

Our results show that CS/CMC multilayers, up to 5 bilayers, without the addition of an anchoring layer do not coat Si-SiO₂ wafers completely. With addition of PEI as an anchoring layer, prepared nanofilms are thicker and fully coat the wafer. Moreover, we also prepared highly concentrated solutions of CS as an anchoring layer which replicated the effects of PEI. Finally, the addition of NaCl to starting polyelectrolyte solutions resulted in the formation of thinner films.

Keywords: polyelectrolyte multilayers, ellipsometry, atomic force microscopy, nanofilm growth, surface properties

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Addressing the role of hydrophobic interactions to tune thermoresponsiveness in model polymeric systems

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Thermoresponsive polymers undergo a temperature induced solubility phase transition in solution. This feature makes these systems optimal candidates for the development of smart materials with controlled characteristics. For instance, thermoresponsive polymeric nanoadsorbers can be designed and tuned in order to adsorb predetermined cargos and then release them in response to an induced thermal stimulus. In fact, the temperature change leads to a modification of the quality of the interactions of the polymer with the solvent. As a consequence, the average size of the polymer turns into a more or less collapsed structure. Understanding the origin of the thermoresponsiveness would allow to control the thermal behaviour of polymers in solution [1].

Polymer solubility is governed by the balance between polymer-solvent interactions and intra and/or inter polymer interactions, as a result of both enthalpic and entropic contributions. However, the nano-scale dimension of these systems complicates the scenario: in fact, the possible three-dimensional conformations of the solute and the inherent fluctuations, the chemical nature of the atoms exposed to the solvent and the surface topography dramatically affect solvation. All these aspects can be well-reproduced by atomistic simulations.

We herein propose a theoretical-computational study to address the role of hydrophobic interactions in the thermoresponsive behavior of a class of thermoresponsive polymers, i.e. polyoxazolines [2,3]. By changing the chemical complexity of the side-groups bound to the common scaffold, we highlight the role played by hydrophobic groups in the definition of the average polymer conformation. Aim of this study is hence to show how local effects affect macromolecular properties, thus paving the way to the design of systems with controlled dimension.

Keywords: polyoxazoline, thermoresponsiveness, atomistic molecular dynamics

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The impact of molecular architecture of block copolymers on lubrication efficacy in non-aqueous media

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Transportation consumes 27% of global energy [1] and a staggering 33% of this is consumed to overcome friction. Different chemical additives have been designed as friction modifiers in intimate contact in oil (e.g. in engines), including organic friction modifiers, organometallics and **functionalised polymers**.

In collaboration with Infineum (a world-leading engine-oil additive manufacturer), novel, custom designed polymers of varying molecular architectures (random, diblock, multiblock and homopolymer) consisting of **polar, hydrophilic** blocks and **non-polar, hydrophobic** blocks in *n*-dodecane solvent (model oil) have been compared for their friction-mediation efficacy. Both the normal and shear forces are measured using the surface force apparatus (SFA) [2], from which the interfacial structures and lubrication mechanisms have been proposed, with the diblock copolymers exhibiting the lowest friction coefficient (Fig. 1). Furthermore, complementary data from small-angle neutron scattering (SANS, Fig. 2) and x-ray reflectivity (XRR) provide understanding of their properties in the bulk solution and at the interface, respectively, pointing to possible aggregate adsorption at the interfaces for effective friction reduction. Such fundamental studies will assist rational design of future polymeric friction-modifying additives for mechanical lubrication, which is of immense environmental and economic importance.

Key Words: Polymers, Surface Forces, Friction

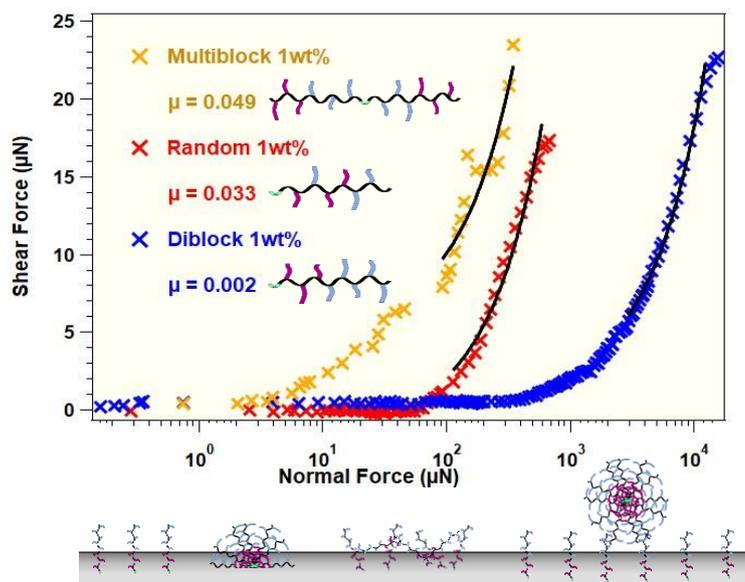


Figure 1. Shear force measurements of different polymer molecular architectures as a function of normal force alongside a schematic of potential diblock layer structures.

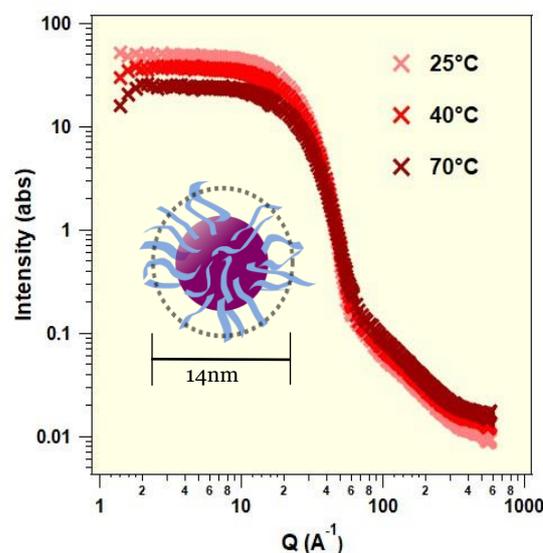


Figure 2. SANS of 1 wt% diblock copolymer in dodecane at different temperatures.

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Interrogating the factors which influence post-polymerization functionalization.

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Efficient, long-range transport of excitons (electron-hole pairs) is an ongoing and non-facile challenge in the design of molecular materials. We are developing a new approach to the design of molecular photonic materials that combines biologically inspired design principles with the exciting new physics of strong light-matter coupling.[1] In our systems, long-range exciton transport is achieved through the immobilization of pigments at plasmonic interfaces. Polymer brushes (arrays of end-tethered polymer chains) act as scaffolds which allow for the regulation of the 3D arrangement of pigments.[2] The incorporation of pigments into polymer brushes occurs post-polymerization. Here, we have expanded upon our prototype brush-pigment system,[2] and examined the factors which influence the post-polymerization functionalization of a water-soluble aldehyde-functional polymer brush (PAGEO5MA) through reductive amination chemistry.

The conjugation of pigments with reactive amine moieties to PAGEO5MA brushes was monitored by XPS, allowing for the extent of brush functionalization to be calculated. Variations in the brush grafting density, size of the pigment and the reaction conditions each affected brush functionalization. Generally, brush functionalization increases when steric barriers to pigment penetration into the brush are reduced, with the greatest pigment functionalization occurring at reduced grafting densities and in good solvent conditions. Understanding the regulation of post-polymerization functionalization is essential for the rational design of boutique molecular photonic materials.

Keywords: Polymer brushes, surface-reactions, exciton transport

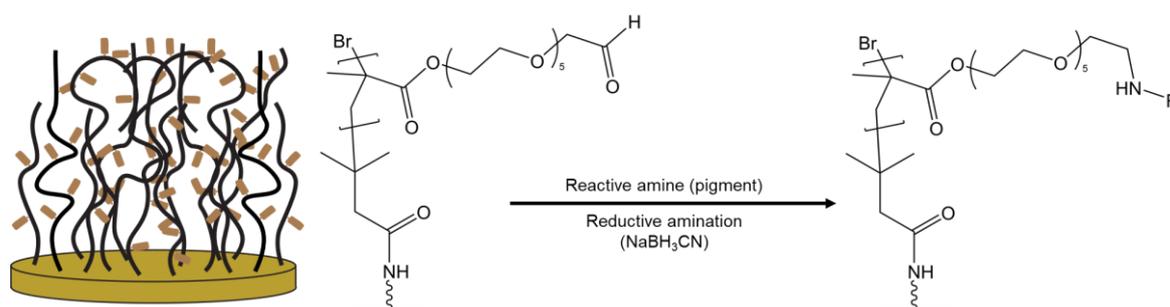


Figure 1. Cartoon of a polymer brush functionalized with pigment molecules. Generalized reaction of PAGEO5MA brushes with amine molecules to anchor pigments at interfaces.

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Impact of charge in disordered peptide tails on PAMAM - DNA binding

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Many proteins in eukaryotic cells possess domains with a large conformational entropy, named intrinsically disordered regions. DNA-binding proteins often contain ordered DNA-binding domains flanked by disordered regions, for example the tumor suppressor protein p53 [1]. It was assumed that these regions mainly act as tethers of the binding domains, however it has been shown that they can have a vital effect on the binding, such as increasing the specificity and affinity of binding [2]. In the past decades the knowledge of the role of such disordered domains has evolved to a picture when they participate more actively in the binding and binding domain search [2].

By using PAMAM dendrimers as a model of a (non-specific) DNA-binding domain and conjugating them with disordered peptide tails, we investigated the impact of charge distribution of the tails using both experimental techniques and Monte Carlo simulations.

Dye exclusion assays and gel electrophoreses showed variations in DNA condensation ability, based on charge distribution on the peptide tails, with positively charged tails increasing DNA binding significantly. These findings were further supported by Monte Carlo simulations using two different length scales, one probing the DNA condensation and complex morphology using a bead and spring model for the DNA, and the other using a more detailed coarse-grained description of the double-strand showing a close-up of the DNA – conjugate dendrimer interaction. It was also found that conjugated dendrimers with positively charged peptide tails lead to the formation of more ordered DNA structures.

These results can give further insight into how proteins utilize disordered tails to increase DNA binding and how this interaction can be fine-tuned by changing the charge distribution of the peptide tails. In addition, the knowledge can be explored for the delivery of nucleic acids using dendrimers.

Keywords: Intrinsically Disorder Proteins, Monte Carlo Simulations, Protein – DNA interactions

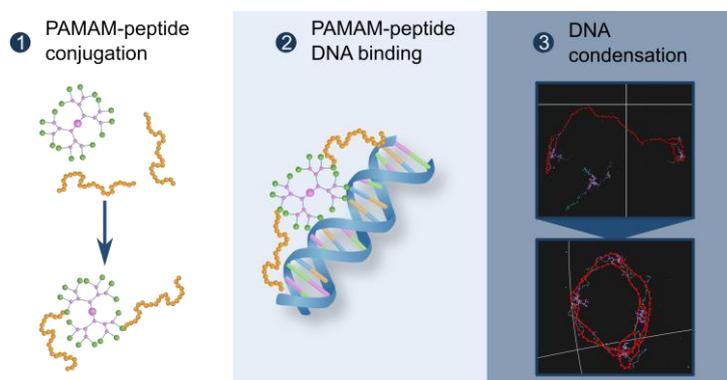


Figure 1. PAMAM dendrimers conjugated to peptide tails can increase DNA condensation.

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Solvent quality effects on DNA minicircles

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The characteristic helical conformation exhibited by double stranded DNA, owing not only to the formation of stabilizing hydrogen bonds between nitrogenous bases, but also to the inward facing spatial arrangement of bases, that minimizes interactions with the surrounding solvent, is a feature uniquely observed in aqueous solutions. In biological processes where replication or recombination of DNA is required, cells expose regions of the genetic material in partially hydrophobic environments that induce strand separation and base de-stacking. Recent experimental studies further exemplify the possibility of such solvent induced conformational transitions, occurring not only on a local base-pair level,¹ but also affecting the overall size of DNA structures as complex as the kinetoplast.²

The objective of the work presented here is the computational study of the equilibrium conformation and dynamics of double stranded DNA minicircles, the individual constituents comprising a kinetoplast network, in solvents of varying quality. Binary aqueous mixtures of two types are employed: a) a mixture of water, itself a good solvent for DNA, with another good solvent such as ethylene glycol, and b) a mixture of water with a bad solvent such as ethanol. The effects of varying solvent compositions are investigated via molecular dynamics and the simulation results are evaluated on the basis of available experimental data, as well as the theoretical predictions of the free energy of mixing of liquid mixtures (Kirkwood-Buff type treatments).³

Keywords: DNA minicircles, DNA stability, binary liquid mixtures

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The physicochemical aspects of subcutaneous drug delivery: Gel models and microfluidic screening tools

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There is a growing amount of peptide and protein-based pharmaceuticals with low oral bioavailability. For these biopharmaceuticals the subcutaneous route is often a suitable alternative, but the bioavailability can vary greatly between different pharmaceuticals. The basic process of absorption from the subcutaneous formulation to blood and lymph is quite well explored, but there is a lack of understanding of how the interactions between biopharmaceuticals and the subcutaneous extracellular matrix (ECM) affects the bioavailability. [1] We aim to provide a greater mechanistic understanding of how pharmaceuticals interact with the polyelectrolytes (eg. Hyaluronic acid, Chondroitin sulfate) of the ECM from a physicochemical perspective.

To quantify interaction strength and characterize aggregation behavior of biopharmaceutical in contact with the ECM, microgels consisting of cross-linked polyelectrolytes from the ECM are used. The interactions between these microgels and different biopharmaceuticals in solution are investigated by a number of microscopy techniques. These include visual light, fluorescence, confocal laser scanning microscopy, and confocal Raman microscopy. Different scattering methods (SAXS, DLS, SLS) are used to gain information about the structure and size of interaction complexes formed.

The work this far has resulted in a novel microfluidic-based *in vitro* screening method which utilizes the above mentioned microgels to investigate interaction and aggregation behavior of biopharmaceuticals. Initial results are promising and more extensive investigations are underway. The results from these will provide the basis for a deeper understanding of the behavior and bioavailability of subcutaneously administered pharmaceuticals. It will in addition assist in the development of new subcutaneous formulations with microgels as carriers.

Keywords: Microgels, Polyelectrolytes, Subcutaneous injection, Microfluidics

Acknowledgments: This research was performed with funding from the Swedish Drug Delivery Center (Swedeliver).

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Antifouling properties of poly(2-oxazoline)s and poly(2-oxazine)s: Direct comparison of polymer-coated gold surfaces at same coating parameters

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Poly(2-oxazoline)s (PAOx) and poly(2-oxazine)s (PAOzi) represent emerging types of polymers with significant potential in biomedical applications [1-3]. Recent reports demonstrated excellent antifouling properties of water-soluble PAOx and PAOzi when exposed to blood components, outperforming the widely used poly(ethylene glycol) [2]. In this study, we critically compare the antifouling properties of PAOx and PAOzi-coated surfaces at the same surface-related parameters. First, we synthesized a library of four different polymers, namely poly(2-methyl-2-oxazoline), poly(2-ethyl-2-oxazoline), poly(2-methyl-2-oxazine), and poly(2-ethyl-2-oxazine), each of them in three different degrees of polymerization (DP = 25, 50, and 100). The polymerizations were terminated by a xanthate agent to introduce chain-end sulfur-containing moiety for gold substrate attachment. Subsequently, the polymers were used to coat gold wafers by a “grafting to-” approach. The thickness, surface-related parameters, and the covalent structure of the resulting polymer brushes were determined via various surface-sensitive techniques, such as spectroscopic ellipsometry, FTIR, XPS, and water contact angle measurements. Finally, the antifouling properties of prepared brushes were measured by surface plasmon resonance experiments. All polymers reduced the fouling from the blood plasma compared to the bare gold surface. The comparison of the synthesized PAOx and PAOzi brushes led us to the conclusion that at the same surface-related parameters, PAOzi brushes show significantly better antifouling properties, which is in line with the recent report by Benetti and Hoogenboom [3].

Keywords: poly(2-oxazolines), poly(2-oxazines), surface coating, antifouling properties

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Counterion effects on thermoresponsive cationic microgels with ionic liquid moieties

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Poly(ionic liquids) are an emerging field of interesting materials due to their broad applicability ranging from self-healing material, to “green solvents”, environmental cleanup, and bioelectrochemical devices. While providing the properties of typical ionic liquids, such as crystallinity with low melting temperatures, and ionic conductivity, poly(ionic liquids) can also show thermoresponsive behavior. This property, as well as the possibility for enhanced solubility of, e.g. proteins and enzymes, make the incorporation of their respective monomers into crosslinked colloidal polymer networks, i.e. microgels, interesting for different applications. Since the chemical and physical properties of poly(ionic liquids) are dominated by the interionic interactions between the respective anion and cation, the study of different counterions in combination with polymerizable ionic liquid monomers is of high interest for the latter application thereof.

We studied the incorporation of different ionic liquid monomers based on alkylated positively charged *N*-vinylimidazolium derivatives into poly(*N*-vinylcaprolactam) based microgels with regard to resulting microgel morphology, solution and swelling behavior, as well as surface charge. Typical anions in the context of ionic liquids with varying chaotropic nature were applied in the synthesis, e.g. bromide and tetrafluoroborate, as well as varying concentrations thereof within the microgel network. The temperature-responsive solution behavior and morphology of obtained microgels was found to be strongly dependent on both parameters. Specifically, a suitable comonomer concentration and present counterion can lead to the presence of two phase transitions (LCST and UCST, respectively), as well as an asymmetric microgel morphology with highly-ordered nanostructures.

Our studies provide access to new microgel systems with controllable and tunable complex swelling behavior. The incorporated positive charges of these multifunctional microgels can be applied in the field of electrostatic immobilization of active biomolecules, and potentially allow for cascade reactions. Moreover, the chaotropic nature of the present anion can increase the stability of immobilized payload.

Keywords: microgels, poly(ionic liquids), polyelectrolytes

Effect of pH on the complexation and secondary structures of self-assembling polypeptides

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Charged polypeptides represent a class of biopolymers with attractive properties, such as biocompatibility, biodegradability, and non-toxicity. This makes them ideal materials for biomedical applications, including drug delivery and functional coatings. In solution, polypeptides form assemblies with highly ordered secondary structures like natural proteins. Polypeptide properties and assembly formation can be controlled by external stimuli, such as the solution pH. However, little is still known about the relations between the factors governing the polypeptide assembly at the molecular level.

Here, we present a study of the effect of pH on the complexation and secondary structures of oppositely charged poly(L-glutamic acid) (PGA) and poly(L-lysine) (PLL) [1]. With atomistic molecular dynamics (MD) simulations and experimental circular dichroism, electrophoretic mobility, and zeta potential measurements, we show that the pH-controlled ionization degrees of the polypeptides clearly affect their intermolecular interactions and consequently complex formation. The ionization degrees of PGA and PLL also dictates their secondary structures: the fully charged PGA and PLL form β -sheets, while partially charged PGA leads to α -helical structures (Figure 1). Our findings provide new understanding on the impact of pH on charged polypeptide assemblies. These guidelines for secondary structure changes can advance future design of self-assembling polypeptide materials with well-defined properties.

Keywords: polypeptides, self-assembly, secondary structure, molecular dynamics

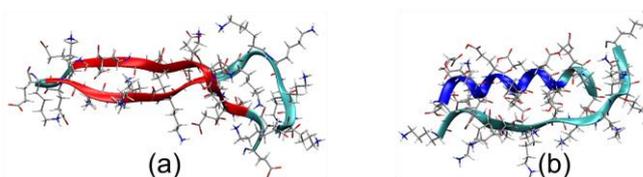


Figure 1. Secondary structures predicted by the MD simulations for the complexes of the fully charged PLL with either (a) the fully or (b) partially charged PGA. The β -sheets and α -helix structures are colored red and blue, respectively.

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From a single molecule to smart material - understanding the polypeptide complexes formation and properties

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Poly l-lysine (PLL), and poly l-glutamic acid (PGA) often serve as a model pair of polypeptides. Their biodegradability and biocompatibility make them perfect candidates for the design and assembly of advanced materials for biomedical applications. Properties and self-assembly of polypeptide complexes can be controlled by external factors, such as the solution ionic strength or pH. However, little is still known about the relations between the factors governing the formation and final complex structure at the molecular level.

The investigation was conducted to reveal the effect of pH on the PLL and PGA properties in bulk solution, such as hydrodynamic radius, electrophoretic mobility or secondary structure. Then, using this knowledge, we reveal the complexation mechanism via several experimental techniques, including circular dichroism (CD), isothermal titration calorimetry (ITC), dynamic light scattering (DLS), laser Doppler velocimetry (LDV) and quartz crystal microbalance (QCM-D). The experimental results are supported with atomistic molecular dynamics (MD) simulations.

We show that the pH has major impact on the assembly mechanism and properties of the resulting PGA/PLL complexes. We developed two stage complexation model to interpret the LDV results at various pHs. Using CD method, we were able to follow the changes in the secondary structure during the complexation, and to extract the secondary structure of the resulting complexes. The pH related changes in the complex structure were connected via QCMD with the properties of bulk materials, i.e., LbL films. With ITC method, we gain insight in thermodynamics of complexation and show distinct differences in the complexation mechanism at various pHs. The MD method confirm the changes observed in experiments and serve as a complementary tool to explain the complexation mechanism via changes in the ionization degree and hydrogen bonding formation.

Our findings provide new understanding on the effect of pH on PGA/PLL assemblies and enable for a better assembly process control and quantitative connection between its conditions and the final structure of the complex.

Keywords: polypeptides, self-assembly, polyelectrolyte complexes,

Acknowledgements: The study was supported by the National Science Centre Research Grant Sonata, UMO 2018/31/D/ST5/01866 and Academy of Finland.

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GelMA-Dextran Aqueous Two-Phase Systems with Tuneable Pores Organization

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Hydrogels are excellent candidates for constructing scaffolds in bioengineering applications. Besides their biocompatibility and stiffness properties, the porosity of hydrogels is essential for promoting cell growth and nutrients transfer. Determining this porosity remains a challenge for biomaterial development [1].

In this work, hydrogels with tunable pore size and organization (disconnected or interconnected) are developed from an aqueous two-phase system composed of gelatin methacryloyl (GelMA) and dextran, a polysaccharide used as the sacrificial template [2]. The segregative phase separation of GelMA (polyampholyte) and dextran (neutral) is driven by the counterions entropy. The demixing is therefore triggered by either controlling the pH near the GelMA isoelectric point or by salt (NaCl) addition to the mixture. This leads to a shift of the binodal – the delimitation from monophasic to biphasic regime – of the established phase diagrams to lower GelMA and dextran concentrations.

The resulting microstructure of the casted hydrogels is controlled by quenching through photo-crosslinking the GelMA phase under UV exposure. The hydrogels' microstructure – tuned by controlling the competition between the phase separation and gelation kinetics – is investigated by confocal laser scanning microscopy (CLSM), whereas their mechanical properties and stability are measured by rheological methods. The resulting microstructures (Figure 1) are tuned by varying the components' concentrations, pH or ionic strength, leading to a phase separation through nucleation and growth or spinodal decomposition that results to disconnected or interconnected porous hydrogels after GelMA crosslinking, respectively [3]. CLSM reveals that the initial pH affects the phase separation kinetics. Salt addition may act either during the early spinodal decomposition stage with a percolation-to-cluster transition or by favoring the nucleation and growth mechanism. Although the role of charges at the water-water interface for NaCl-based hydrogels is under investigation [4], the developed hydrogels with controllable pore size and interconnectivity have great potential in 3D-bioprinting applications.

Keywords: gelatin methacryloyl (GelMA), porous hydrogels, segregative phase separation, nucleation and growth, spinodal decomposition.

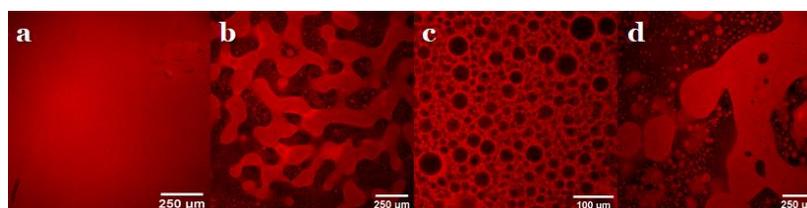


Figure 1. GelMA-Dextran hydrogels as (a) monophasic, (b) bicontinuous, (c) porous and (d) phase inverted systems.

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Mussel-inspired stimuli-responsive PNIPAM microgels

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Microgels are cross-linked polymer particles, which exhibit sizes of colloidal dimension (several nanometers to micrometers [1]). They are highly swollen in a solvent like water and respond fast to outer stimuli [2]. Microgels based on poly(N-isopropylacrylamide) (PNIPAM) undergo a volume phase transition (VPT) when heated above the lower critical solution temperature (LCST) of 32°C. PNIPAM microgels can be easily synthesized with a narrow size distribution [3] by surfactant-free precipitation polymerization [4]. In addition, the co-polymerization of PNIPAM with comonomers of different features like charges or hydrophobicity is a well-defined technique to design unique microgel systems.

The catechol-based monomer Dopamine methacrylamide (DMA) can be found in marine organisms like mussels and is mainly responsible for their unique adhesive properties. The combination of PNIPAM with DMA offers great advantages in the biological and medical engineering field or for adhesive polymer coatings. For biomedical applications, mechanical strength and high elastic moduli are important to significantly improve their use in vivo environments. For polymer coatings, the influence of the substrate onto the microgel properties and its internal structure needs to be understood.

In the present study, DMA was incorporated into PNIPAM microgels. Therefore, a suitable synthesis strategy was developed by studying the consumption of the different educts at different times during the synthesis by mass spectrometry. The incorporated DMA was verified by UV-Vis standard addition and NMR spectroscopy. Nanomechanical properties of the microgels have been studied by AFM indentation measurements.

Keywords: mussel-inspired PNIPAM microgels; catechol chemistry; nanomechanics; indentation measurements

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The Effect of Macromolecular Architecture on the Conductivity-Mechanical Modulus Relationship in Single-ion Polymer Blend Electrolytes

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Solid polymer electrolytes (SPEs) are ideal electrolytes because they possess good electrochemical and mechanical resistance that could eliminate Li dendrite formation in lithium metal batteries. Conventional SPEs are formed by dissolving Li salt in a polymer host that solvates the lithium salt and conducts ions. Such systems are dual conductors as both anions and cations are mobile. In these systems, the fraction of conductivity from the cations (Li^+ transference number, t_{Li^+}) is only a small fraction of the overall conductivity (~ 0.5) and the large contribution from the anions leads to a strong concentration gradient as anions accumulate at the electrode, leading to deleterious effects. The research effort in SPEs has been prevented by the inability to design materials that possess simultaneously, high ionic conductivity, good mechanical properties and cation transference number close to unity (i.e. single-ion solid polymer electrolytes, $t_{\text{Li}^+}=1$). In this talk, we introduce the use of novel, stiff/glassy, polyanion particles, composed of high functionality poly(lithium 4-styrenesulfonyl trifluoromethylsulfonyl imide), PSTFSILi, star-shaped polymers as additives to liquid, low molecular weight poly(ethylene oxide), PEO, electrolytes for the synthesis of SPEs that are single-ion by design while exhibit an unprecedented combination of high modulus and ionic conductivity, at room temperature. The resulting single-ion SPEs exhibit simultaneously higher conductivity and mechanical strength compared to their linear PSTFSILi blend analogues. The reason is the morphology and the ability of the PSTFSILi nanoparticles to disperse within the liquid PEO electrolyte permitting the development of a highly interconnected network of pure liquid PEO that promotes high ionic conductivity. In addition to this, Raman spectroscopy shows a strong effect of macromolecular architecture on the degree of ion dissociation. The proposed macromolecular design approach offers a tremendous potential for the design of high performance single-ion solid polymer electrolytes because gave us the opportunity to control the antagonistic properties of ion-conductivity and shear modulus, which currently limit in the use of single ion polymer electrolytes in lithium metal batteries.

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Structure and viscoelasticity of fibrillar collagen suspensions utilized in regenerative medicine scaffolds

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Collagen I, the most abundant structural protein in humans, is utilized extensively in biomaterial applications. Literature emphasizes on collagen I hydrogels, yet there is limited information on porous scaffolds made of lyophilized suspensions of fibrillar collagen I [1], despite their established utilization in regenerative medicine grafts. Our main goal is to deepen our understanding of the self-assembly of collagen molecules and its role on the viscoelasticity of formulations used in regenerative medicine applications. For this purpose, we apply phase contrast microscopy and cryo-TEM to observe and analyze the multi-scale structure of fibrillar collagen I in acetic acid solutions. Rheology is used to probe the viscoelastic and flow properties at different temperatures. Our findings indicate a correlation between the rheological response of the suspensions, their entangled structure, and the swelling degree of the fibers.

Keywords: fibrillar collagen, fiber suspensions, gel rheology, regenerative medicine

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Structural Transformation and Charge Regulation of Heparin- and Amino-Acid-Mimicking Polyampholytes

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Highly sulfated heparin-mimicking polyelectrolytes act as anticoagulants with additional advantages, including the ability to tailor their structure and to tune parameters such as sulfation percentage and molecular weight dispersity. However, the complex charge regulation of the polymer chain and the mechanisms controlling the structure of such polyelectrolytes remain unclear.

Sodium poly((sulfamate-carboxylate)isoprene) is a high-charge-density polyelectrolyte containing two negatively charged groups of different pH sensitivity at the same monomeric unit. The pH-dependent sulfuric group, which resembles the one found in heparin, undergoes N-S bond cleavage in acidic pH, which leads to the chemical transformation into a polyzwitterionic poly((amino-carboxylate) isoprene) [1-3].

To investigate the variation of ionization with pH, the mechanism of structural changes, and the charge regulation of such a polymer, we synthesized sodium poly((sulfamate-carboxylate)isoprene) and subjected this polyelectrolyte to a post-functionalization reaction, resulting in a zwitterionic poly((amino-carboxylate)isoprene). The structure of both hydrophilic polymers and the cleavage of the sulfuric group were confirmed by ¹HNMR, FTIR, elemental analysis, and pH-dependent zeta-potential and dynamic light scattering measurements. The charge on the polymer was determined by potentiometric titration. Based on those results, we performed molecular simulations to gain insights into zwitterion charge regulation. The biocompatibility and non-toxicity of the polymer was confirmed in a MTT assay. In addition, the heparin-mimicking abilities of the polymer were assessed by measuring the activated partial thromboplastin time (aPTT), which showed that the polymer acts as an anticoagulant.

Therefore, our in-depth study of the mechanisms that control the structure of sodium poly((sulfamate-carboxylate) isoprene) combining experimental methods with molecular simulations contributes to advancing the field of polyelectrolytes by fostering research on blood-clot prevention.

Keywords: polyelectrolytes, charge regulation, polyzwitterion, polyampholyte

Acknowledgements: The authors acknowledge the financial support from Grant Agency of Charles University, project number 405122.

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New wound care material based on bacterial cellulose and flavonoid rutin

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Diabetes is a disease that compromises the immune system of individuals and can lead to foot ulceration, which is difficult to heal, leading to the development of bacterial infection and limb amputation. Nanostructured materials containing flavonoids have demonstrated healing activity [1]. The aim of this work is to develop suitable materials for wound care dressings based on bacterial cellulose-rutin or rutin-Zn. The production methods investigated were the co-precipitation of rutin and rutin-Zn directly on bacterial cellulose membrane (MB) and the entrapment of rutin and rutin-Zn in nanoparticles and their immobilization [3] in MB. The co-precipitation tests were performed at different concentrations (1 to 3% rutin and rutin-zinc). The best deposition on the membrane was obtained in the 3% rutin aqueous solution at pH 7 and for rutin-zinc in 3% methanolic solution. Around 0.2% of rutin and rutin-zinc were entrapped in the nanoparticles to be immobilized in MB. All materials were characterized by Infrared (FTIR), Raman spectroscopy and Scanning electronic microscopy (SEM). The FTIR and RAMAN results showed the interaction of the rutin or rutin-zinc in the bacterial cellulose membrane (Figure 1). Since the MB membrane has healing action [2], the combination between these materials could lead to a membrane with biological properties of great interest.

Keywords: rutin; wound healing; dressing; bacterial cellulose

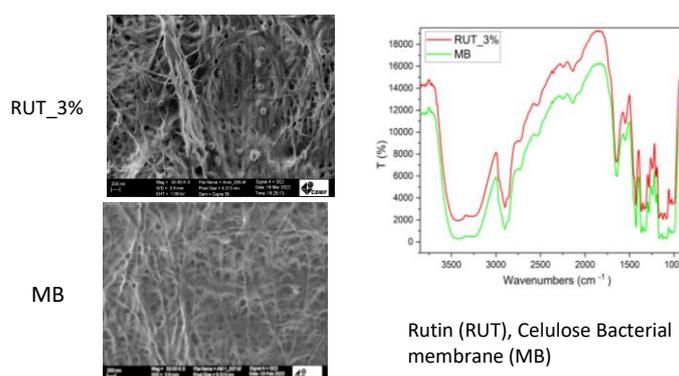


Figure 1. Infrared and scanning electron microscopy of bacterial cellulose membranes (MB) and rutin (RUT).

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Assessment of the muco-adhesion potential of green extracted gums from plant seeds

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The term “mucoadhesion” refers to the ability of a polymeric material to adhere to a mucosal membrane of the body. Mucoadhesive polysaccharides such as sodium alginate, celluloses, pectins or chitosan are well-known for their ability to modulate the tactile and olfactory sense stimuli during oral processing and affect the nutritional impact of food products throughout gastrointestinal transit [1]. In the latter case, mucoadhesive polysaccharides can be used for programming the release and cellular uptake properties of bioactive compounds and nutrients, whilst they can influence the gut cell epithelial adhesion of beneficial probiotic bacteria. Plant seed coat or endosperm extracted biopolymers are emerging food ingredients of multifaceted techno-functionality e.g. thickening, gelling, and interfaces stabilising ability [2]. Hereby, we aimed at the comparative study of plant seed gums (PSG) isolated from chia, flax, psyllium, alfalfa, fenugreek, and quince seeds as concerns their ability to interact with mucins isolated from pig gastric mucosa. Their mucoadhesion potential was assessed in terms of a) viscoelastic and viscosimetric response of PSGs/mucin blends, b) tackiness of PSGs to a mucin based xerogel (dried at 70°C) layer, and c) ζ -potential and particle size changes of mucin/PSGs complexes and compared to that of selected industrial gums. In addition, the nature of the PSGs induced quenching mechanism of mucin fluorescence and therefore the thermodynamics of the PSGs/mucin binding interactions were also assessed.

Keywords: Mucilage; Rheological properties; mucoadhesion

Acknowledgements: This work was supported by the Luxembourg National Research Fund (FNR) (Project PROCEED: CORE/2018/SR/12675439)

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Rheological, structural and thermophysical characteristics of thermo-reversible hydrogels filled with beeswax structured oil-in-water emulsions

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Oil-in-gel emulsions (emulgels), have been largely exploited in food and nutraceutical applications owing to their ability to impart structuring, texturing and stabilizing functionalities to food matrices [1]. Stemming from their composite material characteristics, emulgels may permit the programming of the food matrix disintegration and micronutrients release profile leading to tailorable health-conferring bio-functionalities [2]. Structure-engineering approaches such as the incorporation of solid lipid nanocarriers or the direct physical structuring of the liquid lipid phase may improve the colloidal stability of emulgels and therefore, they can prevent the untimely release conveying bioactives during storage and/or post-ingestion, enhancing their biological activity.

The present work aimed at exploring the role of beeswax as a physical co-structurant of the lipid phase in thermo-reversible (gelatine based) emulgels. The liquid phase (rapeseed oil) of the o/w emulsions was substituted by beeswax at incrementing ratios (i.e. 0, 25, 50, 75 and 100%) and emulgels were prepared according to the procedure illustrated in Fig. 1. Oscillatory thermo-rheology (OTR) coupled with differential scanning calorimetry (DSC) were used to monitor the gelation and melting behaviour of the emulgels. The effects of cold storage induced ageing (t=1 & 30 days) on the lipid droplet mean size and microstructural aspects of the emulgels were assessed by means of static laser light scattering (SLS) and confocal laser scanning microscopy (CLSM).

Beeswax addition resulted in a double sigmoidal pattern of the OTR spectra, indicative of the occurring structure conformational changes i.e. gelatine's random-coil to helix transition (<30° C) and lipid phase crystallisation (30-50°C). On cooling, beeswax addition induced a significant elevation of $T_{sol-gel}$ values approx. by 3 to 6 °C. CLSM and oscillatory rheology revealed that beeswax presence was associated with stiff, cohesive and fine-tuned hydrogel structures suggesting the active filler behaviour of the semi-solid lipid droplets. According to the van der Poel - Smith model, beeswax increased the proportional contribution of the lipid phase to the total hydrogel matrix stiffness as compared to gelatine ($G'_{lipid} > G'_{gelatine}$).

Keywords: Beeswax; emulgel; microstructure; dynamic rheology; colloidal stability; active fillers

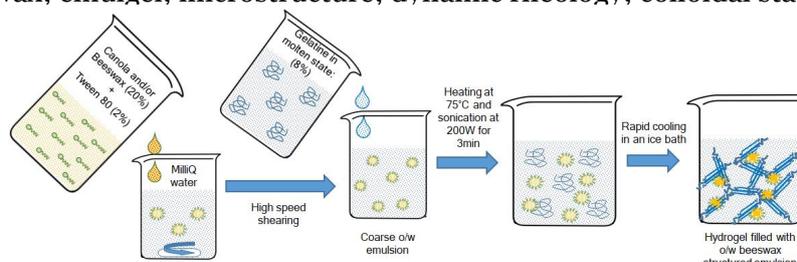


Figure 1. Experimental setup for the production of gelatine-based hydrogels filled with o/w beeswax co-structured emulsions.

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Novel *in vitro* models for subcutaneous administration – Peptide diffusion in polyelectrolyte gels

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Background Subcutaneous (SC) injection is a common route of administration in clinical medicine today, in particular for sensitive biopharmaceuticals with poor oral bioavailability [1]. However, for many biopharmaceutical formulations administered via the SC route the bioavailability is variable and incomplete, being in the range of 20-100 % [2]. Currently there is no standard accepted medium for simulation of the human SC environment [3]. Therefore, there is a need to develop and validate physiologically relevant *in vitro* models for subcutaneous administration of drug formulations.

Aim The aim of this project is to study physicochemical aspects of the absorption of drug molecules after subcutaneous administration. The interactions of model drugs with the biopolymers present in the human extracellular matrix (ECM) e.g. hyaluronic acid (HA) and collagen (COL), are investigated as well as the contribution of diffusion and convection to their transport.

Method Hydrogels of cross-linked hyaluronic acid and collagen were synthesized and the diffusion of fluorescently labelled model peptides through these gel matrixes was investigated using confocal laser scanning microscopy (CLSM). Fluorescence recovery after photo bleaching (FRAP) was used to determine diffusion coefficients [4].

Results The obtained diffusion coefficients in neutral control gels were in the range of free diffusion of the compounds in water. The diffusivity of cationic peptides in gels containing anionic HA was hindered significantly, whereas neutral compounds were largely unaffected. Peptide aggregation inside the gel matrixes could be observed as immobile fractions in FRAP experiments. The method will be further used to study model peptides with systematically varied physicochemical properties, as well as drug compounds with subcutaneous administration route.

Keywords: diffusion, hydrogels, peptides, FRAP

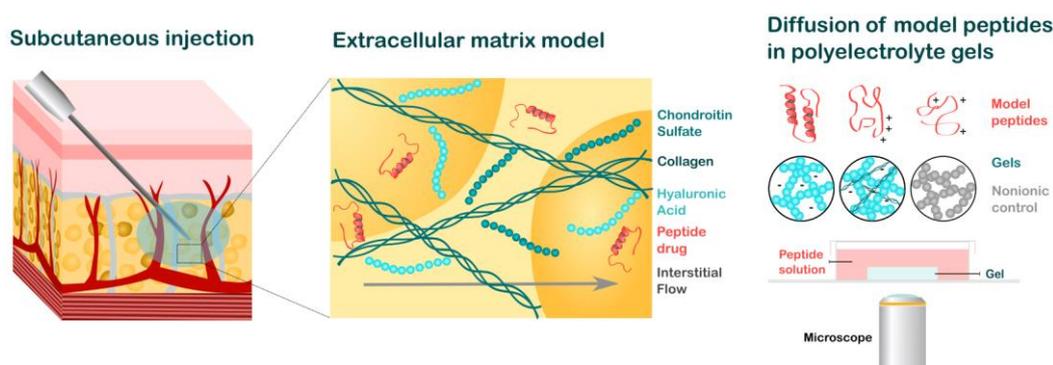


Figure 1. Schematic illustration of subcutaneous injection, the extracellular matrix model and experimental setup.

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Differential Dynamic Microscopy to Characterise Fluctuating Nematic Liquid Crystals

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Stiff, yet highly thinning, viscoelastic gels can be formed upon mixing colloids with homeotropic alignment into a nematic liquid crystalline medium due to the entangled network of defect lines that percolated throughout the sample. Theoretical and experimental results by Katyan et al. [1] have shown that the value of the elastic constant (K) determines the storage (G') and loss (G'') moduli of the gel. Cellulose nematic phases can be created from biorenewable ingredients obtained from wood and seaweed. The ability to measure viscoelastic ratios will help us understand how composition and the aspect ratio of nanocrystals affect the performance.

During this project, we set out to determine the range of viscoelastic ratios (K/η) using Differential Dynamic Microscopy for thermotropic and, for the first time, lyotropic nematic liquid crystals. This approach is an effective alternative to light scattering and avoids any requirement to apply an electric field which creates the movement of charged entities forming a lyotropic nematic state. Differential Dynamic Microscopy [2] allows for the extraction of scattering information directly from microscope images collected between crossed polarisers. Dynamic analysis of the images of different geometries is performed, providing the splay, twist and bend viscoelastic ratios.

Keywords: Lyotropic, nematic, viscoelastic ratios

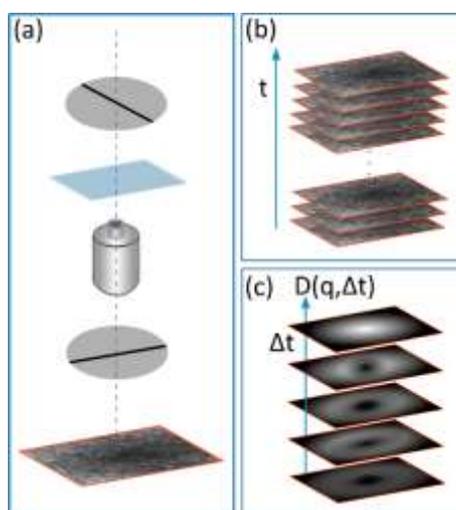


Figure 1. Sketch of the DDM experimental and data analysis procedure. (a) The sample cell is positioned on the microscope stage between two polarising elements. (b) A stack of digital images of the sample is acquired with a fixed frame rate. (c) For each Δt , the 2D image structure function ($\vec{q}, \Delta t$) is calculated by averaging the Fourier power spectrum of the difference of images separated in time by the same time delay Δt .

Acknowledgements: This work was funded by BBSRC.

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Light-cleavable polyacylhydrazone-based drug carriers

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Photo-cleavable polymers have emerged as an attractive class of materials for use in a broad range of applications including drug delivery, photopatterning, recyclable materials, and others [1]. The design and development of new photo-labile polymers, exhibiting enhanced degradation rates under low irradiation energies as well as bio- and eco-friendly photodegradation products are of particular interest [2,3].

In the present work, we have developed a new type of main-chain, photo-cleavable polymers based on hydrophilic polyacylhydrazones [4]. The polymers were synthesized via a polycondensation reaction of adipic acid dihydrazide (AA) with a dibenzaldehyde terminated poly(ethylene glycol), under mild conditions to afford hydrophilic poly(PEG-*alt*-AA) alternating copolymers. The main-chain photo-scission of the copolymers, upon UV light irradiation at $\lambda = 254$ nm, was studied by size exclusion chromatography, proton nuclear magnetic resonance and UV-vis spectroscopies. Next, a hydrophobic anticancer drug, Doxorubicin (DOX), was attached onto the hydrazide end-group(s) of the polymer via an acylhydrazone bond, to afford an amphiphilic P(EG-*alt*-AA)-DOX conjugate. The polymer-drug conjugate self-assembled in aqueous media to produce spherical nanoparticles evidenced by scanning and transmission electron microscopies. Photo-irradiation of the self-assembled nanostructures resulted in the photolysis of the acylhydrazone bonds along the polymer chains, causing the disintegration of the nanoparticles and the release of the DOX molecules. Moreover, the synergistic effect of an acidic solution pH and light irradiation was further exploited onto the combined photo- and acido-lysis of the acylhydrazone bonds and the disruption of the self-assembled prodrug nanostructures.

Keywords: polyacylhydrazones, photodegradable polymers, polymer-drug conjugates

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Filtration through hydrogels with controlled permeability

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Pressure-driven membrane technologies, such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis, have proven their effectiveness in a broad range of water treatment applications [1]. Hydrogels, which are networks of polymer chains in water, have been the subject of recent work in the context of filtration. For example, thin coatings of hydrogels deposited on classical filtration membranes allow to increase their hydrophilicity and to decrease their fouling by hydrophobic proteins. An important remaining challenge is to control the selectivity and permeability of the hydrogels.

We have developed a series of hydrogels with controlled permeability obtained by the photopolymerization of poly (ethylene glycol) diacrylate, (PEGDA) under UV light in the presence of non-crosslinkable PEG chains. The resulting hydrogels are turbid, which suggest that a phase separation between the PEGDA matrix and the PEG chains occurs.

The permeability K of the resulting hydrogels, varies over several orders of magnitude as we vary the PEG concentration and molar mass (Figure 1). It shows a maximum with PEG concentration, obtained for the overlapping concentration C^* of the PEG chains. To account for this behavior, we suggest that the concentration of free PEG chains in the pores of the PEGDA matrix controls the hydrogel's permeability. At low PEG concentration, the pores are closed and an open porosity is obtained around C^* . Above C^* , the PEG concentration in the pores increases sharply which causes the permeability of the hydrogels to drop.

In conclusion, this work has shown how to prepare new hydrogels with variable permeability using PEG/PEGDA mixtures. Moreover, these model filtration experiments are an interesting technique to study the transport of flexible polymer chains through these hydrogels. This study opens new perspectives for the design of flexible hydrogel membranes with controlled permeability and their application in water treatment and bioseparation.

Keywords: Filtration, permeability, PEGDA, PEG chains

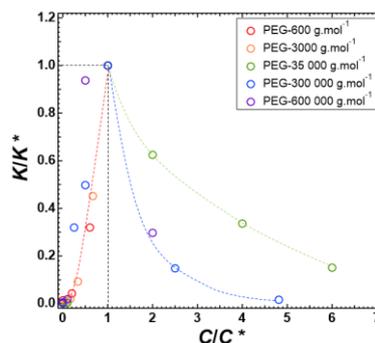


Figure 1. Variation of the water permeability as a function of the PEG concentration added to the hydrogel membrane with various molecular weight.

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Novel diblock copolymer coatings with self-renewable antimicrobial properties

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Microbial infectious diseases can occur as a result of the contamination of surfaces with pathogens and constitute a growing threat to human health, with major risks in food packaging and storage, water filtration-purification, household sanitation and the biomedical field. The development of effective, long-lasting and environmentally friendly coatings to eliminate bacteria adhesion and growth on surfaces has attracted great research interest [1].

In this work, we have developed novel polymeric materials exhibiting controllable biocidal and polishing properties in the solid state. These polymers comprise environmental-friendly cationic biocidal species and can self-organize into nanostructured films with controlled self-polishing and biocidal features. Amphiphilic diblock copolymers containing hydrophobic and hydrolyzable tetrahydropyranyl methacrylate (THPMA) units and hydrophilic 2-(dimethylamino)ethyl methacrylate (DMAEMA) moieties were synthesized by group transfer polymerization (GTP) [2] and were characterized by gel permeation chromatography (GPC) and proton nuclear magnetic resonance spectroscopy. Thin films of the symmetric diblock copolymers organized lamellae structures oriented parallel to the substrate, as verified by independent X-ray reflectivity (XRR) and Grazing incidence small angle X-ray scattering (GISAXS) measurements. Propyl iodide was used to quaternize the DMAEMA units and introduce cationic biocidal groups onto the polymers (see Figure 1). The self-polishing behavior of the quaternized diblock copolymer thin films in aqueous media, over a period of ~1 year, was monitored by ellipsometry. Furthermore, the quaternized block copolymer thin films exhibited good antimicrobial properties against both Gram-positive and Gram-negative bacteria strains.

Keywords: Biocidal surfaces, polymer self-assembly, polyelectrolyte

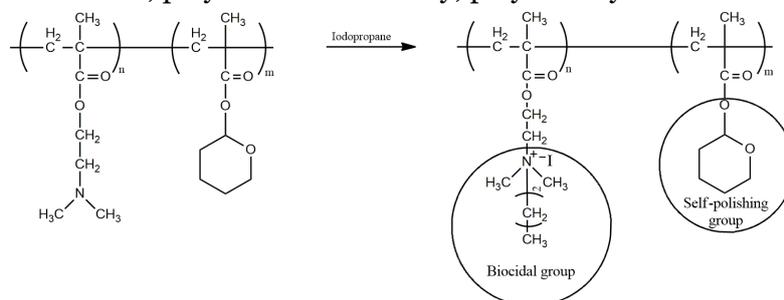


Figure 1: Quaternization of the PDMAEMA-b-PTHPMA diblock copolymer

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3D printed scaffolds based on graphene oxide particles and poly(styrene-butadiene-styrene) thermoplastic elastomer

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The main task of this work is to fabricate and analyze the new type of scaffold based on thermoplastic elastomer (SBS - styrene-butadiene-styrene block copolymer) as a matrix and plus electrically conductive particles (modified graphene oxide) as a filler. This combination is a suitable base for 3D printing, easy manipulation and finally, for cultivation of neural cells on it. Typically, scaffold can be made in the form of a complex structure and it would show improved physical properties in terms of mechanical stability and electrical conductivity. The fabricated masterbatches suitable for 3D printing will be characterized as listed below and will provide suitable mechanical properties, expectedly self-healing ability and will be in the same time electrically conducting, which is important from the neural tissue engineering [1].

The composites are examined using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), rotation rheometry in oscillatory mode. All mentioned tests are performed to obtain knowledge about material behavior and adapt the parameters of the 3D printing process suitably. The last crucial test will be measurement of scaffold cytotoxicity, where it is expected that fabricated materials based on graphene oxide and SBS matrix will be evaluated as non-cytotoxic.

Keywords: Thermoplastic elastomer, scaffold, 3D printing, graphene oxide

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Apparent Young-violating concave-convex switching of curved oil-water menisci

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Controlling the curvature of the meniscus is crucial in a wide range of technologies, ranging from interfacial assembly methods to liquid lens technologies, microfluidics, direct-write 3D printing, thermal management and printing of microelectronic devices, and more. The physics of menisci and their shapes is also fundamental for many natural phenomena. However, while the existing methods allow the curvature to be controlled only by varying the chemical composition of the sample, by surface treatment, or by external fields, reversible convex-concave curvature switching of menisci by simply varying the temperature has never been hitherto reported.

I will demonstrate, that such temperature-controlled curvature inversion is possible for a capillary-contained macroscopic water:oil interface. This phenomenon occurs under the joint, interrelated, action of two nanoscale effects: one is the interfacial freezing, whereby a crystalline monolayer spontaneously forms at the interface between two liquid bulk phases, at a temperature T_s . The freezing switches the temperature-slope of the oil:water interfacial tension γ_{ow} from slightly negative at $T > T_s$, to strongly positive at $T < T_s$, causing γ_{ow} to decrease upon cooling, and vanish at some T_{SE} , above the bulk freezing point of the oil. The second effect is a unique hydrophilic-hydrophobic transition of the liquid-containing glass capillary's walls. While thermal hydrophobicity-hydrophilicity transformations have been observed under nano confinement conditions, no such transformations have been hitherto reported for bulk materials contained in macroscopic capillaries. Such transformations may allow the direction of capillary action to be reversed, significantly influencing wicking, imbibition, wetting, narrow channel or soil penetration, as well as other nanotechnology-related phenomena. Remarkably, I will demonstrate that the shape of the meniscus strongly depends on the width of the containing capillaries, in an apparent violation of Young's equation. We elucidated the mechanism of this dependence by a combination of systematic optical microscopy measurements and computer simulations.

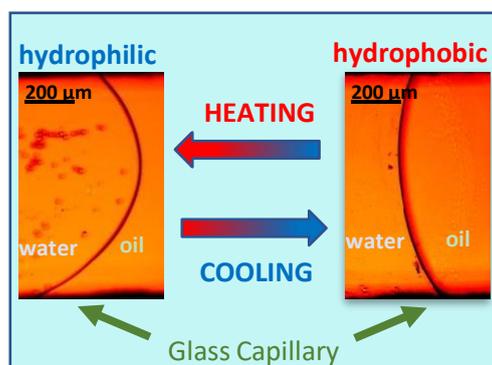


Figure 1. Raw experimental images of the meniscus, taken at different temperatures, for capillaries with cross-sections: $w \times h = 1 \times 0.1$ mm. The aqueous phase is on the left, and the $C_{16}OH$ concentration is 0.3%

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Adsorption and aggregation properties of hydrophobically functionalized polyanions. Novel materials for pH sensitive nanostructures formation.

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Polymeric micro- and nanocarriers have attracted broad scientific interest in recent years. We considered as the building blocks for nanostructures, hydrophobically functionalized polyelectrolytes (HF-PE) based on the poly(4-styrene sulfonic-co-maleic acid) copolymer (PSS/MA) with hydrophobic alkyl side chains grafted to the backbone chain via the pH-labile amid or ester linkers [1].

We investigated the effect of the alkyl chain length and grafting density on the aggregation and adsorption properties of the polymers. Fluorescence spectroscopy was used to confirm the self-assembly of polymers and the formation of hydrophobic domains, whereas the dynamic light scattering allowed for determining the size and zeta potential of polymeric structures. As a measure of polymer pH responsiveness, acid and base hydrolysis were studied in different temperature ranges with the GC-MS. The results were correlated with the stability of HF-PE based nanoparticles.

The linker dependent differences in the dependency of interfacial tension on the HF-PE concentration and molecular dynamics simulations led us to conclude that copolymers with ester linkers can form more tight hydrophobic domains along the (PSS/MA) backbone [2].

HF-PE copolymers were adsorbed on a solid surface coated by polyelectrolyte multilayer (PEM). The sequential adsorption process was monitored using QCM combined with ellipsometry and FTIR-ATR. It was proved that hydrophobic copolymers form stable thin films on solid surfaces and change the structure of water. Furthermore, contact angle analysis proved that HF-PE modified the wetting of the PEM surface [2].

Our research demonstrated that HF-PE based on PSS/MA copolymers are a promising material for creating nanocarriers for the controlled release of hydrophobic substances and thin polymer films modifying the surface properties of materials.

Keywords: hydrophobized polyelectrolytes; adsorption; nanocarriers; thin polymeric films

Acknowledgements: The work was supported by the NCN project 2017/25/B/ST4/02450.

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Slow phase transition of Poly(methacrylic acid) in semi-diluted regime

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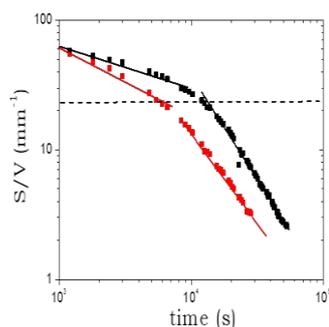
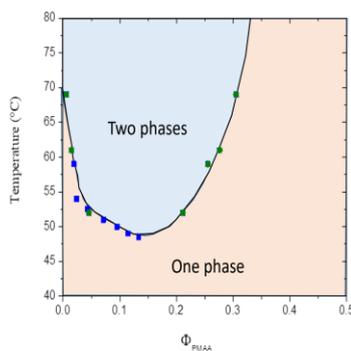
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Poly(methacrylic acid) (PMAA) is an interesting polyelectrolyte, the conformation of which may be tuned by pH and/or ionic strength but also by temperature. PMAA have been reported a long time ago to form thermoreversible gels which are obtained at low pH when PMAA stands in its acidic conformation ($\alpha \sim 0$) [1]. This compartment is due to the balance between the hydrophobicity due to the methyl group and the hydrophilic one due to the carboxylic acid function. A really small ionization of the chain moves the balance in the hydrophilic direction and hinders this thermosensitive behavior.



This Lower Critical Solution Temperature (LCST) behavior of PMAA solutions has been poorly addressed in literature. In this presentation we will address an original way to construct the phase diagram of this polymer in order to determine binodal curve and LCST temperature (figure 1.A)

In a second part, we will look at the structure at nanoscale of PMAA in semi diluted regime with the help of SANS measurements (figure 2.B). Surprisingly, this transition is really slow in comparison to other LCST-behavior polymer like PNIPAM [2].

This transition occurs in two different steps which reveal two mechanisms. This complete study will help us to explain the formation of gel-like structure above cloud point.

Keywords: LCST, polyelectrolyte, phase transition

Acknowledgements: This work was supported by the LABEX MMCD.

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Post-polymerization modification of polymer brush surface coatings based on active esters

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Surface coatings derived from polymer brushes and their unique properties enabling control over the interaction between material and environment have attracted attention not only in polymer science, but also in fields like biosensing, bioadhesion, tribology, etc. So far, various synthetic paths for introducing target functionalities to polymer brush coated surfaces and interfaces were developed. Amongst them, the post-polymerization modification of reactive polymer brushes arises as a versatile tool for avoiding the difficulties with direct surface polymerization of monomers containing functional groups incompatible with the polymerization system.

In this contribution we report a straightforward strategy for the post-polymerization modification of polymer brush coatings based on N-methacryloxysuccinimide. This strategy consists of two steps- the surface-initiated atom transfer radical polymerization (SI-ATRP) of the active ester monomer, which was performed in mild conditions, followed by the post-polymerization amidation reaction of the active ester side groups. The polymerizations were performed on both Si and glass flat surfaces, modified with a self-assembled monolayer of the ATRP initiator. The desired layer thickness of 10 nm was achieved by optimizing the polymerization conditions. The following amidation reaction with various primary amines, including fluorine-containing amines and 5-amino-fluorescein, was performed so that precise control over the reaction conversion was obtained. Additionally, hierarchical block-copolymer brushes with a second block containing N-methacryloxysuccinimide monomeric units were synthesized and modified in the same manner in order to demonstrate the potential of the strategy for designing complex polymer architectures. The properties of all surface coatings were detailedly studied utilizing spectroscopic ellipsometry (SE), X-ray photoelectron (XPS) and infrared reflection-absorption (IRRAS) spectroscopies. Fluorescent microscopy performed over the fluorescein-modified polymer brushes demonstrated the homogeneity of the modified films.

Keywords: surface coating, polymer brush, surface modification

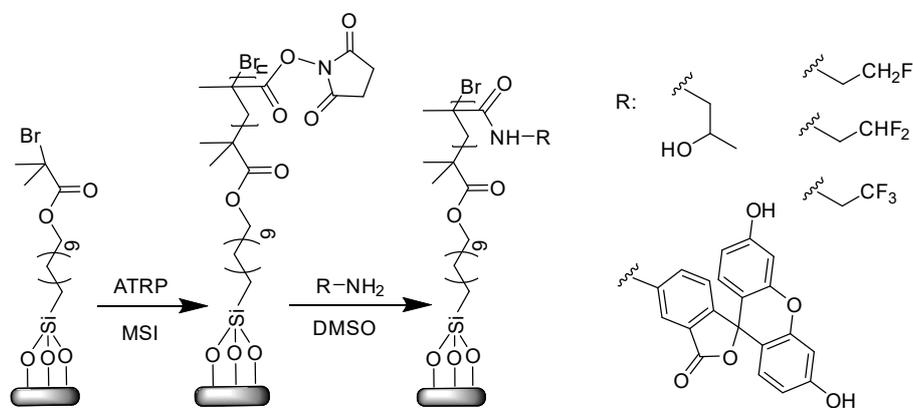


Figure 1. Synthesis of modified surface coatings

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pH-induced Changes in Formation and Stability of Polypeptide Monolayers: Experimental Studies and MD Modeling

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Polypeptides constitute a group of biopolymers composed of physiologically active aminoacids. Poly-L-lysine (PLL) and poly-L-arginine (P-Arg) have been extensively studied combining *in situ* streaming potential method, QCM-D and molecular dynamics (MD) modeling.

The macroions were characterized in bulk using the dynamic light scattering (DLS), electrophoretic mobility (LDV) and viscosity measurements. The hydrodynamic diameter of PLL and P-Arg equals to 22 nm and 12 nm, respectively. From LDV experiments, it is shown that PLL molecules are positively charged up to pH 10.5 (IEP), above which the reversal in charge is observed. In contrary, P-Arg molecules remain positively charged under the whole examined pH range [1,2]. From the viscosity measurements the basic parameters such as the conformation, the length of a single molecule (L_c) and its diameter (d_c) was determined. It was revealed that the length of the molecules decreases with increasing ionic strengths reaching 182 nm and 66 nm for $10^{-4}\text{M} - 0.15 \text{ NaCl}$ for PLL and 70 nm and 36 nm for PARG molecules for $10^{-4}\text{M} - 0.15 \text{ NaCl}$.

Knowing the bulk characteristics, the adsorption of the macroions on negatively charged mica and Si/SiO₂ substrates was studied by QCM-D and *in situ* streaming potential measurements and interpreted in terms of the 3D electrokinetic model and MD modeling. The studies confirmed the side-on adsorption of PLL molecules with the fraction of side-on with crossing adsorption for the coverage above 0.3. Moreover, using the streaming potential method, the stability of the monolayers, evaluated via desorption kinetic measurements, was determined. This allowed us to evaluate the equilibrium adsorption constant and the binding energy for the macroions at various ionic strengths and pHs. It was shown that PLL and P-Arg molecules adsorbed in the side-on conformation remain irreversibly bound with the surface. Such stable polypeptide monolayers can be efficiently used as supporting layers for nanoparticle and protein immobilization.

Keywords: polypeptides, self-assembly, streaming potential measurements, PLL and P-Arg monolayers formation and stability

Acknowledgements: The study was supported by the National Science Centre Research Grant Sonata, UMO 2018/31/D/ST5/01866 and Academy of Finland.

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Poly-L-arginine and Poly-L-lysine Molecule Characteristics in Simple Electrolytes: Experiments and Molecular Dynamic Modeling

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Polypeptides constitute a group of biopolymers composed of physiologically active aminoacids. Poly-L-lysine (PLL) and poly-L-arginine (P-Arg) have been extensively studied as drug nanocarriers, antibacterial and antimicrobial agents, anticancer vaccines etc. Even though the interactions of polypeptide molecules with other macroions as well as proteins and surfaces depend on physicochemical parameters such as: molar mass, specific density, size, geometry and surface charge, only few investigations were carried out focused on their thorough physicochemical characteristics in electrolyte solutions. Here we present the studies comprising physicochemical properties of PLL and P-Arg molecules in NaCl solutions determined by molecular dynamics (MD) modeling and various experimental techniques. Primarily, the molecule conformations, the monomer length and the chain diameter were theoretically calculated for each of the macroions. These results were used to interpret experimental data, which comprised the molecule secondary structure (CD measurements), the diffusion coefficient and the hydrodynamic diameter (DLS measurements) and the electrophoretic mobility (LDV measurements) determined at various ionic strengths and pHs. Using these data, the electrokinetic charge and the effective ionization degree of PLL and P-Arg molecules were determined. In addition, the dynamic viscosity measurements for dilute PLL and P-Arg solutions allowed to determine the molecule intrinsic viscosity, which was equal to 2420 and 120 for PLL and 500 and 90 for P-Arg molecules and ionic strength of 10^{-5} and 0.15 M, respectively. This confirmed that both PLL and P-Arg molecules assume extended conformations and approached the slender body limit at the low range of ionic strength. The experimental data also enabled to determine the molecule length and the chain diameter, which agreed with theoretical predictions. Exploiting these results, a robust method for determining the molar mass of positively charged and elongated macroions, the molecule hydrodynamic diameter, the hydrodynamic diameter, the radius of gyration and the sedimentation coefficient was proposed.

The study was supported by the National Science Centre Research Grant Sonata, UMO 2018/31/D/ST5/01866.

Keywords: polypeptides, bulk properties of PLL and PARG molecules, bulk characteristics of polypeptides, new method for determining molar mass of elongated macroions, viscosity of polypeptide solutions

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Reversible Electro-thermally Bending Soft Gripper with Triple-Layered Polymers and a Dry Adhesive Surface

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Soft grippers have attracted great interest in the soft robotics research field [1-3]. Many types of soft grippers have been reported, including air-powered soft robotic grippers, and soft actuators based on shape-memory polymers, electroactive polymers, liquid crystalline elastomers, ionic polymer-metal composites, and so forth. Due to the lack of deformability and control over compliance, it is not so easy to grab or lift objects of too large or too small sizes. In particular, compliant objects are vulnerable to large grasping force. Therefore, it is crucial to be able to manipulate the rigidity of the gripper materials in response to external triggers such as light, heat, electric or magnetic fields, etc.

In this study, a soft gripper is presented consisting of a triple-layered polymer structure. An exterior layer made of an ecoflex-graphene composite embedding electric wires is adopted as a heat source by applying a direct-current potential. The generated heat will not only deform the first layer, but will also transfer heat to the middle layer of thermoplastic polyurethane (TPU), allowing for adjustable bending by varying the electro-thermal energy. Consequently, the modulus of the TPU layer can be reversibly tuned by electrical heating and natural cooling. As for the bottom layer, a polydimethylsiloxane replica from a microstructured mold is used as a gecko-inspired dry adhesive surface. With deformation of the external thicker layers of polymer, the dry adhesive layer can adhere to various irregular surfaces of either rigid or flexible objects. By this means, it is feasible for an assembled soft gripper to grab objects like a glass beaker, shuttlecock, tennis ball, and so on. This research may offer an insight in the fabrication and application of practical soft grippers.

Keywords: soft gripper, thermoplastic polyurethane, polydimethylsiloxane, ecoflex-graphene composite, gecko-inspired dry adhesive, electro-thermal bending

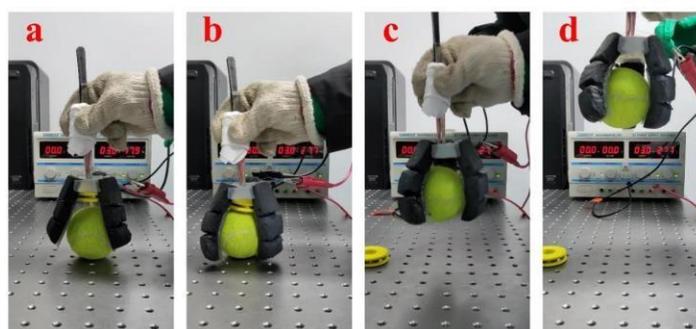


Figure 1. Demonstration of soft gripper grabbing a tennis ball with triple-layered polymer structure

Acknowledgements: This work is partially supported by funding of China Scholarship Council.

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The Impact of Surfactant-Free Mesostructured Liquids on Free-Radical Polymerizations in Those

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Today, several systems for polymerizations are known, but especially polymerizations in (micro)emulsion and (micro)suspension comprise an attractive technique. By using microemulsions it is possible to tune the polymer size and morphology, while yields are usually good and temperature control is not a problem. However, the surfactants or auxiliary colloids might have an impact on the latter polymer properties. For example, surfactants have been shown to accelerate the release of small molecules (plasticizers) from a polymeric workpiece into the environment. [1]

Surfactant-free microemulsions (SFME) are ternary, mesostructured liquids consisting of an oil, water, and a hydrotrope. SFMEs were firstly postulated in the late 1970s and found their way to applications as mesostructured reaction systems in the context of enzymatic reactions in the 1980s [2,3]. However, it took until the last two decades that SFMEs were investigated in more detail. In terms of polymerizations, only a limited number of studies in SFME were presented in the last years. All of them present quite special applications. [2]

This study shows the use of SFME as a template for free-radical polymerizations. We present a simple system composed of water, the monomer methyl methacrylate as the oil phase, and small-chain alcohols (iso-propanol, n-propanol, tert-butyl alcohol) as hydrotropes. The polymerizations can be performed by using commercially available thermal or UV activated initiators, such as peroxodicarbonates. The polymerization is affected by the exact composition of the ternary mixture in the phase diagram, as well as the choice of the different hydrotropes, and thus the mesoscale structures. We observe remarkable differences in the morphology, yield, and mean molar mass of the derived polymers. [3]

Keywords: surfactant-free microemulsions, mesostructured aggregates, structured reaction media, polymerizations, free-radical polymerizations

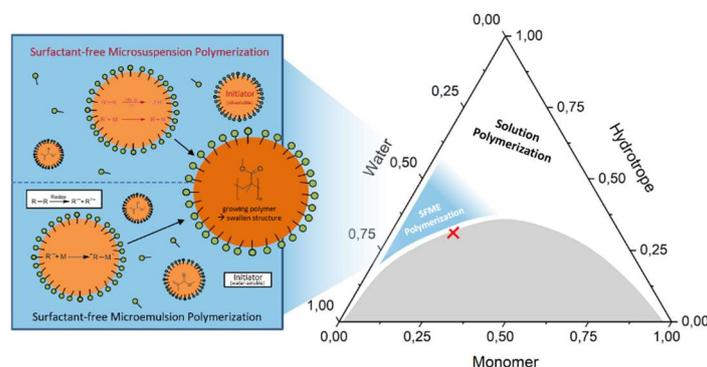


Figure 1. Water – alcohol – (vinyllic) monomer structured mixtures (SFME), for which polymerizations can be fine-tuned, concerning morphology, yield, and mean molar mass.

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Confining effects of transparent PEG hydrogels on microgel transport

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Many attractive phenomena from physics to biology, applications from medicine to environmental science are associated to the colloids' diffusion through 3D heterogenous matrices. The detailed knowledge of matrix's morphology is the key to understand the relation between diffusion properties of micro and nanometric particles, and the structural features of the confining network. Effects of confinement were well-studied in quasi-2D and highly ordered 3D matrices [1-2], nevertheless, prediction of particles' transport in disordered porous natural-like media requires additional efforts.

In order to relate the diffusion properties with the confining disordered matrices, we developed transparent porous hydrogels of poly(ethylene glycol) (PEG). The photo-polymerization of the diacrylated monomer, and the subsequent freeze-drying of the resulting hydrogel allows the synthesis of transparent 3D networks with tunable porosity at the micron scale. A detailed analysis of the hydrogel structure combining different techniques [3], including confocal microscopy applied to fluorescently labeled networks, allowed us to determine the 3D porosity of the hydrogels. This revealed complex, interconnected, channel-like porous networks, in which the section of the channel decreases as a function of increasing monomer concentration in the pre-reaction mixture.

The confining effects imposed by the porous structure of the hydrogels were tested on thermoresponsive pNIPAM microgels. Trajectories and mean square displacements obtained from particle tracking analyses highlight a slowdown of the microgels dynamics as a result on the increasing confinement degree. The extrapolated effective diffusivity coefficient and the diffusion exponent were related to the 3D porous structure through the confinement length, the particle area fraction, and the pore volume fraction of the confining hydrogels.

The precise characterization of the porous network is crucial for the complete understanding of colloids' transport processes in disordered porous natural-like media. Our work represents an excellent starting point for the investigation of more complex system (i.e., bacteria) with interesting implication in colloids' filtration, anti-bacterial strategies, and selective absorption.

Keywords: Transparent Hydrogel, Tortuosity, Morphological characterization, Particle Tracking, Transport properties, Micrometric Confinement

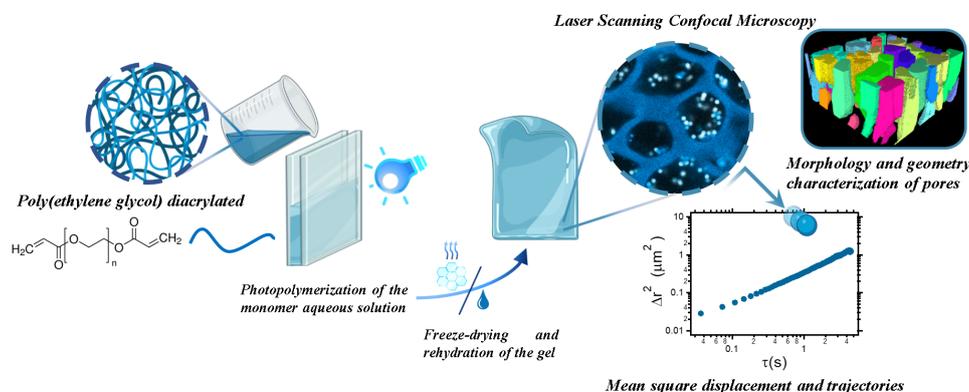


Figure 1. Synthesis of the hydrogel followed by structural characterization and particle tracking analysis of the diffusing loaded particles.

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Synthesis, structure, and gelling power of γ - In_2S_3 nanoribbons with large aspect ratio

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Indium sulfide is a widegap semiconductor material which could be an ideal candidate for various opto-electronic applications. We report the synthesis of ultrathin indium sulfide In_2S_3 nanoribbons (NR) which display a giant aspect ratio using a simple and fast solvothermal method. We show that these NR have a thickness controlled at the atomic level below the nanometer, a width of 8.7 ± 0.1 nm and a length which can reach several micrometers. We determined the atomic composition of the inorganic core by Rutherford backscattering spectrometry (RBS) and measured by X-ray photoelectron spectrometry (XPS) an oleylamine surface coverage of 2.3 ligands per nm^2 . X-ray diffraction experiments and simulations as well as high-resolution dark-field STEM point towards a $P\text{-}3m1$ trigonal crystallographic structure (γ phase).

Their lateral dimensions can be tuned by the amount of water present in the reaction medium: anhydrous synthesis conditions lead to hexagonal nanoplates whereas controlled addition of water induces a symmetry break yielding long NR with a rectangular shape. Depending on the dispersion solvent, these long ribbon-like nanoparticles can form either well dispersed colloids or bundles in which they stack face to face. Their large aspect ratio induces the formation of gels at volume fractions as low as 1.3×10^{-4} .

We believe our work could open valuable perspectives for the design of functional highly anisotropic and ultrathin nanomaterials [1] since it could serve as a starting point for further ion exchange with potential applications beyond toxic Cd and Pb based semiconductors.

Keywords: indium sulfide, nanoribbons, crystallography, shape-controlled synthesis, TEM, gel

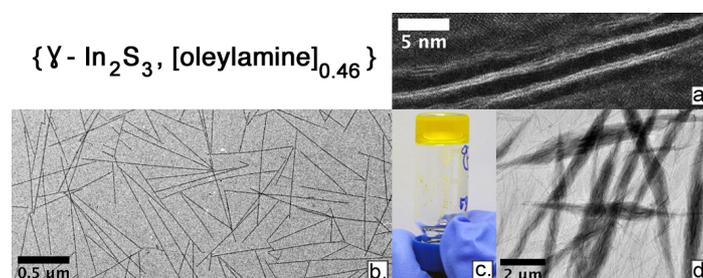


Figure 1. TEM images of In_2S_3 nanoribbons: a. lying on their edge ; b. lying flat - c. Image of a gel of In_2S_3 nanoribbons colloidal solution – d. Bundles of In_2S_3 nanoribbons.

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Stack cluster formation in dense solutions of DNA mini-rings: a simulation study

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Semiflexible ring polymers in dense solutions are known to form a cluster-glass phase, in which rings assemble into cylindrical stacks. The phenomena emerge mainly as a consequence of topological constraints due to the ring-like architecture of the macromolecules. The same topological effects play an essential role in organization of DNA in living systems and therefore, ring polymers can serve as a model for human chromosomes. Unfortunately, most of our knowledge about ring polymers comes from computer simulations of generic neutral macromolecules, and the interpolation to the DNA is not straightforward. For instance, the electrostatic interaction present between DNA segments, is often omitted in generic polymer simulation models. In this study, we employed molecular simulations to explore the differences between behaviour of ssDNA ring polyelectrolytes, and their neutral counterparts. We found out that at low polymer concentrations, polyelectrolytes form cluster-glass phase, very similar to the phase of neutral rings. However, at higher concentrations, polyelectrolyte rings shrink, due to the interaction with their counterions. Consequently, polyelectrolytes in this concentration regime do not form cluster stacks, in contrast to their neutral counterparts. Ultimately, our results show that connection between particular DNA macromolecules and generic models should be done with caution.

Keywords: ring polymers, polyelectrolytes, computer simulations

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Effective interactions between ring polymers of different sizes and flexibilities

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Ring polymers can be found in nature in the form of plasmids, bacterial DNA or kinetoplasts. Certain features of organization and regulation of these circular biomacromolecules in the living systems are of generic and universal nature, underlining the need for understanding the fundamental aspects of physics of ring polymers. In this study, we use computer simulations to derive effective potentials between ring polymers differing in flexibility and size. We also analyze threading effects between the rings and correlated them with threading-induced changes in shape and geometry of the respective polymers.

Keywords: ring polymers, coarse-graining, threading effects

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GSHU, a parameter to generalize and regulate the degree of enzymolysis on the granule starches

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Starch is the second most abundant biological polymer, after cellulose, produced on earth. Native starch exists in the form of granules of different sizes and shapes, that depend on the botanical source. Porous starch is a modified starch that is non-toxic and economical adsorbent extensively used in food, pharmaceutical and environmental applications. It consists of abundant pores that are distributed on the granule surface and extend towards the central cavities, without changing the granular structure. Enzymolysis of raw starch granule at sub-gelatinization temperature is a good way to make porous starch. The alternating structure of amorphous and crystalline layers of starch guarantees the continuity of this hydrolysis.

In this work, we form porous starch from 10 native starches from different botanical sources by hydrolysis with amylase. We study the structure and morphology using advanced electron microscopy methods, and additionally defined the concept of GSHU (Granule Starch Hydrolysis Units) and prove it is a useful tool to regulate double-amylase hydrolysis treated with UHP (Ultra high-pressure processing). GSHU reflects the difficulty of how granular starches are attacked by enzyme and it can be a good way to unify the degree of hydrolysis of granule starch. With UHP treatment, lower amount of enzyme (or shorter processing) is needed to reach the same porosity compared to untreated samples. The GSHU parameter can guide the selection of catalysts to achieve similar porosity.

Keywords: granule starch, enzymolysis, porous starch

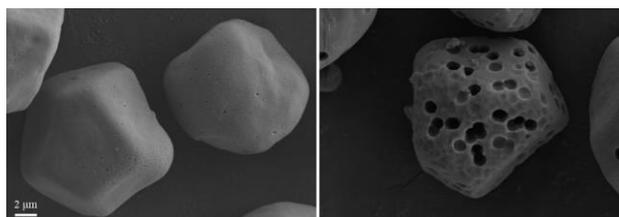


Figure 1. Native starch (left) and porous starch made via enzymolysis (right).

Structure and electrostatic properties of polyelectrolyte dendrimer brushes

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Being ubiquitous substances in Nature and technology, the theoretical study of polyelectrolytes is a vast and highly relevant topic in the field of polymer physics. Among their many applications, polyelectrolytes have been extensively used to functionalize the surface of very diverse materials, including colloidal particles, frequently as polymer brush coatings. For instance, polyelectrolyte brushes are broadly used to stabilize electrostatically colloidal particles in suspension. Another interesting application that is being actively studied nowadays is the electrostatic adsorption of ions and charged molecules on the polyelectrolyte shell of colloidal particles for separation purposes. To this regard, the usage of polyelectrolytes with hyperbranched structure instead of the conventional linear one provides a large and well defined number of tunable functional groups in both, the surface and internal regions of the polyelectrolyte shell, as well as a large number of internal cavities that can host the adsorbed substances [1].

Despite their interest, polyelectrolyte dendrimer brushes have been poorly studied theoretically to date [2]. In this work we present an extensive computer simulation study of the structure and electrostatic properties of these systems by means of Langevin dynamics simulations with a primitive model. In particular, we focus on planar brushes made of PAMAM G5 dendrimers, analyzing their properties as a function of the grafting density, the degree of protonation of the dendrimers and the surface charge of the grafting surface, as corresponding to different pH conditions. Preliminary steps to develop an accurate Poisson-Boltzmann theory on the basis of these results and their extension to spherical surfaces will be also outlined.

Keywords: dendrimers, polyelectrolyte brushes, electrostatics, modeling

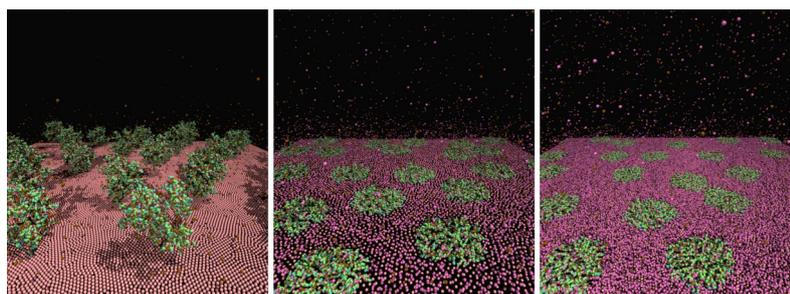


Figure 1. Simulation snapshots with examples of equilibrium structures of a sparse dendrimer brush under different pH conditions.

Acknowledgements: Research supported by the project “Computer modeling of magnetic nanosorbents”, funded by the University of the Balearic Islands and the European Regional Development Fund.

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Influence of poly(ϵ -caprolactone) end-groups on the temperature-induced macroscopic gelation of Pluronic in aqueous media

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Amphiphilic block copolymers with different architectures and chemical compositions that self-assemble and form hydrogels in the semidilute concentration regime in response to external stimuli constitute an essential class of soft materials, with applications in areas such as drug delivery, gene delivery, tissue engineering, and smart surface coatings.

One of the most studied commercially available amphiphilic copolymers are the Pluronic triblock copolymers, composed of hydrophilic poly(ethylene oxide) (PEO) at both ends and a hydrophobic poly(propylene oxide) block as a spacer. Decades of experimental and theoretical studies have established a solid insight into the self-assembly, micelle and gel formation, structures, and phase behavior of Pluronics.

However, because of the rather low hydrophobicity of the PPO-block in Pluronics it has been pointed out that this type of copolymer is not suitable as a long-term drug delivery vehicle since it has short gel duration (less than 1 day) after implanting the hydrogel in the subcutaneous layer.

To strengthen the hydrophobicity and to be able to design a durable and degradable thermogel, we synthesized modified versions of the copolymer of the type PEO-PPO-PEO (Pluronic, F127) with short poly (ϵ -caprolactone) (PCL(5)) or long (PCL(11)) PCL blocks at both ends. We investigated what kind of structures and rheological behavior appear in the semidilute concentration regime and in the hydrogels formed at elevated temperatures by performing rheology and SANS experiments, complemented with gel phase separation studies.

The aim of this work was to understand the impact of the PCL end-groups in the formation of the transient network in the semidilute concentration range and how the gel-formation evolved at higher temperatures will be affected by the PCL-groups. It was revealed that the PCL modification of Pluronic leads to significant alterations of the rheological features, as well as consequences on the local structure probed by SANS.

Keywords: Self-assembly, amphiphilic polymers, drug delivery, gels assembly and supramolecular structures

Controlled deposition of cellulose nanocrystals for tuning ultrafiltration membrane performance

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Cellulose nanocrystals (CNCs) are nanorods of ca. 20 nm diameter and 200 nm length, derived from cellulose via acid hydrolysis. They exhibit good colloidal stability due to sulfate groups on their surface formed upon sulfuric acid hydrolysis. Their aqueous suspensions assemble into chiral nematic structures above a certain concentration and show nematic order under shear (*Figure 1.a*). In this study, we utilized the shear alignment of CNCs for tuning the interparticle distance in CNC deposit layers formed on porous supports in tangential flow filtration. Furthermore, we showed that we can also tune the interparticle distance in these CNC layers by varying the ionic strength of the CNC suspension using NaCl (0-50 mM). After deposition of the CNC layer on the porous support, a highly concentrated AlCl₃ solution was permeated through the deposit to diminish electrostatic repulsion between nanocrystals and cause irreversible coagulation of CNCs. The CNC layers obtained as such showed ultrafiltration membrane properties, where the separation performance varied with shear rate and ionic strength used during CNC deposition. Alternatively, we also showed that membrane layers formed of carboxyl-functionalized CNCs can be chemically crosslinked via Ag(I)-catalyzed oxidative decarboxylation, providing an additional means of stabilizing the membrane layer [1].

During filtration of aqueous CNC suspensions, as shear rate increased, we observed an increase in alignment of nanocrystals in the membrane layer (*Figure 1.b and c*) and this increased the membranes' rejection towards a probe molecule, blue dextran (5 kDa), which implies that with increasing extent of alignment, CNC packing became denser [2]. When the nanocrystal suspension contained an increasing concentration of NaCl during deposition, dextran rejection increased which is attributed to screened electrostatic interactions allowing the nanorods forming the membrane layer to deposit in a more compact form. Pure water permeances of CNC membranes were comparable to commercial membranes of similar rejection behavior.

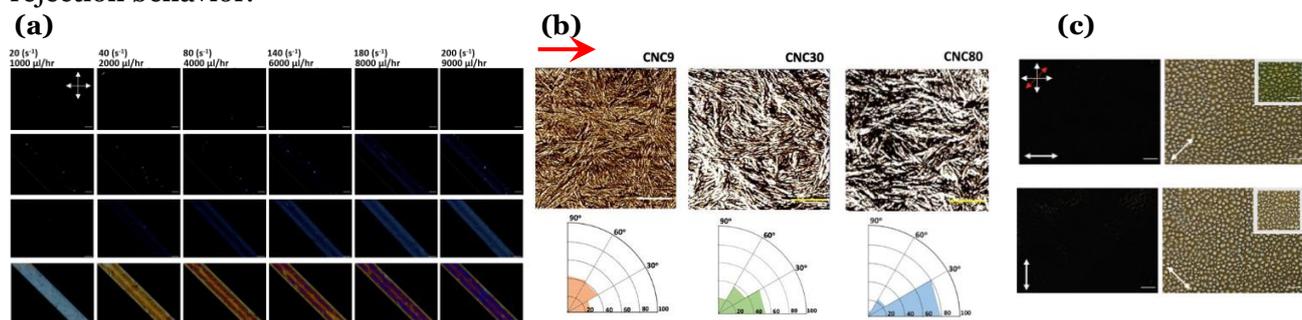


Figure 1. (a) Polarized optical microscopy images of cellulose nanocrystal suspension flow in capillary tube at different concentrations: 1.5, 2.0, 3.2 and 6.4% (w/v) from top to bottom, (b) AFM phase images of membrane surfaces fabricated under increasing tangential flow rate during nanocrystal deposition (9, 30 and 80 mL/min for CNC9, CNC30 and CNC80, respectively), (c) Polarized light images of CNC80 membranes. Single white arrow: feed flow direction. Crossed arrows: direction of analyzer and polarizer. Scale bars: 250 µm (Insets: First order retardation plate images. Additive red arrow to crossed polarizers represents the direction of first order retardation plate. Inset scale bar: 100 µm)

Keywords: Cellulose nanocrystals, ultrafiltration, nematic liquid crystal, shear alignment

Acknowledgements: The authors thank financial support by TUBITAK, Grant No: 119M828.

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Polyelectrolyte multilayer membranes via layer-by-layer assembly of cellulose-based polyelectrolytes

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Polyelectrolyte multilayer membranes fabricated via layer-by-layer (LbL) assembly have gained increasing interest in the past decades owing to the precise control over fabrication conditions they offer and therefore over membrane properties. Natural nanofibers, which have been demonstrated in other applications of the layer-by-layer assembly technique, have not yet been exploited in membrane applications. Within this context, cellulose nanocrystals and nanofibers are especially interesting due to the liquid crystalline behavior of cellulose nanocrystals which enables additional control in their assembly [1] and the excellent solvent resistance of cellulosic materials, enabling their use in organic solvent nanofiltration [2].

We used cellulose nanofibrils (CNF) containing carboxyl groups and poly(diallyldimethylammonium chloride) (PDADMAC) in fabricating membranes by layer-by-layer assembly at different salt concentrations (5 and 50 mM NaCl) during deposition (Figure 1).

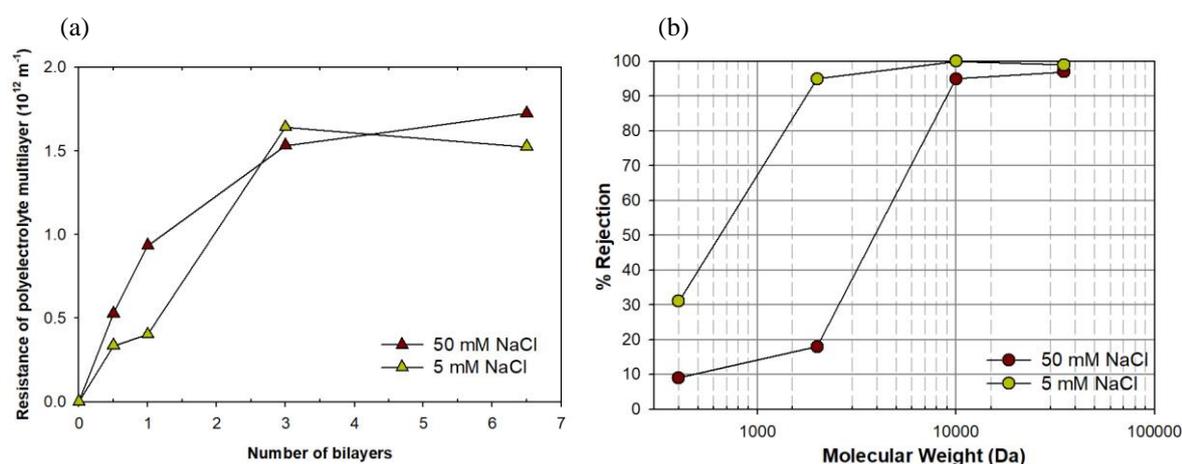


Figure 1. (a) Resistance of polyelectrolyte layers (b) Rejection of polyelectrolyte multilayer membranes for poly(ethylene glycol) probes of varying molecular weight. Support is negatively charged so half bilayers are PDADMAC-terminating and full bilayers are CNF-terminating.

Deposited on a negatively charged cellulose ultrafiltration membrane (Millipore, Ultracel 10 kDa) as support, for 6.5 bilayers the resistance increase upon polyelectrolyte deposition was similar when the PDADMAC solution and CNF suspension contained 5 and 50 mM NaCl. The rejections on the other hand were higher when the NaCl concentration was 5 mM, which probably implies a thinner and denser deposit.

Keywords: Cellulose nanocrystals, cellulose nanofibrils, polyelectrolyte multilayer membranes, layer-by-layer assembly

Acknowledgements: The authors thank Prof. Dr. Sedat Ondaral for supplying CNF and financial support by TUBITAK, Grant No: 121M320.

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Simulations and potentiometric titrations enable reliable determination of effective pKa values of various polyzwitterions

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We synthesized three different polyzwitterions: poly(N,N-diallylglutamate) (PDAGA), polydehydroalanine (PDha), poly(2-(imidazol-1-yl)acrylic acid) (PIAA), and investigated how their ionization states respond to changes in solution pH. We used molecular simulations to determine how the net charge per monomer and the ionization states of individual acidic and basic groups differ from the ideal (Henderson-Hasselbalch) behavior. To complement the theoretical predictions, we performed potentiometric titrations and zeta potential measurements of all studied polyzwitterions. By comparing these experiments with theoretical predictions we could show that molecular simulations can predict and explain the origin of the differences between the effective and bare pKa values of individual titratable groups. Furthermore, we have shown that it is not possible to obtain these effective pKa values directly from the equivalence point recognition criterion (ERC), commonly used in potentiometric titrations. However, the effective pKa values can be reliably obtained by calculating the net charge per monomer from the potentiometric titration curves and validating these results against theoretical predictions. The approach we propose works reliably for polyzwitterions in which the ionization response is dominated by electrostatic interactions, such as PDAGA or PDha, however, it fails if other specific interactions contribute significantly, such as in the case of PIAA.

Keywords: charge regulation, polyzwitterion ionization

PDha: Polydehydroalanine

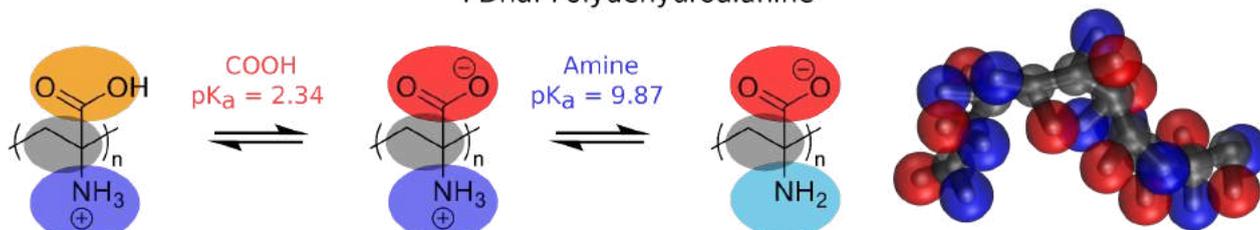


Figure 1. Schematics of the chemical structure of polydehydroalanine with its different ionization states. The simulation snapshot represents the coarse-grained model used in our simulations. Colour code: grey = backbone; red or orange = acidic side-chain; cyan or blue = basic side-chain.

Charge-Regulation and Charge-Patch Distribution Can Drive Adsorption on the Wrong Side of the Isoelectric Point

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The mechanism of protein–polyelectrolyte complexation on the wrong side of the isoelectric point has long puzzled researchers. Two alternative explanations have been proposed in the literature: (a) the charge-patch (CP) mechanism, based on the inhomogeneous distribution of charges on the protein, and (b) the charge-regulation (CR) mechanism, based on the variable charge of a weak acid and base groups, which may invert the protein charge in the presence of another highly charged object. To discern these two mechanisms, we simulated artificially constructed short peptides, containing acidic and basic residues, arranged in a blocklike or alternating sequence. Our simulations of these peptides, interacting with polyelectrolytes, showed that charge patch and charge regulation alone can both lead to adsorption on the wrong side of the pI value. Their simultaneous presence enhances adsorption, whereas their absence prevents adsorption. Our simulation results were rationalized by following the variation of the charge regulation capacity and dipole moments of these peptides with the pH. Specifically for lysozyme, we found that charge patch prevails at physiological pH, whereas charge regulation prevails near the pI, thereby explaining seemingly contradicting conclusions in the literature. By applying the same approach to other proteins, we developed a general framework for assessing the role of the CP and CR mechanisms in existing case studies and for predicting how various proteins interact with polyelectrolytes at different pH values.[1]

Keywords: Adsorption, Peptides and proteins, Acid and base chemistry

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Data-driven Investigations on Topologically Constrained Conformal Fluctuations in Entangled Polymer Melt

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In entangled linear polymer melt, motion of a typical chain is constrained in a "tube"-like region while equilibrium dynamics is dominated by "reptation", whereby kinks or structural defects propagate along the chain. We employ a data-driven approach to understand the shape fluctuation, and relate this conformational changes with the dynamics. To this end, Cartesian and internal coordinates are used to form the higher dimensional feature space. The measurements of these observables are extracted from equilibrium molecular dynamics simulations of long semiflexible polymer chains in a melt. Principal component analysis (PCA), and time-lagged independent coordinate analysis (TICA) are employed to embed the data to a lower dimensional space. We relate PCA modes to structure, and interpret TICA modes in terms of both structural and dynamic properties.

Keywords: Entangled Polymer Melt, Machine Learning, Sub-diffusion

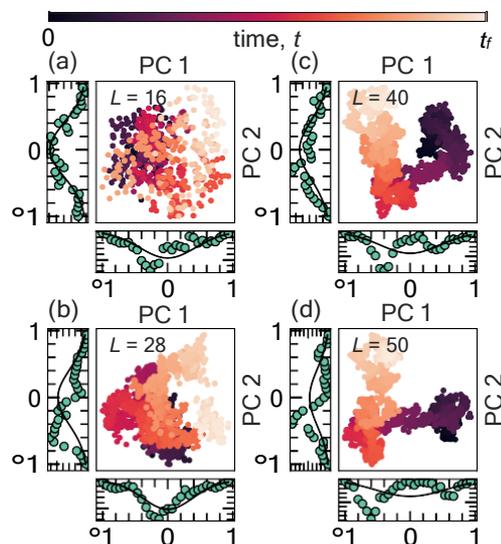


Figure 1. PCA projections corresponding to polymers of different sizes. Distinct "U-shape" pattern, characteristic of correlated input data, emerge beyond entanglement length.

Biofunctional polymer brush coatings on the nanoscale

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Biofunctional polymer layers composed of antifouling polymer brushes and containing extracellular matrix-derived peptide motifs offer promising new options for biomimetic surface engineering [1]. We utilize grafting-to and grafting-from synthesis methods for attaining the polymer brush conformation, and further functionalize the brushes with various biomimetic peptide sequences, such as RGD and TYRAY. The characterization of obtained systems goes beyond the state-of-the-art findings based on far-field analytical techniques for proving the brush character of the synthesized polymer structures, their antifouling character and the biofunctionality induced by the presence of various peptide motifs. By utilizing mid-infrared nanoscopy methods of scattering type scanning near-field optical microscopy and nanoFTIR we unravel the conformation and orientation of the individual polymer chains constituting the polymer brush films [2] and directly determine the distribution of bifunctional peptides with a nanoscale resolution. We foresee that measurements under controlled temperature, humidity, or in liquids will give further physicochemical insight into bioactivity of these polymer brushes architectures [2,3].

Keywords: biofunctional polymer brushes, near-field spectroscopies, sSNOM, nanoFTIR, conformation, orientation

Acknowledgements: Financial support from Czech Grant Foundation (grant No. 20-07313S and 22-02836S) and is gratefully acknowledged. Research was partly carried out within the NANOPOL H2020-MSCA-RISE-2018 (Project Nr.823883) consortium.

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Encapsulation of Phycocyanin in hydrogels

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Phycocyanin (PC) is a highly degradable light-harvesting protein produced in cyanobacteria. Its distinct blue color is produced by its chromophore, phycocyanobilin (PCB), bound to the protein via a thioether bond. So far, PC has found several applications in the fields of biotechnology, food science, cosmetics and pharmaceuticals, owing primarily to its ability to be used as a blue dye and its potential as an antioxidant [1].

This work has aimed to produce cyanobacterial extracts of high PC content from commercially available *Arthrospira maxima*, whose production has not been designed for increased PC yields. PC extraction has focused on the use of facile, existing protocols, involving biomass lysis, protein precipitation, dialysis and further isolation and purification by ion exchange and size exclusion chromatography.

Subsequently, PC was encapsulated in polymeric hydrogels. Hydrogels represent a simple and affordable tool for the creation of an environment that maintains the properties of biologics [2]. They consist of three-dimensional networks, generated by hydrophilic polymers. These networks enclose high water content, allowing the encapsulation of hydrophilic molecules. The encapsulation of PC in hydrogels created by natural biopolymers like chitosan and cellulose is investigated towards the ability to increase the stability of the color associated with the protein against high temperatures, extreme pH and light-induced color loss. Our work aims to validate protein stability in hydrogel systems via evaluation of its antioxidant properties by Electron Paramagnetic Resonance (EPR).

Keywords: Phycocyanin, Hydrogels, Spirulina, *Arthrospira maxima*, Antioxidant activity

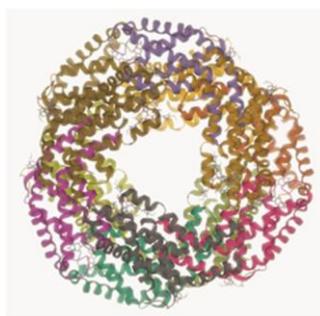


Figure 1. Phycocyanin.

Acknowledgements: Part of this work was financially supported by ANSO Project No. ANSO-CR-PP-2021-01.

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Structure-rheology relationships in gelling carrageenan hydrocolloids

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Gelling carrageenans are hydrocolloids used extensively in the food industry, but the structure–elastic relationships in the gel network are still to be clearly established [1]. After reviewing the structures and rheological properties documented so far for gelling carrageenans, selected linear and nonlinear elastic models for filamentous gels will be introduced. Then, preliminary results for the concentration scaling of the strain hardening exhibited by iota-carrageenan and hybrid-carrageenans will be presented. In addition, the nonlinear elastic properties of blends of kappa- and iota-carrageenan will be systematically compared with those of hybrid-carrageenan gels exhibiting equivalent disaccharide contents. Finally, the effects on normal stress build up during gelation on the nonlinear elastic properties will be questioned.

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Core-shell interfacial interpenetration control forms microgels with switchable elasticity

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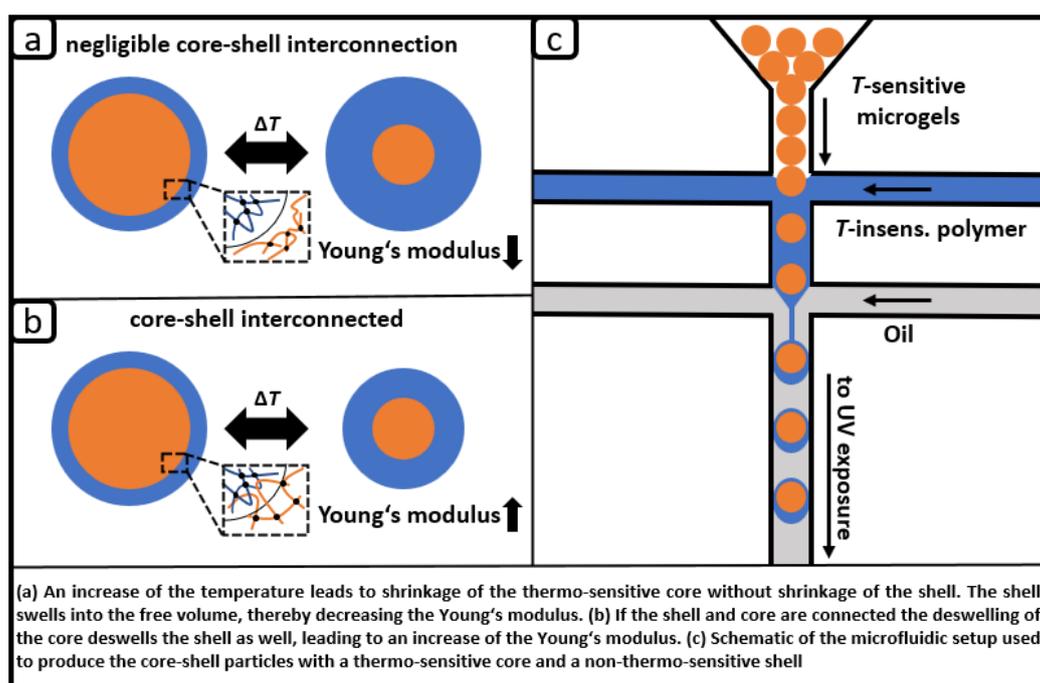
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Thermo-sensitive gels exhibit controllable swelling-deswelling transitions upon change of temperature, thereby switching their elastic and Young's moduli. On top of that, the transition leads to a change in their adhesiveness. To decouple these two effects, we form core-shell particles with a thermo-sensitive core and a thermo-insensitive shell. These microgels take advantage of the swelling-deswelling transition, while the outer adhesiveness remains constant.

To achieve this goal, droplet-based microfluidics serves us to form microgel core-shell particles of about 400 μm diameter, containing a thermo-sensitive hydrogel core made of poly(N-isopropylacrylamide) (pNIPAAm) about 300 μm in diameter and a non-thermo-sensitive shell made of an about 100 μm thick shell of polyacrylamide. Through variation of the time of gelation of the shell via UV irradiation, the extent of interpenetration of the core and shell is varied, resulting in core-shell particles with interconnected cores and shells and particles with negligible core-shell interconnection. Due to the thermo-sensitive core of the core-shell particles, the core deswells upon an increase of the temperature, changing the particle surficial Young's modulus in a way that decisively depends on the interconnection of the shell and core.

Keywords: core-shell particles, interpenetration, thermoresponsivity, droplet-based microfluidics, switchable elasticity



Electrostatically cross-linked chitosan nanoparticles intended for agricultural use

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Chitosan (CS) is an abundant cationic natural biopolymer derived by the alkaline N-deacetylation of chitin [1]. It is biocompatible, non-toxic, has antimicrobial properties and acts as a phytostimulator (elicitor), inducing plant defense mechanisms and preparing them for impending attack by bacteria, fungi and viruses [2]. Therefore, its potential use in agriculture for the control of pathogens constitutes a promising alternative to traditional chemical fertilizers and pesticides that raise concerns related to public health, environmental protection, and development of resistant pests [2].

In this work we report on the preparation of chitosan nanoparticles (CS-NPs) utilizing electrostatic cross-linking with suitable organic molecules (e.g., tannic acid), that can be subsequently loaded with organic/biological substances, relevant to their intended agricultural use (i.e., adjuvants, metabolites, etc.). Different formulations in regard to CS concentration, mixing ratios, and preparation protocols were investigated aiming to the development of stable nanosized products. The resulting nanoparticles were characterized as to their mass, size, size distribution and effective charge by dynamic and electrophoretic light scattering (DLS and ELS). Further structural insight was obtained through UV-Vis and fluorescence spectroscopic measurements.

Overall, the produced chitosan nanoparticles exhibit favorable properties that deem them suitable for use in agriculture, where they can act as a means of controlling plant diseases and at the same time improve plant health.

Keywords: chitosan, nanoparticles, cross-linking, plant health

Acknowledgements: This work is co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE - INNOVATE (project code: T2EDK-02113).

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Biobased flame retardant coatings based on polyphenol-polyphosphazene colloids

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The design of new biobased and environmentally-friendly flame retardants (FR) is of great importance, especially in the construction, electrical and textile industries. Due to updates of safety and environmental regulations, syntheses of FR materials continuously meet new challenges. Therefore, the current interest is the development of new, halogen-free FR to reduce the environmental and health impact.^[1]

The present work is concerned with the development of sustainable halogen-free cyclomatrix polyphosphazene coatings for textiles. This will be realized by combining the phosphornitrilic chlorid trimer (HCCP) with biobased polyphenols extracted from lignin. The synthesis is started by base addition and the cyclomatrix colloids are formed by a precipitation polycondensation. Mild reaction conditions, simple purification and scalability are favorable to improve the sustainability even further.^[2] This new FR material promises high thermal stability, low degradation, and high charring conditions due to a high phosphorus and nitrogen content.

After deposition of the FR coating on the surface of textile fibers the flame retardant activity was evaluated. The flame-retardant activity of polyphenol-polyphosphazenes can be directly influenced by the polymer composition and the coating amount. The influence of the chemical composition of the biobased polyphenol-polyphosphazenes colloids on the thermal stability and performance as FR was systematically investigated in bulk and as coatings on textiles by various analytical methods like thermogravimetric analysis, vertical flame tests and Limiting Oxidation Index (LOI) measurements.

Keywords: precipitation polycondensation, synthesis, functional coatings, biobased flame retardants

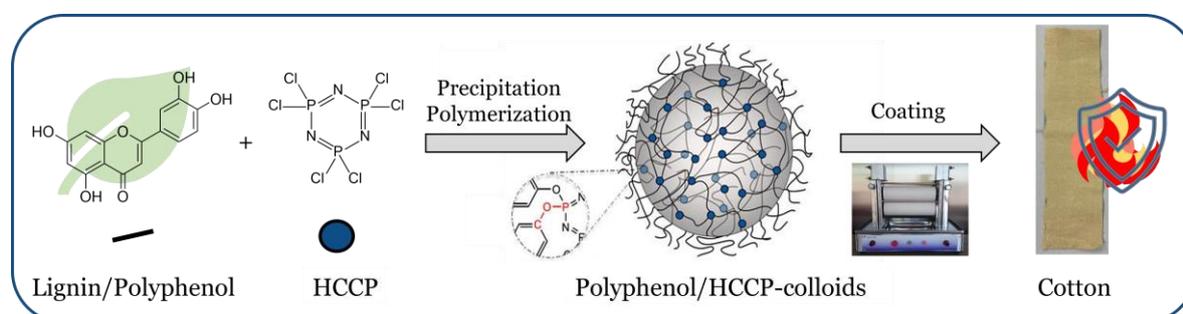


Figure 1. Synthesis of polyphenol-polyphosphazene-(HCCP) colloids subsequent coating process.

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Silver Nanoparticles stabilized with citrate and L-cysteine: structural and toxicological studies.

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Heavy metal ions in water are released through industrial, agricultural, and domestic activities, and it is well known their toxicity and negative impact on humans and the environment [1-2]. For this reason, there is an increasing need of innovative systems able to interact selectively and effectively with heavy metals ions, that can be used for water remediation. With this aim, we synthesized silver nanoparticles (AgNPs) stabilized with L-cysteine and citrate, and analyzed their electronic and molecular structure, as well as their morphology, in the presence of arsenic and cadmium ions. The characteristic structure at the interface between ligands and AgNPs was probed by complementary synchrotron radiation induced techniques (SR-XPS and NEXAFS). The sensitivity to the presence of cadmium and arsenic was assessed in water by UV-visible absorption. In addition, we evaluated in vitro the toxicological profile of the innovative nano-system using a human epithelial cell line (HEK293T). We analyzed cell viability after AgNPs treatment as well as the activation of the antioxidant response. In fact, the possibility to design nano-system able to chelate selectively heavy metal ions can represent an interesting perspective in the field of therapies for heavy metal poisoning in human.

Keywords: silver nanoparticles, heavy metals ions, toxicology

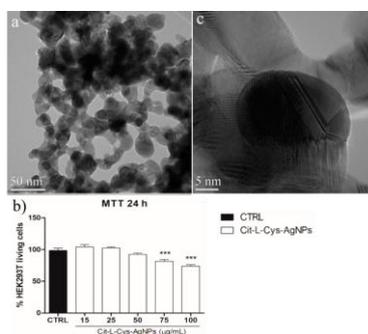


Figure 1. of AgNPs/L-cys/citr: (a) TEM and (c) HRTEM image; (b) Effect on the viability of HEK293T cells [3].

Acknowledgements: The authors gratefully acknowledge the Grant of Excellence Departments, MIUR (ARTICOLO 1, COMMI 314–337 LEGGE 232/2016) and Regione Lazio, through Progetto “Gruppi di ricerca 2020”-POR FESR Lazio 2014-2020-Azione 1.2.1 prot. A0375-2020-36521.

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Controlling Self-Propelled Motion of Polystyrene Particles with Pt Spots Deposited by UV Irradiation Technique

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Self-propelled particles are one of the micro-nano devices, and it has been actively studied for their potential applications in chemical sensors and drug delivery systems. The self-propelled particles are composed of a based particle with catalytic metal loaded on a specific site of the based particle. The self-propelled motion of their particles is generally difficult to control because the conventional technique can not control preciously the size, position and number of catalytic metal spots that governing the motion. Therefore, regulating the motion is the challenging topic of self-propelled particles.

In this study, we demonstrate that polystyrene (PS) particles with Pt spots deposited on desired positions of the surface can be prepared by irradiating ultraviolet (UV) light onto the particles floating on aqueous solutions of Pt ions, and the size and position of the Pt spots are adjustable by the power and incidence angle of UV light. We will discuss the effects of the size and position of Pt spots on the self-propelled motion of Pt-PS particles.

The monolayer of PS particles (diameter: 12 μm) were prepared on an aqueous solution of potassium tetrachloroplatinate (II), and UV light was irradiated on the monolayer. SEM images (Fig.1) show that Pt is surely deposited on the surface of the PS particle. Pt deposited PS particles were dispersed in hydrogen peroxide solutions, and the self-propelled motion was observed with an optical microscope. PS particles with a single Pt spot (Fig. 2a) showed a straight motion and the moving speed increased with the size of Pt, which was controlled by the irradiation time of UV light. Interestingly, PS particles with double Pt spots (Fig. 2b) showed a zigzag motion. Further, we also demonstrate that tuning the shape of PS particles affords to produce PS particles with a rotational motion.

Keywords: Self-propelled particles, Polystyrene, Platinum

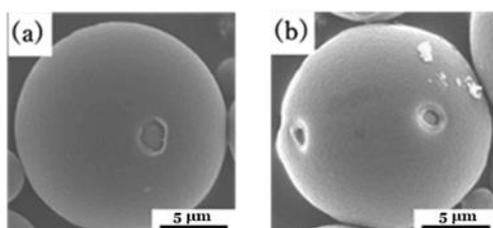


Fig.1 SEM images of PS particle with (a) 1 Pt spot and (b) 2 Pt spots

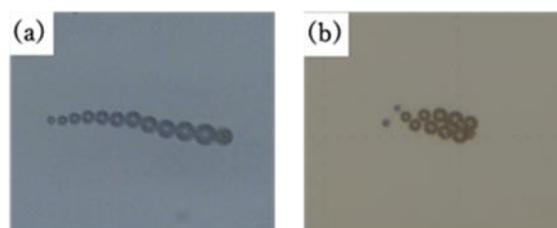


Fig.2 Self-propulsion of PS particle with (a) 1 Pt spot and (b) 2 Pt spots

Dual-responsive P(DEGMA-co-DIPAEMA) hyperbranched copolymers as drug-loaded self-assembled nanocarriers

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Hyperbranched copolymers and dendrimers belong to a well-known family of highly branched macromolecules with a three-dimensional dendritic-like architecture. Over the last years hyperbranched copolymers have gained the interest of polymer science and industry as well, due to their unique macromolecular topologies and remarkable physicochemical properties. [1-3]

Herein we report on the synthesis of novel hyperbranched copolymers, prepared by RAFT polymerization, their self-assembly into functional colloidal structures, and their co-assembly with a hydrophobic drug, namely indomethacin (IND), in order to study their utilization as nanocarriers. The poly(diethylene glycol methacrylate-co-di-isopropyl amino ethyl methacrylate), H-P(DEGMA-co-DIPAEMA), hyperbranched copolymers are dual-responsive in various stimulus such as temperature, pH and ionic strength. According to physicochemical studies, involving the implementation of light scattering and fluorescence spectroscopy techniques, the hyperbranched synthetic macromolecules present self-organization into nanoparticulate structures. In addition, the hyperbranched copolymers were able to encapsulate indomethacin in different feed ratios. IND release experiments were accomplished at pH7, where it was revealed that a high amount of the entrapped IND is strongly attached to the hydrophobic domains of the hyperbranched copolymer aggregates. The acquired data are encouraging for the potential of these novel hyperbranched copolymers to be used as nanocarrier systems for drug delivery applications.

Keywords: hyperbranched copolymers, colloid properties, drug release

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Highly stable colloids of barium hexaferrite nanoplatelets coated with tannic acid

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Colloidal stabilization of magnetic nanoparticles is one of the most important steps in the preparation of magnetic nanoparticles for potential biomedical applications. A special kind of magnetic nanoparticles is barium hexaferrite nanoplatelets (BHF) with hexagonal shape and a permanent magnetic moment [1]. Until now, there are a few stabilization strategies for stabilization of BHF in aqueous media, for example, coatings with citric acid, dextran, silica, and phosphonates [2, 3].

In contrast to the listed coatings, we propose a polyphenol coating with eco-friendly tannic acid on BHF. Tannic acid has a dendritic polyphenol structure with five di-galloyl ester units covalently attached to a central glucose core. Tannic acid contains large numbers of phenolic groups that are attractive for numerous applications acting as antioxidants, antibacterial, anticarcinogenic material, and as a ligand for metal ion coordination [4]. It is proven that catechol groups provide a high reduction ability to transform/reduce metal ions to metal nanoparticles. The reduction of metal ions onto tannic coating is followed by immobilization of the newly formed metal nanoparticles, especially plasmonic nanoparticles [5].

In our research, we tested how different concentrations of tannic acid influence the formation of polyphenolic coatings, the formation of porous structures, and their optical and magnetic properties of coated BHF. Also, we tested the in-situ production and immobilization of plasmonic nanoparticles and the antimicrobial activity of new magneto-tannic-plasmonic material.

Keywords: barium hexaferrite nanoplatelets, tannic acid, stabilization, antimicrobial activity.

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Non-cross-linked, hollow polymer capsules derived from amphiphilic diblock copolymer brushes in aqueous media

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In this work, we report the synthesis of water-dispersible, non-cross-linked, hollow polymer nanocapsules derived from polymer coated inorganic colloids. First, well-defined diblock copolymer brushes, comprising a hydrophobic poly(methyl methacrylate) (PMMA) inner block and a hydrophilic poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA) outer layer, were grown from the surface of silica spheres via atom transfer radical polymerization (ATRP) [1-3]. The hybrid core-shell particles allowed the preparation of water-dispersible, hollow polymer nanocapsules, following the etching of the inorganic core under acidic conditions [4]. In the absence of chemical cross-links, the molecular weight of the solvent-incompatible hydrophobic PMMA block proved to be crucial for the structural integrity of the hollow polymer capsules, while the hydrophilic PDMAEMA block endowed the dispersibility of the capsules in aqueous media.

Critical parameters that were shown to affect the morphology of the hollow polymer capsules and the flexibility and thickness of the capsule wall were investigated, including the molecular weight and composition of the diblock copolymer, the grafting density of the polymer chains onto the inorganic surface and the glass transition temperature (T_g) of the hydrophobic inner block. The present work constitutes a proof-of-principle study of a generic approach that can be applied for the preparation of hollow polymer capsules of controlled size, as well as morphological and physicochemical features in any solvent medium and at high yield, upon the appropriate selection of the solvent-incompatible inner block and the solvent-compatible outer block.

Keywords: non-cross-linked hollow nanocapsules; hybrid core-shell spheres; ATRP

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Chemical Structure Engineering of Naphthalene Spacers in Low-Dimensional Perovskites

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Organic-inorganic hybrid low-dimensional perovskites have attracted great attention for optical and optoelectronic applications due to their excellent stability and structural diversity. The use of various organic cations leads to the formation of 2D, 1D or 0D-structures depending on how the metal halide octahedra are connected to each other. Even insignificant differences in the structure of organic cations can lead to a sharp change in the structural and, as a consequence, optoelectronic properties of perovskite systems.

Incorporation of functionalized ammonium molecules into the perovskites makes it possible to design a variety of new organic-inorganic hybrids, where functionalized organic layer assembled with an inorganic semiconductor layer at a molecular scale. Recently, special attention has been drawn to systems with inorganic exciton-to-molecular triplet energy flow [1]. These systems have potential application in optoelectronics, photoredox catalysis and solar energy conversion. One of the ways to impart such properties is to use small conjugated organic spacer cations.

In this work, a series of low-dimensional hybrid perovskites, based on isomeric naphthalene amine cations and lead iodide were fabricated and their structures and properties were investigated. Examination of the influence of organic cation on the structure-property relationship reveals that the number and position of amino groups in naphthalene rings has an effect on the perovskite dimensionality (Fig. 1) and related optoelectronic properties.

Keywords: halide perovskites, π -conjugated molecule, photoluminescence

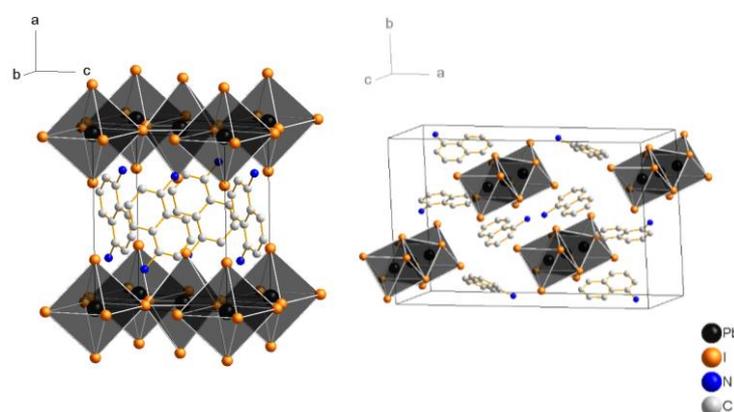


Figure 1. Formation of 2D (left) and 1D (right) perovskite framework depending on the organic spacer structure.

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Control of Particle Size, Particle Size Distribution and Morphology of Silica Coated Iron Oxide Nanoparticles (SIONPs)

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Recent years have seen an exponential increase in research work on nanomaterials in biomedicine with applications ranging from contrast agents in medical imaging to carriers for gene delivery. Among these, Iron oxide nanoparticles (IONPs) find extensive applications in novel diagnostics, drug delivery, magnetic resonance imaging (MRI) and protein purification, etc because of their unique properties such as superparamagnetism, tunable surface chemistry, low cytotoxicity among others.[1]

To warrant their use in these aforementioned applications, they should possess high magnetic saturations, overall narrow particle size distributions (PSD) and high colloidal stability. A silica shell atop the IONPs not only helps in controlling the interparticle interactions and hence magnetic properties, but also offer possibilities to further functionalize their surface with biomolecules by exploiting the surface silanol groups. Here, we present a detailed understanding of the correlation between size, morphology and magnetic saturation of silica coated iron (SIONPs) as a function of various reaction parameters.

A full factorial design of experiments shows that nature of the solvent and concentration of catalyst (ammonium hydroxide) are the most significant factors affecting size and PSD of SIONPs. These parameters in addition to mass ratio of IONPs to silica precursor lead to formation of four distinct morphologies (Figure 1 (a)), which further impact magnetization saturations (Figure 1 (b)).

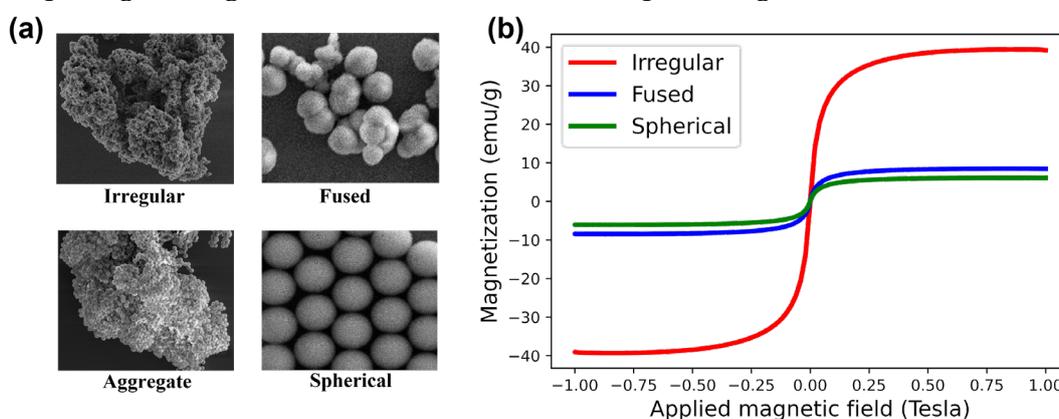


Figure 1. (a) Various Morphologies obtained during silanization of IONPs and (b) Magnetic saturations of obtained morphologies showing superparamagnetic behaviours of SIONPs.

Keywords: Iron oxide nanoparticles, silica coated iron oxide nanoparticles, morphology, superparamagnetism

Acknowledgement: Regina Lopez Fyllingsnes

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Synthesis of polymeric particles with multiple lobes

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The formation of particles with multiple lobes has been in the focus of several investigations [1-3], because of their potential applications as colloidal molecules. Such particles can be used as a building blocks in the processes of self-assembly, or they can be used as carriers of different substances, because each lobe can be different from the others in the same entity. In the production of multi-lobed particles, it is important to develop protocols that are reproducible and robust, with good yield, and where it is easy to recover the particles at the end of the synthesis.

If one wants to form non-spherical particles, the interfacial tension that drives a particle to adopt a spherical shape must be overcome. Here will be shown how this can be achieved by using a method based on multiple swelling and polymerization steps, starting from simple polystyrene colloids. By combining hydrolyzed 3-(trimethoxysilyl)propyl methacrylate with styrene, with the possibility of introducing a crosslinker, we have been able to induce phase separation. This allowed us to create multi-lobed particles whose morphology changes with the quantity and ratio of monomers (Figure 1.). In this work, we will show how the control of the hydrolysis of 3-(trimethoxysilyl)propyl methacrylate is playing a crucial role in defining the final shape of the particle.

Keywords: multi-lobed particles, phase separation, emulsion polymerization

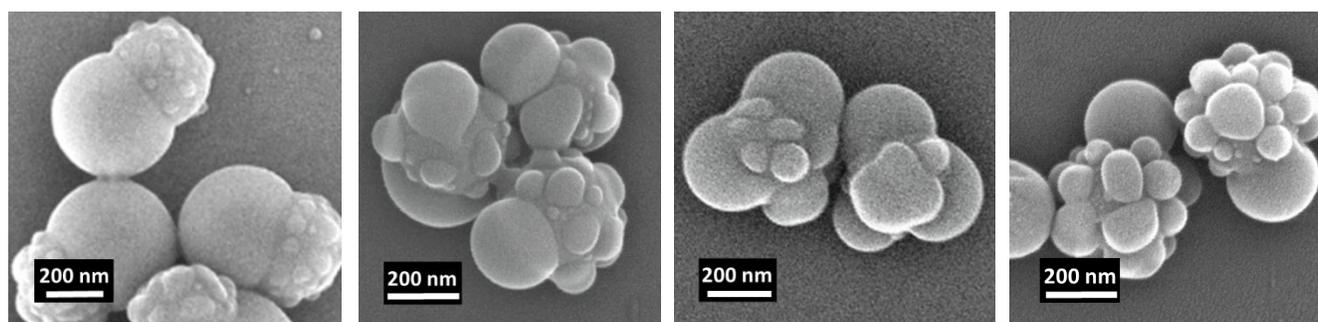


Figure 1. Changes in the morphology of particles by changing ratios between styrene and hydrolyzed 3-(trimethoxysilyl)propyl methacrylate

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Functional Janus particles from complex emulsions: simple design of nano-to-microscale precision objects

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We are motivated to explore methods that synthesize functional particles in new and simple ways. Many impressive tools exist to break symmetry during particle synthesis to generate unique functionality and morphology. Utilizing bottom-up and top-down approaches, these methods are either flexible in the end product or easily scalable, but rarely both. By using a dynamically reconfigurable emulsion template which has multiple interfaces, we generate particles with defined shape. Complex emulsions generated in one step with a thermal phase separation approach enable the generation of particle templates in the nano- to micro-scale with uniform geometry. In total, we utilize gentle heating to generate the particle templates, amphiphile self-assembly to design functionality, and light to photo-polymerize the final particle with defined function and form[1]. Controlling self-organization at each interface enables further avenues for functional control.

The ability to generate anisotropic or spherical Janus particles with defined morphology benefit from interfacial behavior tuned by shape. For amphiphilic particles, by controlling the surface area balance of the hydrophilic or oleophilic phase, particles which readily stabilize water-in-air, or air-in-water are generated from uniform materials. Shape and hydrophobic-directed self-assembly of these colloids can further enable the trapping of gas, for delivery to a liquid-phase catalytic oxidation reaction[2]. Furthermore, by generating shape-templated water-in-oil droplets from the thermal phase separation of aqueous two-phase systems, morphology-tuned hydrogels molds are generated. Self-organization within these APTS droplets before polymerization, enable the generation of compartmented micro reactors in one step. Interfacial organization within oil-in-water and water-in-oil complex emulsions enable a simple yet powerful pathway for the design of complex particles with self-organized function, where size, shape, and functionality are controlled in one scalable step.

Keywords: functional soft matter, complex emulsion droplets, templates

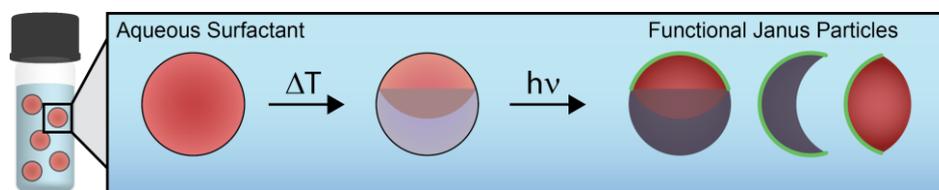


Figure 1. Functional Janus particles generated from templated complex emulsions.

Acknowledgements: We acknowledge funding from the Max-Planck Society and the Emmy-Noether program of the German Research Foundation.

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Structural study of non-graphitizable carbons from corn cobs for negative sodium ion battery electrodes

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Sodium-ion batteries (SIBs) are an attractive alternative to lithium-ion batteries for large-scale energy storage applications because they are made from low-cost, abundant, and less toxic raw materials [1]. Non-graphitizable carbons are the best option for the negative electrode in SIBs. We performed a detailed structural study of non-graphitizable carbon powders from corn cobs prepared at different carbonization temperatures from 900 °C to 1600 °C. It is based on scanning transmission electron microscopy (STEM) and small- and wide-angle X-ray scattering (SWAXS) curves, which contain structural information over a wide range of structural length scales, as shown in Fig. 1. These curves were fitted by an equation with three main contributions, from which a number of structural parameters were obtained [2,3]. The results show a trend of increasing structural order with increasing carbonization temperature, as demonstrated by unconventional parameters such as the correlation at which order is lost, the fractal cut-off length, and the lengths of the locally flat regions.

Keywords: SAXS; SWAXS; XRD; pores; carbonization process.

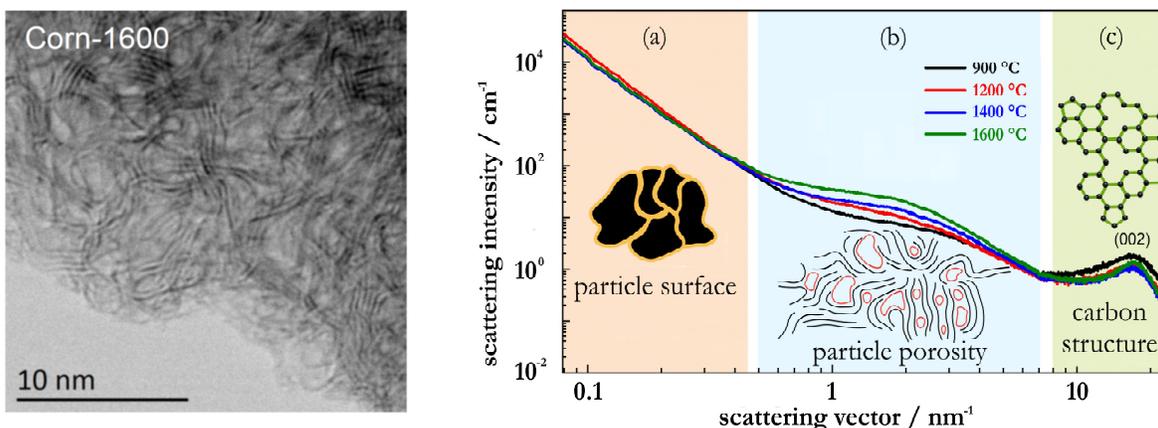


Figure 1. STEM image and schematic representation of SWAXS curves and related structural length-scales.

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Dispersions of Delaminated Double Hydroxides in Ionic Liquids

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We studied the delamination of layered double hydroxide (LDH) particles into the nanosheets, which was triggered in the liquid phase and resulted in stable dispersions. The mesoporous LDHs were prepared by a template-free method [1] and dispersed in two different ionic liquids (ILs), i.e., ethylammonium nitrate (EAN) and 1-butyl-3-methylimidazolium thiocyanate (BMIMSCN). Small-angle X-ray scattering (SAXS), X-ray diffraction (XRD) and atomic force microscopy (AFM) were used. The latter provided the height profile of the dried dispersed nanoparticles on a freshly cleaved mica. The generalized inverse Fourier transform method [2] was used to analyze the SAXS data and provided the corresponding thickness-pair distance distribution functions (tPDDFs) of the dispersed nanosheets in bulk solutions. Delamination of the LDHs was confirmed in ILs but not in water.

Keywords: LDH; IL; nanosheets, AFM, SAXS, XRD.

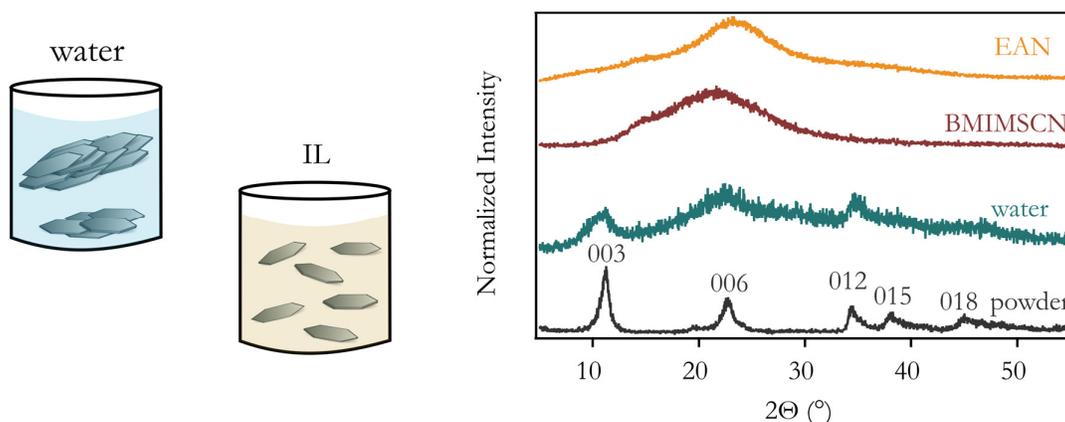


Figure 1. Schematic representation of LDHs in water and ionic liquids and the corresponding XRD results.

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Design and synthesis of stimuli-responsive polymers for wastewater treatment

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Since the first preparation, poly(2-alkyl/aryloxazoline)s (PAOxs) have undoubtedly been recognized as a valuable polymer class characterized by uncommon synthetic versatility and good biocompatibility, features that give straightforward access to highly functionalized and adaptable materials [1]. PAOxs are prepared through Cationic Ring-Opening Polymerization (CROP), which, avoiding termination reactions and suppressing chain transfer, allow a facile regulation of polymer chain length by simply changing the reaction conditions. Furthermore, the large available number of monomers with different side-chain modifications opens the path toward fabricating innovative smart materials with a manifold of applications. [2,3]

Taking into account such observations, we devoted several efforts to the preparation of block-copolymers featured by: (i) a polar side chain, capable of exploiting electrostatic and hydrophilic interactions with a predetermined cargo (e.g. heavy metal ions, organic pollutants, active principles), and (ii) a thermoresponsive scaffold, able to change the interaction with the media by modifying external stimuli [3]. Once grafted the copolymers onto iron oxide nanoparticles, the adsorption properties were initially evaluated by Isothermal Titration Calorimetry (ITC), which revealed a surprising removal efficiency for heavy metal ions.

Prompted by these results, we have engaged in the optimization of the CROP reaction conditions for developing a protocol for gram-scale production of several PAOxs whose side chains differ in terms of steric hindrance and electronic demand. The adsorption properties of the synthesized homo and copolymers are further validated by employing Atomic Fluorescence Spectroscopy (AFS) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). In this communication we will summarize the results of our investigation.

Keywords: polymers, polyoxazolines, wastewater treatment

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Correlation between physicochemical and emulsion-stabilizing properties of insoluble soybean fibre obtained by different ultrasound-assisted autoclaving alkaline treatments

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Insoluble fiber has been considered as a promising stabilizer or dietary supplement, especially when rationally modified. In this study, insoluble soybean fiber (ISF) derived from okara was subjected to an ultrasound-assisted autoclaving alkaline treatment by adjusting the ultrasonication time (20-60 min), autoclaving temperature (105 vs. 121 °C) and time (10-30 min).

Increasing the ultrasonication time, autoclaving temperature and time were effective in improving the treatment intensity. At elevated intensity, hydrogen-bonding interactions were enhanced and the crystalline index first increased and then decreased slightly, as determined by Fourier transform infrared spectrometry and X-ray diffraction analysis, respectively. The particle size progressively increased with the opening of the tightly stacked structure. The ζ -potential and three-phase contact angle both varied depending on the net removal of negatively charged groups and the further release of internal hydroxyl groups. A higher viscosity and elastic modulus could be observed with enhanced treatment intensity. The results revealed that the overall treatment intensity played a dominant role in the effects of ISFs, while the autoclaving temperature may be a secondary key factor, as confirmed by Pearson correlation analysis. The mean droplet size of ISF-stabilized emulsions was positively related to the particle size and was also influenced by the contact angle, viscosity and elastic modulus of the ISF used. In addition, hydrogen bonding may favor the approach of oil droplets, which was reflected by flocculation as seen from the optical microstructure.

Understanding the correlations between these characteristics provides a theoretical basis for designing ISFs with desired properties and advancing their applications.

Keywords: insoluble soybean fiber, ultrasound, autoclaving, initial structure, particle properties, emulsion

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Graphite oxide/nickel ferrite nanocomposites for magnetic hyperthermia

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Magnetic iron oxide nanoparticles (MNPs) are well-known for their great potential for biomedical use (e.g., drug-delivery, MRI contrast enhancement and hyperthermia), hence their possible diagnostic and therapeutic application has been in the focus of many studies recently. However, the bare MNPs require biocompatibilization with the application of a highly hydrophilic protecting layer [1]. Beside magnetite, nickel-ferrite nanoparticles also seem to have favorable magnetic properties for utilization in magnetic hyperthermia. Graphite oxide (GO) is a hydrophilic material, with high surface area and tunable pH-dependent surface charge properties, thus it might serve as a carrier for the nanomagnets. Synthesizing GO/MNP nanocomposites by heterocoagulation method, it is possible to further enhance the heat production induced by an alternating magnetic field during hyperthermia sessions [2].

To study the effect of the composition and the influence of the protective layers on the particle surface, the nanocomposites were prepared with 1/5 and 1/10 GO/MNP mass ratios. The nickel content was 0%, 10% and 20% within the magnetic core, while two different polymers (PAM and PEGMA-AA) were used to coat the nanomagnets. The bare nanomagnets showed spherical morphology according to the TEM images, and the mean diameter slightly decreased with increasing the Ni content. In the case of the GO/MNP composites we could observe the anisometric character of the GO sheets, while the MNPs were almost homogeneously distributed on them. All the nanomagnets exhibit amphoteric surface charge characteristics, the IEP was varied between pH~6 and ~8 depending on the composition. The salt tolerance was monitored by dynamic light scattering (DLS), and the coagulation kinetics of the various nanocomposite samples showed that there are notable differences in their colloidal stability. The critical coagulation concentrations were higher when PAM polymer was used, and the nickel ratio also influenced the stability of the nanocomposites, the CCC shifted towards higher NaCl concentrations. Exposing the nanocomposites to an alternating magnetic field for 5 minutes revealed that increasing the frequency (at the same magnetic field strength) resulted in higher heat production.

Keywords: nanomagnet, composite, colloid stability, magnetic hyperthermia

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Noble metal nanoclusters with structure-tunable fluorescent properties: synthesis, characterization and biomedical utilizations

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Metallic nanoclusters (MeNCs) have become one of the most important nanostructured materials that have been extensively investigated in several research fields. They exhibit molecule-like characteristics as their size approaches the Fermi-wavelength of electrons. Due to the discrete energy levels, MeNCs possess different electric, optical and chemical properties from those of larger metal nanoparticles. Their characteristic feature is the strong photoluminescence. Due to the facile synthesis, good quantum yields, tunable fluorescence emission, large Stokes shift and high photostability they are excellent nano-objects in biomedical applications as well. Therefore, there is a continuous demand to prepare new MeNCs having biocompatible features via development of mainly cost-effective “green” synthetic approaches using small biomolecules, peptides and commonly used proteins.

In actual presentation, we demonstrate several “green” preparation protocols for fabrication of Au NCs using proteins (bovine serum albumin (BSA); lysozyme (LYZ), gamma-globulin (γ G)), nucleotide (adenosine monophosphate (AMP) and amino acids (histidine (His); tryptophan (Trp), cysteine (Cys) *etc.* which result in different nanostructures having tunable blue, green, yellow and orange emissions [1-3]. The main goal of this work was to investigate the spontaneous interactions of AuCl_4^- and the studied biomolecules as well to optimize the gold/biomolecule ratios and pH on the formation of gold nanosized objects by several physico-chemical techniques. Based on the experimental results we provided important information on the structure and optical features. Moreover, we plan to present the application possibilities of these fluorescent Au NCs for selective detection of different transition metal ions and small molecules. Furthermore, the potential utilizations of these fluorescent nanostructures in bioimaging/biolabeling will be presented.

Keywords: gold nanoclusters, tunable fluorescence, biosensor, bioimaging

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Design of experiments to model the size of AgNPs in microfluidic synthesis

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Silver nanoparticles (AgNPs) possess unique optical, antibacterial and catalytic characteristics which facilitate their application in multiple industrial fields. Therefore, the determination of fabrication and synthesis routes is a very critical step to fulfil application requirements. Microfluidics has been demonstrated as a useful platform for AgNP synthesis which allows the manipulation of small volumes of reagents and the precise control of operational parameters [1]. If used together with powerful tools such as design of experiments, regression analysis and response surface methodology it can further increase the synthesis effectiveness in terms of size and sustainability.

This study is concerned with the development of a predictive response surface model for AgNP size, based upon experimental data obtained in a T-junction microfluidic device, as a function of hydrodynamic and reaction conditions. The continuous flows of silver nitrate and tannic acid/trisodium citrate were supplied by two tubes meeting at T-junction, whereas the reaction was performed in the outlet tube. The particle size distributions obtained were measured by dynamic light scattering (Z-sizer) and transmission electron microscopy (TEM). Both techniques were in very good agreement as shown in Fig.1.

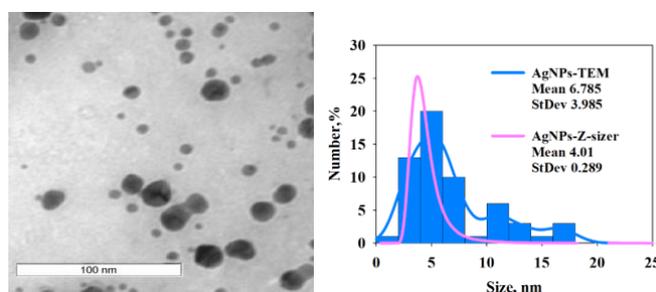


Figure 1: AgNPs size distributions at optimal conditions measured by TEM and light scattering.

The effects and interactions of pH of the solution, relative concentration of trisodium citrate, curvature of the outlet channel, flow rates of reagents and storage temperature on the size of the AgNPs were examined at two/three levels through a D-optimal design (162 runs).

The experimental data of the size of AgNPs were fitted to a second-order polynomial function with average prediction error around 12.68 %. The obtained model was validated by subsequent experiments (12 runs) within the limits of the experimental factors with average prediction error around 8%. The response surface methodology revealed the optimum combination of parameters for minimum size of particles with prediction error around 7.0%.

Keywords: silver-nanoparticles, microfluidics, design-of-experiments, regression

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Inducing defects in colloidal crystals

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Crystal defects are imperfections that can occur in any crystalline material and can crucially influence the mechanical, structural, and optical properties of the material. Colloidal crystals are useful model systems to study defect phenomena due to their similarities with atomic/molecular crystal systems. Although defect structures in colloidal crystals have been addressed, little is known about how (point) defects interact and the mechanisms of their diffusion in 3D, due to the lack of experimental control over the defect formation.

The aim of this project is to develop a colloidal system in which defect formation in 3D crystals can be controlled *in-situ*. For this the aim is to embed thermoresponsive colloids in a crystal of non-responsive particles. By heating or cooling, the thermoresponsive particles can collapse or swell, and will subsequently induce vacancy-like defects or interstitials, respectively (Figure 1a). To realize this system, we synthesized thermoresponsive colloids with a poly(*N*-isopropyl acrylamide) microgel shell and non-responsive poly(2,2,2-trifluoroethyl methacrylate) (pFEMA) core [1], and non-responsive core-shell pFEMA particles of the same size that can be refractive index matched. Using a confocal microscope equipped with a temperature-controlled stage, the mixed system is visualized on a single particle level (Figure 1b). By changing the particle mixing ratios, volume fractions and temperature ramps, we have studied if point defects can be created upon switching. Using existing particle tracking and image analysis procedures, we have further studied if local stress- and strain-fields around these crystal defects can be visualized [2]. Ultimately, this project aims to provide fundamental insight into the formation and dynamics of defects.

Keywords: colloidal crystals, defects, PNIPAM, particle tracking

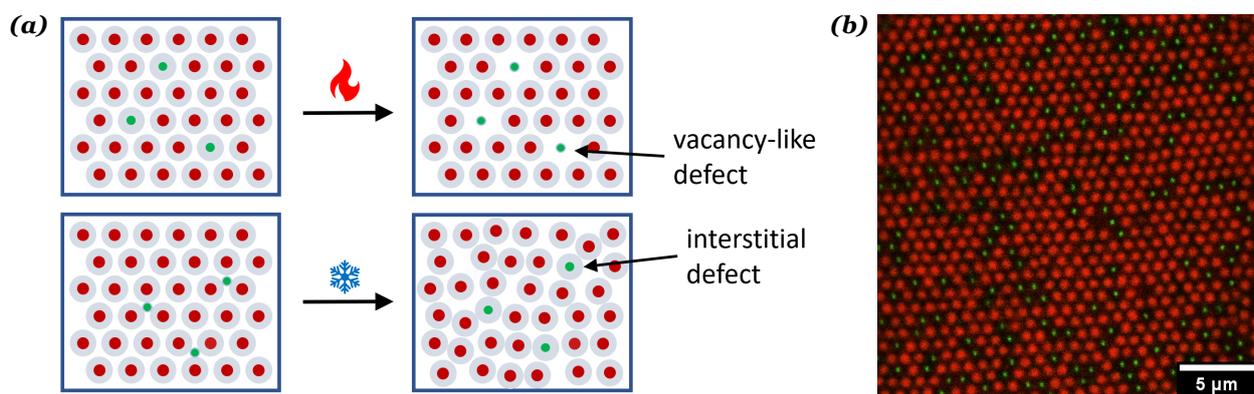


Figure 1. (a) Conceptual visualization of inducing vacancy-like and interstitial defects using thermoresponsive particles. (b) Confocal image of successful embedding of swollen thermoresponsive microgels (green) in a crystal of non-responsive particles (red) at 20 °C.

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Size-Controlled Co-Fe Alloy Wrapped on Nitrogen-Doped Graphitic Carbons as Highly Selective Catalysts for CO₂ Hydrogenation

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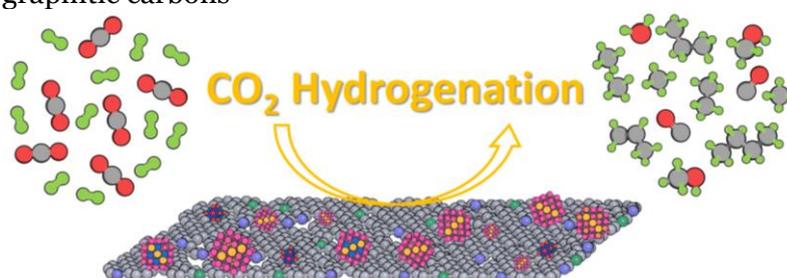
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As a nontoxic, abundant and renewable carbon source, the chemical utilization of CO₂ into value-added carbon-containing products is attractive since it will contribute to diminishing atmospheric CO₂ emissions and the replacement of dwindling fossil fuels. However, CO₂ is a well-known highly stable molecule, [1] the activation and conversion of carbon dioxide are energy-demanding processes. Therefore, CO₂ hydrogenation, using H₂ obtained from renewable energy, could be a promising research direction. Considering the particle size plays a significant role in CO₂ hydrogenation, metal alloy nanoparticles (NPs) wrapped on N-doped graphitic carbons with various particle size distributions were performed as highly selective catalysts for CO₂ hydrogenation towards target products, CH₄, CO and C₂-C₄ hydrocarbons.

When Co-Fe alloy NPs wrapped on N-doped graphitic carbon obtained with broad particle size distributions, catalysts for the Sabatier reaction exhibited remarkable selectivity of CH₄, reaching the highest conversion of 87 % with a CH₄ selectivity of 91 %. [2] Small clusters of Co-Fe alloy NPs supported on N-doped graphitic carbon matrix are highly selective catalysts for the reverse-water-gas-shift reaction, achieving a conversion of 56 % with 98 % CO selectivity. These catalysts with the metal loading even below 0.2 wt.% exhibit a higher selectivity and better performance than the ones with larger NPs (1-4 nm) and higher metal loading in a similar composition. [3] By the preparation of Co-Fe alloy NPs with a narrow particle size distribution ranging from 7 to 17 nm, it has been possible to drive the selectivity of CO₂ hydrogenation towards C₂₊ hydrocarbons, including ethane, propane, n-butane, ethylene and propylene together with methane and CO. Under optimized conditions, a selectivity towards C₂₊ hydrocarbons of 45 % was obtained with CO₂ conversion closing to 60 % and remarkable selectivity values of ethylene and propylene as high as 30 % were detected at CO₂ conversion of 34 %. [4]

Keywords: Particle size-controlled metal nanoparticles, Co-Fe alloy, CO₂ hydrogenation, defective N-doped graphitic carbons



Scheme 1. Illustration of particle size-controlled Co-Fe alloy wrapped on defective N-doped graphitic carbon as highly selective catalyst for CO₂ hydrogenation.

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Interplay between magnetic properties and colloidal stabilization in bio-ferrofluids

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The present work reports a comparative study on the magnetic behavior of spinel iron oxide nanoparticles (MNPs) coated with different ligands aiming to investigate the interrelationship between the magnetic properties and colloidal stability of the ferrofluids.

Spherical spinel iron oxide (magnetite) nanoparticles ($d_{\text{TEM}} \sim 10$ nm) from the same batch, synthesized by chemical coprecipitation were used as identical cores and various biocompatible ligands, double layer of oleic acid (OAOA), polyethylene glycol with oleic acid (PEG-OA), polyacrylic acid (PAA), polygallic acid (PGA) and a carboxylated PEG copolymer (PEGMA) were chosen to cover the MNPs surface by post coating method. At low temperature, PAA and PGA coatings generate an increase in the saturation magnetization (M_s), while the presence of OAOA and PEG-OA shell induces a clear decrease in M_s after coating, while at the same time excellent colloid stability was observed even at high electrolyte concentrations (~ 500 mM NaCl). ΔM plots showed that the MNPs were slightly interacting systems, which is significantly reduced in the MNP<PEG-OA@MNP<PAA@MNP order. Magnetic hyperthermia efficiencies also increase upon PAA and PGA coating, as shown by their maximum values of specific absorption rate (SAR) of 220 Wg^{-1} and 217 Wg^{-1} , respectively, as compared to the SAR of naked particles (196 Wg^{-1}). Nearly linear relationship between the SAR and saturation magnetization values was observed for the coated nanomagnets demonstrating that the post synthetic surface modification of magnetite has a crucial effect on the magnetic behavior in aqueous dispersions.

Keywords: nanomagnets, biocompatible coating, colloid stability, magnetic hyperthermia

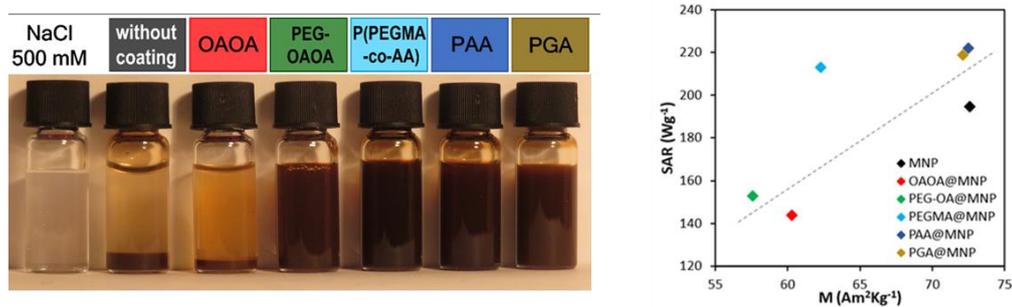


Figure 1. Salt tolerance (left) and hyperthermic efficiency of the coated nanomagnets (right)

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Cold-bursting and double emulsion formation in mixed triglyceride particles undergoing polymorphic phase transitions

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It was recently shown that a solid-to-solid phase transition (α -to- β , gel-to-crystal), commonly observed in many lipid substances, causes nanopore network formation in micrometer sized particles dispersed in surfactant solutions. These nanopores become spontaneously impregnated by the aqueous phase. As a result, the initial particles with diameters up to 100 μm may disintegrate in nanoparticles with diameters down to 20 nm just by cooling and heating of the initial dispersion. Furthermore, in some cases – the penetrated aqueous phase become entrapped in the moment of particle melting and instead water-in-oil-in-water double emulsion formation is observed [1,2].

The aim of the current study is to understand how the presence of multiple mixed triglyceride oils in the droplets affects the observed phenomena. Different mixtures prepared from monoacid triglycerides (fatty acid chain lengths – between 8 and 18 C-atoms) were investigated.

As a result of the study, suitable combination of surfactants solutions and temperature protocols for effective disintegration and double emulsion formation were found for the studied triglyceride mixtures. In addition, it was shown that it is possible to controllably switch the systems behavior without changing their chemical composition through: (1) Change in the heating or cooling rate, (2) Change in the concentration of the oil soluble surfactant and (3) Change in the phase in which the oil soluble surfactant is added. The main governing factors are systematically explored and the mechanisms controlling the observed phenomena are discussed.

Keywords: solid lipid nanoparticle, double emulsion, polymorphic phase transition, triglyceride

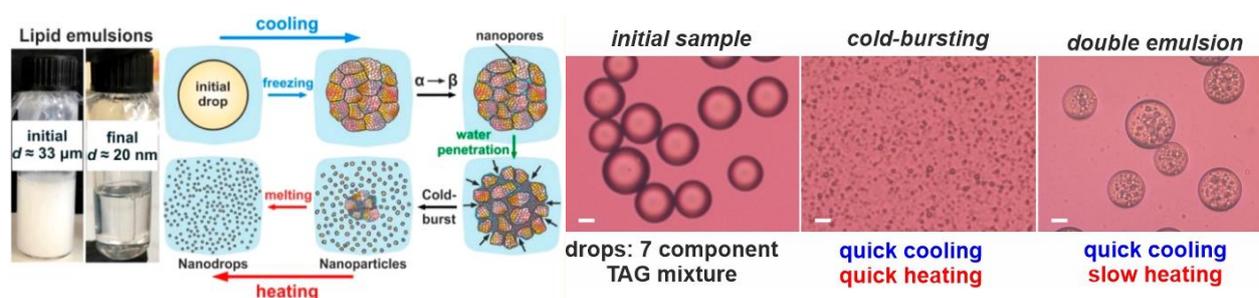


Figure 1. Schematic illustration of the cold-burst method for preparation of lipid nanoparticles. Optical microscopy pictures showing the effect of cooling-heating protocol for emulsion drops composed of 7-component triglyceride mixture. Scale bars = 20 μm .

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AFM-based size statistics of Au nanoparticles generated on amino-terminated TEOS silica surfaces for biosensors

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Gold nanoparticles have been generated on the surface of silica ultrathin layers through a novel method of varying ratios of tetraethyl orthosilicate (TEOS) and (3-aminopropyl)triethoxysilane (APTES) deposited onto glass disc substrates by spin coating.

AFM scans (Dimenson 3100 AFM, NanoScope IIIa controller, Tapping Mode, 512×512 pixel resolution) were performed in 6 locations for each sample type, starting near the centre of the discs and proceeding in 1 mm steps towards the edge.

Data was pretreated by applying a 1st order plane fit to remove tilt, 0th order flattening to level scan lines, and occasionally erase scan lines. Two built-in analysis routines were compared, respectively used complementarily. The *peak count* module in the *Roughness* routine returned the number of individual peaks higher than the set 2.8 nm threshold. In turn, *Particle analysis* routine provided the count and density, and the mean, minimum, maximum and standard deviation of height, area, diameter, length and width of nanoparticles. The obtained descriptors were 1) plotted against scan location of the same samples (in order to check for homogeneity) and 2) treated as one population per sample type and plotted against APTES content (to check for APTES content dependence).

The two analysis routines gave almost identical particle density distribution vs. scan location and APTES content. While particle density statistics showed no clear trend, size statistics showed a decreasing trend with APTES content, and thus, surface amino group density. These results are useful for further optimization of the nucleation process of surface bound nanoparticles.

Keywords: Au nanoparticles; AFM; TEOS; APTES; silica; biosensors

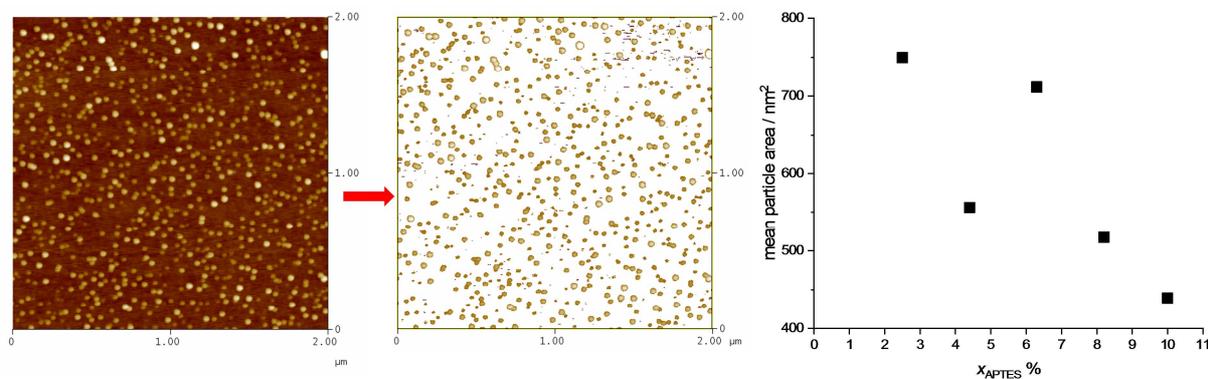


Figure 1. Automatic particle detection from AFM height image and mean area dependence of Au nanoparticles on APTES content of TEOS-APTES silica

Casein Micelles Under Osmotic Stress

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Understanding the stability of milk, and mixed dairy and plant protein dispersions, is vital for the generation of new food or beverage product design. This requires knowledge of the interactions of key components. The particles of primary interest in milk are protein aggregates averaging 200 nm in diameter, called casein micelles. These casein micelles highly hydrated, with 76% of their volume being occupied by water, and are known to be structurally sensitive to calcium and temperature.

The interactions of casein micelles both in the presence and absence of other milk proteins, such as whey, with respect to calcium and temperature, are investigated by means of osmotic stressing. Osmotic stressing offers a non-invasive means for determining the osmotic second virial coefficient via equilibrium dialysis, which describes the total sum of the attractive and repulsive forces occurring in systems. The second virial coefficient is hypothesized to show that the casein micelles deviate from commonly assumed hard sphere behavior, indicating some form of attraction. Mapping this attraction with respect to calcium, temperature and other plant protein or polysaccharide mixtures will help with current understanding of dairy and non-dairy protein mixture behaviors and the future design of milk-based food stuffs.

Keywords: casein micelles, osmotic stress, dairy non-dairy mixtures

The usefulness of phosphatidylcholine-depleted (PC-depleted) lecithin as low-HLB emulsifier to produce W₁/O/W₂ double emulsions

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Water-in-oil-in-water (W₁/O/W₂) double emulsions have the potential to develop low-fat and functional foods. However, the limited range of food-grade hydrophobic emulsifiers hinders their application in food industry [1]. PC-depleted lecithin is characterised by a lower phosphatidylcholine/ phosphatidylethanolamine (PC/PE) ratio, favoring the formation of water-in-oil (W/O) emulsions, and thus can be applied in W₁/O/W₂ emulsions [2]. However, the effects of PC-depleted lecithin are expected to be influenced by the formulation and processing conditions.

In this work, different conditions including different types of osmotic agent, oil type, ratio of inner water and oil phase (W₁/O), homogenization method, concentration of lecithin and the type of hydrophilic emulsifier were combined to study the effect of PC-depleted lecithin on the formation and stability of W₁/O/W₂ emulsions. The emulsions were characterized by morphology, droplet size and entrapped water yield.

Firstly, it was observed that the formation of primary W/O emulsions was highly dependent on the oil type, the homogenization method and the ratio of W₁/O, independent of osmotic agent and lecithin concentration. Most conditions enabled to produce primary emulsions and further double emulsions, except when medium-chain triglyceride (MCT) oil based double emulsions were prepared by microfluidization as well as when a ratio of W₁/O higher than 60/40 was used. Besides, the formation of double emulsions was inhibited by increasing the salt content. Moreover, the stability of the obtained W₁/O/W₂ emulsions during storage was more influenced by the oil type and the type of hydrophilic emulsifier, and less affected by the homogenization method, the ratio of W₁/O, and the concentration of lecithin. Overall, quite stable W₁/O/W₂ emulsions with small droplet size and high entrapped water yield could be produced when using glucose as osmotic agent, MCT as oil phase, a W₁/O ratio of less than 70/30, and a rotor-stator system in the first homogenization step.

Keywords: PC-depleted lecithin, W₁/O/W₂ double emulsions, stability

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Probing in-cage particle dynamics in concentrated suspensions and glasses of hard spheres particles with HF rheometry.

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The cage concept, a central microscopic mechanism, has been utilized in concentrated suspensions to describe a number of phenomena. We probe the evolution of cage formation and shear elasticity with increasing volume fraction in hard sphere suspensions, with emphasis in the short-time dynamics.

To this end we utilize linear viscoelastic (LVE) measurements, by means of conventional rotational rheometers and our home made HF piezo-rheometer [1], to probe the dynamic response in a very broad range of volume fractions up to the very dense regime in proximity to RCP. We focus on the LVE spectra and on times shorter than those corresponding to the G' plateau, where confinement is maximized. In these short times (higher freq.) the caging effect is not evident as the particles cannot fully explore their cage. This results to the virtual solid to liquid transition at elevated frequencies marked by the HF moduli crossover. On the other hand, caging becomes tighter as volume fraction increases and the in-cage rattling becomes more localized. This shifts the HF crossover to higher frequencies (shorter times). Therefore the study of the dependence of the HF crossover properties (frequency and moduli) on volume fraction provides direct insights of the particle in-cage motion, and allows direct comparison with current theoretical models. We find that the above characteristic HF crossover properties exhibit a two regime nearly exponential dependence on volume fraction. This finding is experimentally robust, and consistent with predictions of the microscopic nonlinear Langevin Equation dynamical theory [2] with highly accurate structural input [3].

Keywords: Hard spheres, glass, rheology, high frequency, cage, Langevin.

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Supraparticles: Aggregation of colloids in evaporating dispersion drops

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Evaporating dispersion drops from superamphiphobic surfaces opens a way to fabricate supraparticles with complex structures. The structure formation can be controlled by tailoring the interaction forces between particles and process conditions. In this study, the structure of the supraparticles was investigated by tuning the shape of the primary building blocks and the process conditions. Ellipsoidal polystyrene (PS) particles of different aspect ratios were obtained by adapting the protocol from *Ho et al.*^[1], which followed stretching a polymeric film of spherical particles above the glass transition temperature. Aqueous dispersion drops of the ellipsoidal particles were evaporated from candle-soot templated superamphiphobic surfaces under varying humidity conditions, during which the evaporation process was monitored by a camera. The change in the droplet volume as a function of time and the deterioration from sphericity were quantified through image analysis. Furthermore, the interaction between the building blocks were altered by changing the pH of the medium. Control experiments with spherical PS building blocks were conducted in parallel. The study elucidated the effect of primary building block shape on the final morphology of supraparticles and the transition between a shape-dominated regime and an interaction-dominated regime.

Keywords: evaporation, supraparticles, colloids

Acknowledgements: This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through Research Training Group GRK 2516 (Grant no. 405552959).

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Surface tension decrease with dispersed lignin colloids and their potential capacity as emulsifiers

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Recent progress has been made in substituting petroleum-based colloids with plant-based colloids. Lignins are polyphenolic polymers and represent the most abundant non-saccharidic biopolymers in plant biomass. Despite their high industrial availability in paper industries and biorefineries, they are poorly valorised because of their complex chemical structure and their low solubility in commonly used solvents. Lignin colloids represent a good alternative to adopt sustainable colloids by exploiting their multifunctional physico-chemical properties, such as antioxidant [1], anti-UV [2], antimicrobial and interfacial properties [3]. Nevertheless, there is a strong need to investigate the structure-properties relationships to better understand and exploit their multifunctionalities.

The objective of this research work was to study the physico-chemical properties of lignin colloids with focusing on emulsifying capacities. To this end, both the colloidal stability and the surface properties were studied by dispersing various lignins (e.g. native, fractionated or grafted) in solvents. Lignin solutions and dispersions properties were then investigated by using a series of techniques such as surface tension, granulometry and microstructure observations. Surface tension variations according to the type of lignin used, to their self-assembly in different solvents, to the solubilization process used and to the pH of the colloidal dispersions were evidenced; in addition, one could establish microstructural and granulometry variations depending on the lignin dispersions. Finally, surface tension decrease caused by lignin colloids was shown as strongly related to their granulometry and microstructure. Those results were used for a deeper understanding of lignin colloids as emulsifiers. To this end, emulsions were prepared by incorporating a series of lignin colloids. This allowed demonstrating that lignins could stabilize oil droplets by forming a condensed film around the oil droplets.

Further studies will consist of highlighting other lignin functionalities such as antioxidant, anti-UV and antimicrobial properties with the aim to evidence multifunctional colloidal properties.

Keywords : lignins, colloids, dispersions, surface tension, emulsions

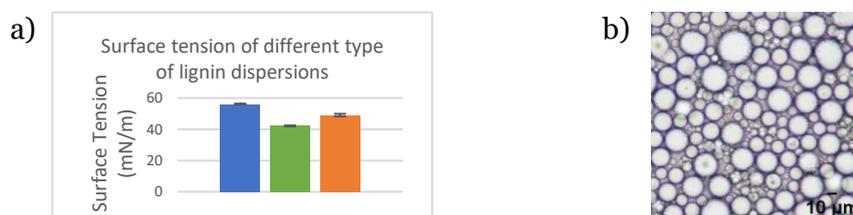


Figure 1: a) Surface Tension decrease of dispersions with different type of lignin colloids (green and orange) compared to a dispersion without lignin colloids (blue) b) Optical Microscopy of a lignin emulsion (Magnification x400)

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Crystallizing depletion colloidal gels by shear

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In this work we present the study of monodisperse attractive colloidal gels using both experiments (rheology and confocal microscopy) and molecular dynamics simulations. The system under study is a depletion gel of (nearly) monodisperse Poly-methyl methacrylate (PMMA) particles at large volume fraction (44%). The attractive interactions are simulated using a Morse potential (harmonic oscillator with cutoff). We find that when such colloidal gels are sheared dynamically (i.e. applying oscillatory shear) they show a drop in their modulus(G) which depends on the applied strain amplitude (γ_0), frequency (ω) and shearing time, similarly to polydisperse colloidal gels, as previously reported [1]. More specifically, in both experiments and simulations the drop of the modulus depends non-monotonically on the strain amplitude, with the maximum decrease in the modulus appearing in the range of $\gamma_0=70$ to $\gamma_0=100\%$ depending on ω . At larger strain amplitudes, the modulus returns to a similar value as the quiescent gels suggesting that any structural transition responsible for the modulus drop occurring in the range of $\gamma_0\sim 100\%$ is destroyed for large strain amplitudes. In this range, MD simulations show that the gels undergo a crystallization transition, observed in similar systems before [2], which depends on the shearing time. At first, small crystallites are formed which later on grow into large crystalline domains, something that is also observed in the experiments using confocal microscopy coupled with rheology. The appearance of crystallization or not depends on both the frequency and the strain amplitude which can allow for tunability of the properties of the colloidal gel as well as the structure from a disordered to an ordered state but also suggests that it is connected with both some characteristic length scale and time scale of the system, and of course raises the question whether shear “pushes” the system toward equilibrium.

Keywords: Colloidal gels, Shear induced tuning, crystallization

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Physical mechanism of erythrocytes sedimentation rate

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Red blood cells (or erythrocytes) sedimentation rate (ESR) is a physical parameter of blood which is often checked in medical diagnosis. It is indeed well known that in case of inflammation, the increase in fibrinogen and other proteins induces a higher ESR.

Until now, researchers thought that the increase of fibrinogen accelerates the ESR by creating bigger aggregates of red blood cells (RBC). Fibrinogen is indeed an aggregation agent of RBCs, and bigger aggregates tend to sediment faster in Stokes regime. However, modeling the ESR measurements with this hypothesis is challenging and often requires physical assumptions specific to this system.

Besides, modern colloidal science has shown that attractive particles form percolating aggregates, as wide as the container. The sedimentation of those colloids then follows a so-called "colloidal gel collapse" regime. Here, we show that RBCs actually follow the same behavior [1]. We present detailed measurements of experimental ESR curves, and original micro- and mesoscopic pictures supporting this claim [2,3]. Besides, those experimental observations are supported by numerical simulations [4].

We also demonstrate that such assumption naturally leads to efficient analytical modeling for the sedimentation curve of RBC.

Keywords: colloidal gel, gravitational collapse, erythrocyte sedimentation

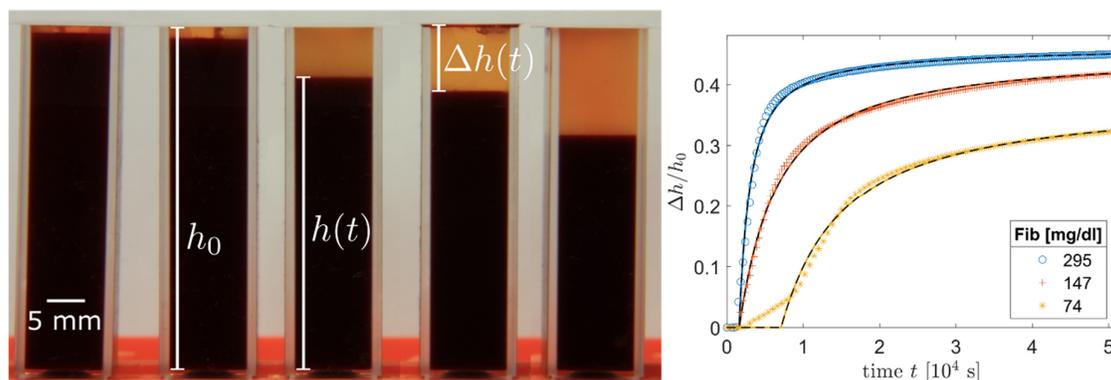


Figure 1. Experimental observation of erythrocytes during sedimentation, along extracted curve and adjusted model.

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Block Copolymer Nanoparticles are Effective Dispersants for Micrometer-Sized Organic Crystalline Particles

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Well-defined sterically-stabilized diblock copolymer nanoparticles of 29 nm diameter are prepared by RAFT aqueous emulsion polymerization of methyl methacrylate using a dithiobenzoate-capped poly(glycerol monomethacrylate) precursor. These nanoparticles are evaluated as a dispersant for the preparation of organic crystalline microparticles via ball milling. This is exemplified for azoxystrobin, which is a broad-spectrum fungicide that is widely used to protect various food crops.

Laser diffraction and optical microscopy studies indicate the formation of azoxystrobin microparticles of approximately 2 μm diameter after ball milling for 10 min at 400 rpm. A uniform layer of nanoparticles adsorbed at the surface of these azoxystrobin microparticles is confirmed by electron microscopy studies. The extent of nanoparticle adsorption on the azoxystrobin microparticles can be quantified using a supernatant assay based on solution densitometry. This technique indicates an adsorbed amount of approximately 5.5 mg m^{-2} , which is sufficient to significantly reduce the negative zeta potential exhibited by azoxystrobin. XPS studies suggest a fractional surface coverage of nanoparticles of approximately 0.24. Moreover, this adsorbed amount appears to be essentially independent of the nature of the core-forming block, with similar data being obtained for both poly(methyl methacrylate)- and poly(2,2,2-trifluoroethyl methacrylate)-based nanoparticles [1].

Finally, we show that this versatile approach is also applicable to five other organic crystalline agrochemicals. TEM studies illustrate a layer of PGMA₅₀-PMMA₈₀ nanoparticles adsorbed at the surface of these microparticles [2]. Overall, this study suggests that sterically-stabilized diblock copolymer nanoparticles may offer a useful alternative approach to traditional soluble copolymer dispersants for the preparation of suspension concentrates in the context of agrochemical science.

Keywords: Nanoparticles, RAFT, Suspension Concentrate, Azoxystrobin

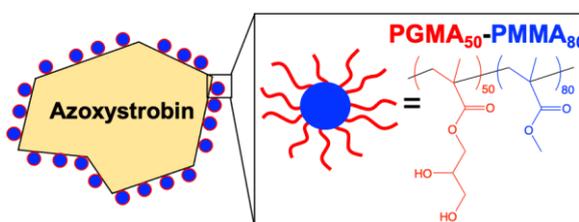


Figure 1. Schematic representation of azoxystrobin microparticles coated with PGMA₅₀-PMMA₈₀ nanoparticles.

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Binary mixture of hard and soft colloids with tuneable interactions

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Industrial and academic researchers have granted a lot of attention to mixture of hard and soft colloids[1] by means of the impact of their softness on rheological properties and phase diagrams. In this work, we broaden these knowledges by studying the implication of an innovative binary mixture where attractive interactions are modulated, not by depletion effect, but by the use of a patchy co-monomer.

To do so, we derived a well-known nanocomposites system[2], [3] of polyacrylamide matrix containing silica particles to a colloidal scale of hard and soft colloids. Our system consists of an aqueous solution where the soft colloids are synthesized polyacrylamide microgels and the hard ones are silica nanoparticles.

Our goals are to study the impact of attractive interactions, brought in the microgel by the use of a patchy co-monomer, onto the flow properties, the structure and the phase diagram of the mixture. In the presentation, I will firstly introduce how we tuned the softness and size of our polyacrylamide microgels depending on the synthesis process. Then, I will show the implication the attractive interaction on the colloidal glass transition, the phase diagram and the structure of the binary mixture.

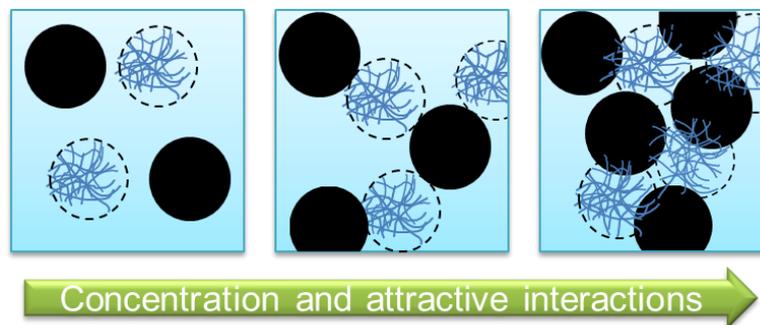


Figure 1. Illustration of our binary mixture of soft (open blue circles) and hard (black circles) colloids.

Keywords: colloids, synthesis, rheology

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Microfluidic osmotic compression of charge-stabilized colloidal dispersions: Equations of state and collective diffusion coefficients

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We show, using a model coupling mass transport and liquid theory calculations for a charge-stabilized colloidal dispersion, that diffusion significantly limits measurement times of its equation of state (EOS), osmotic pressure vs composition, using the osmotic compression technique.

Following this result, we present a microfluidic chip allowing one to measure the entire EOS of a charged dispersion at the nanoliter scale in a few hours, with precisely controlled pH and chemical potential of ions. We also show that time-resolved analyses of relaxation to equilibrium in this microfluidic experiment lead to direct estimates of the collective diffusion coefficient of the dispersion in Donnan equilibrium with a salt reservoir. [1]

The microfluidic chip acting as a “chemostat”, it becomes possible to impose ramps of pH or salt chemical potential to the dispersion and to measure the dependence of the EOS on these parameters easily. With an adequate account of charge renormalisation due to ion condensation, inferring the charge regulation mechanisms at the surface of colloids in concentrated dispersions becomes possible.

Keywords: equation of state, collective diffusion coefficient, colloids, microfluidics, charge regulation

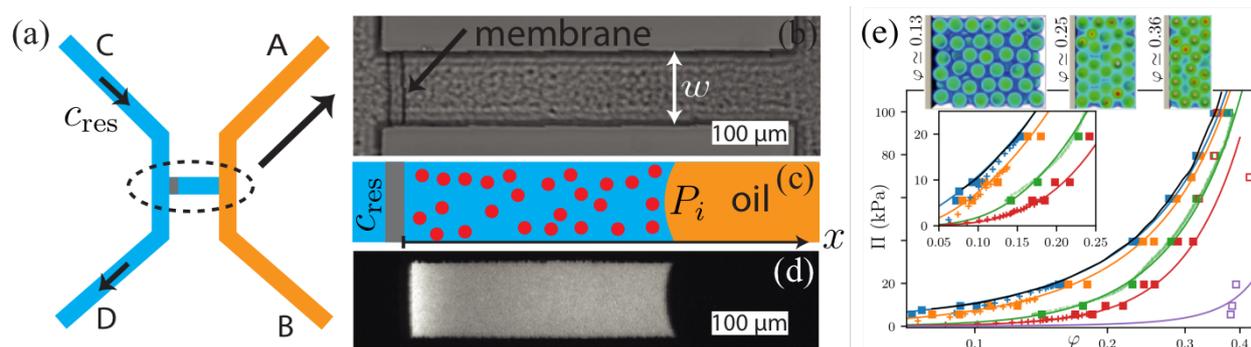


Figure 1. (a) Design of the microfluidic chip. (b) Bright-field view showing the nanoporous membrane in the transverse channel. (c) Compression of the dispersion by an imposed pressure P_i against the reservoir (flowing channel CD) at concentration c_{res} . (d) Typical fluorescence image allowing to measure concentration gradients. (e) Measured equations of states (symbols) compared to theory (OZ + RMSA + EPC renormalization, colored lines) and 3D simulations (black line, top images) for $c_{res} = 0.1, 1, 5, 10$ and 100 mM, from top to bottom.

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Rheology and structural characterization of mild solvolytically fractionated lignin dispersed in alcohols

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The mild thermal solvolysis of lignin in alcohols is a promising technology for obtaining carbon-neutral fuels. Deployment of these fuels and their concentrated dispersions partially depends on their structural and rheological properties. Here, we investigate the structure of mildly depolymerized Protobind 1000 lignin dispersed in ethanol (LEO) and methanol (LiMO) at different percentages of solids. Small-angle X-ray scattering (SAXS) data of diluted and concentrated LEO and LiMO dispersions show that, in these dispersions, lignin exists in two states: individual lignin coils and their aggregates. The lignin coils have few nanometers (3 - 5 nm) in size in both solvents. Direct observation of the lignin coils was achieved by cryo-TEM images and supports the findings of the SAXS measurements. The radius of gyration of the dilute dispersions increases with increasing the lignin content, while in the concentrated dispersions, the opposite trend is observed. It is hypothesized that in the concentrated regime, the lignin coils are more compressed by adjacent coils. The lignin aggregates can be detected in the concentrated dispersions as they exhibit an upturn at low Q. Rheology measurement supported the presence of very fragile aggregates. The concentrated dispersion exhibit Newtonian behavior in the shear rate of 1 – 1000 s⁻¹. Moreover, the viscosities of the LEO and LiMO dispersions are also almost similar at the same lignin weight percent. Furthermore, the measured energy density data shows that the addition of lignin in ethanol and methanol results in high volumetric energy density dispersions relative to ethanol and methanol solvent.

Keywords: Lignin colloids, rheology, small-angle x-ray scattering, and green fuel.

Work of adhesion in soft bodies contact scenario

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Work of adhesion is important for biological, anti-clogging, industrial applications. Recently, Atomic Force Microscopy (AFM) has become one of the most accurate and used ways to detect the adhesion work in scientific applications. This contribution aims to analysis of its output.

The adhesive properties of poly-N-isopropylacrylamide brushes in swollen and collapsed states were investigated using soft colloidal probe (PDMS particle) AFM. The swelling of the brush was controlled with co-nonsolvency effect. 10% 1-propanol water solution was used to trigger deswelling. While the force curve was recorded the contact area between surfaces was measured optically. The comparison of the results was the backbone of this contribution.

Contact area of the soft colloidal probe with the brush was investigated using Reflection Interference Contrast Microscopy. The work of adhesion values for pull-off force detection and optical contact area measurement and fitting the shape of the colloidal probe were compared. Large mismatch in these values was found. Possible reason for such discrepancy was non-equilibrium nature of the pull-off process itself, which was proven by its pronounced rate dependence.

Keywords: Adhesion, AFM, PNiPAAm, Colloidal Probe

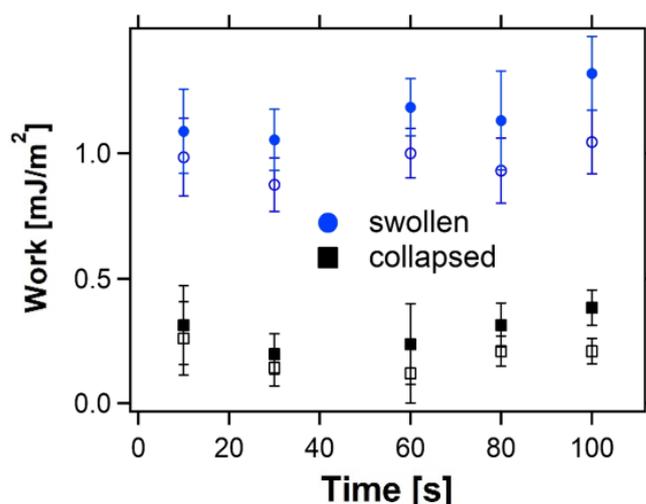


Figure 1. Dependence of work of adhesion on contact time for swollen and collapsed state of the brush. Filled symbols indicate the given contact time. Empty symbols detected in the initial moment of the contact

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Tailoring water resistance properties of environmentally friendly water-based wood adhesive

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Water based polyvinyl acetate – PVAc dispersions are worldwide known due to their advantageous properties, such as low VOC content, high chemical stability and bond strength, fast setting speed, and favourable price [1]. Volatile organic compounds (VOC) are organic chemicals that have a high vapour pressure at room temperature, some of which may have short- and long-term adverse health effects. Most significant consumers are among wood, paper, and textile industry and used in the most various applications (such as tobacco processing, water emulsion paints, wood and paper adhesive formulation) [2].

Water-based wood adhesives can be classified into four durability gradings according DIN EN 204 and DIN EN 205 standards (running from D1 to D4). These tests are carried out using beech wood specimens and are based on the different water-resistance of the adhesives. At industrial level, there is a growing demand from year to year for products that are more affordable but unchanged in terms of the parameters mentioned above in order to keep their competitiveness.

In this paper, the laboratory production and comprehensive testing of industrial wood adhesives formulated with different organic, VOC free materials such as polyvinyl alcohol is presented. The optimal amount of afore-mentioned additives is determined in order to improve the physical and chemical properties of the adhesives and reach more affordable price at the same time. Measurements include long-term stability tests with viscosity measurements and tensile strength determination according EN 204 and EN 205.

Keywords: polyvinyl acetate, wood adhesive, formulation, environmentally friendly

Acknowledgements: This work was supported by the National Research, Development and Innovation Office, Hungary (project no. 2019-2.1.11-TÉT-2020-00184).

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Designing highly water resistant PVAc wood adhesives using cellulose-based fibrous materials

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As a result of technological advances in recent decades, there has been an increased demand for the development of new types of industrial adhesives. In addition to the many existing positive properties of polyvinyl acetate (PVAc) adhesives, such as high initial tack and final bond strength, high chemical stability and low cost, achieving higher water resistance and greater tensile strength would result in an even wider range of possible applications, making it more attractive to the current market.

In the present study, cellulose-based materials of different kinds were used to formulate novel types of wood adhesives. Systematic variation of the different additives allowed us to tailor the properties, such as viscosity, tensile strength, setting time and open time. The water resistance was tested according to DIN EN 204 and DIN EN 205 international standards that classify the adhesives into D1-D4 classes depending on their behavior. Long-term stability measurements were also carried out in order to check the applicability of the different systems.

Two types of commercially available PVAc-based adhesives and four different types of cellulose were used throughout the study. The results will be presented in a systematic fashion which will include the determination of the optimal amount of fibrous materials through the complete evaluation of the different physicochemical properties of the adhesives. In addition, discrepancies will be highlighted between the results obtained and the data available in the literature. [1-4]

Keywords: PVAc, wood adhesives, water resistance, cellulose, formulation, long-term stability

Acknowledgements: This work was supported by the National Research, Development and Innovation Office, Hungary (project no. 2019-2.1.11-TÉT-2020-00185).

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Evidence and modelling of physical ageing in fluid gels

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Fluid gels are suspensions of soft microgel particles above the random close packing point. These systems are obtained by applying shear to a gelling e.g., polysaccharide solution during the sol-gel transition. They possess tuneable material characteristics (e.g., yield stress, shear thinning behaviour, viscoelastic response) which can be modulated by formulation and process parameters. For this reason, fluid gels are extremely attractive for many applications (e.g., suspending agent, foam, and emulsion stabiliser) in several industries. Fluid gels' elastic modulus is known to evolve linearly with the logarithm of time when subject to strains within the linear viscoelastic region. Yet, evidence and modelling of physical ageing in fluid gels is still lacking. We investigated fluid gel ageing using a 3-step repeated cycle method: 1) rejuvenation in oscillation mode to shear melt the system while minimising the relaxing strain from this step; 2) waiting time (t_w) where no stress was applied; 3) creep with a stress below the yield stress to retrieve the relaxation time τ . We observed that $\tau(t_w)$ increases until reaching an asymptotic constant value τ_∞ . We evidence this behaviour, for a Ca^{2+} - bond based fluid gel (using low acyl gellan gum) and a non-ionic fluid gel (using agar). Therefore, we demonstrated the existence of physical ageing in fluid gels, which is not driven by kinetic factors linked to ions' diffusion e.g. Ca^{2+} ions (Figure 1). We are currently investigating if gravity plays a role in the ageing phenomenon. All in all, this study provides a tool to measure more carefully fluid gels' rheological properties by considering their physical ageing. In addition, we hypothesise that the method designed to investigate physical ageing in fluid gels could be used to study the phenomenon in other colloidal glasses.

Keywords: Fluid gel, Physical ageing, Colloidal glass

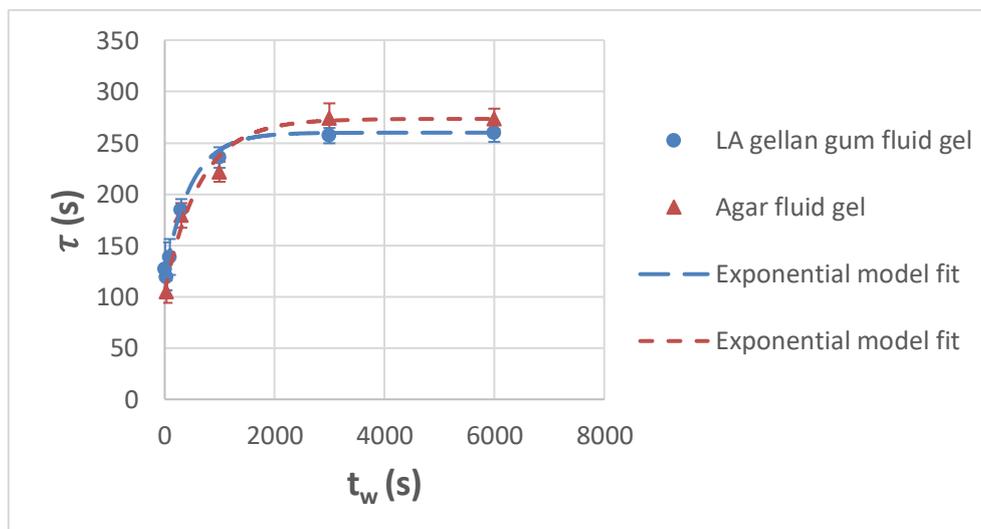


Figure 1. Evolution of $\tau(t_w)$ of low acyl (LA) gellan gum and agar fluid gels.

Abrasion phenomenon in low acyl gellan gum fluid gels

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Fluid gels are jammed suspensions of soft microgel particles which are obtained by applying shear to a gelling e.g., polysaccharide solution during the sol-gel transition. They possess tuneable material characteristics (e.g., yield stress, shear thinning behaviour, viscoelastic response) which can be modulated by formulation and process parameters. For this reason, fluid gels are extremely attractive for many applications (e.g., suspending agent, foam, and emulsion stabiliser) in several industries. Because of their industrial relevance, it is critical to understand how fluid gels' properties evolve after they have been manufactured. We investigated how low acyl gellan gum fluid gels' storage modulus is affected by repeated cycles performed at large oscillatory strain. We found that the storage modulus of our system was logarithmically reduced until reaching a finite steady value. This would suggest that the volume fraction is progressively reduced from cycle to cycle due to abrasion between the fluid gel particle layers, reducing the particles' hydrodynamic volume. The hypothesised mechanism is also supported by preliminary microscopy pictures where small fragments can be observed after several high shear cycles have been performed. We are currently exploring how processing and formulation parameters could impact the abrasion rate of low acyl gellan gum fluid gels. These findings will be very relevant for the successful industrialisation and tailored design of more shear-resistant fluid gels microstructures.

Keywords: Fluid gel, Abrasion, Rheology, Microgel particles

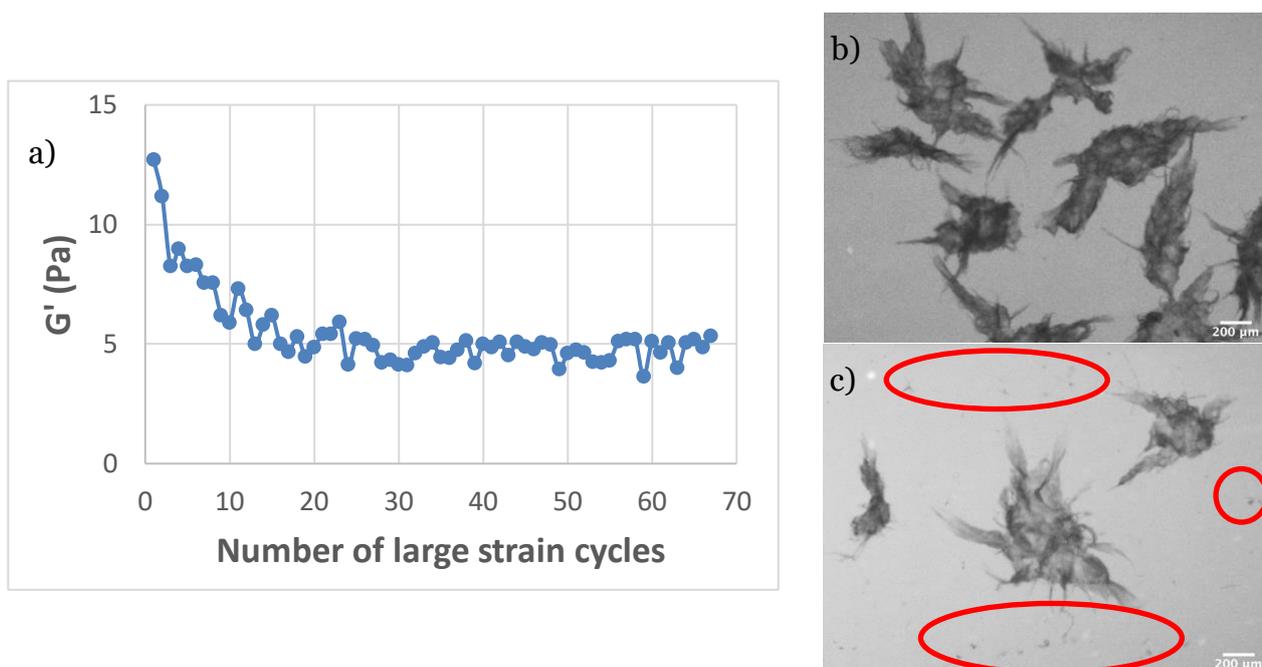


Figure 1. a) G' loss with repeated large strain cycles; particles b) non abraded; c) after abrasion (fragments in circles)

Long-term stability and loading of DPPC-based liposomes

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Nanotechnology is an emerging field in medicine that will display significant therapeutic benefits. Nowadays, challenges in drug delivery include reduce toxicity (side effects), local administration route and low cost. In addition, there is an increasing need for active targeting and controlled of drug release dose. For this, research in nanotechnology is focused on a variety of nanodrug delivery carriers, such as nanoemulsions, lipid or polymeric nanoparticles and liposomes. [1]

Liposomes are spherical vesicles consisting of one or more phospholipid bilayers enclosing an aqueous core, providing a powerful delivery system for several drugs. Liposomes can be synthesized using nontoxic and biocompatible amphiphilic molecules, being coated with different polymers (chitosan, PEG and hyaluronic acid) that enhances its properties as drug delivery systems [2-3]

In this work, liposomes have been synthesized by the rehydration and extrusion method using 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) as phospholipid, obtaining a particle size of ca. 200 nm and polydispersity index of 0.1. Subsequently, two different types of dyes, methylene blue (negatively charged) and bengal rose (positively charged), were encapsulated simulating drugs. Then, exhaustive characterization was carried out using different techniques, such as dynamic light scattering, zeta-potential, confocal microscopy, scanning cryomicroscopy, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy, aiming to study of the long-term stability of the different synthesized emulsions as well as a month of storage after lyophilization process.

Keywords: Drug delivery, Liposome, DPPC, extrusion.

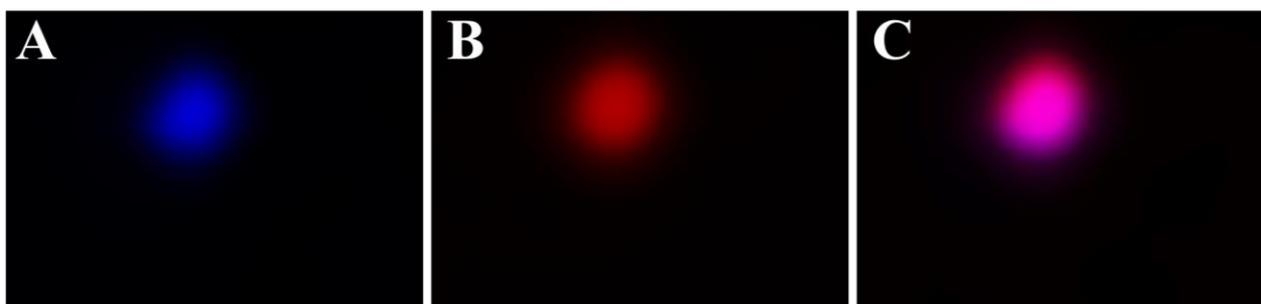


Figure 1. Photographs obtained by confocal microscopy (A) Liposome loaded with DAPI in its aqueous phase (B) Liposome membrane labeled with Nile Red (C) Superimposed images of the membrane and the load

Acknowledgements: FQM-204 Research group; P20_01151 (PAIDI2020) and PID2020-112744GB-I00 projects.

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Properties of interfacial layer in surfactant-laden concentrate titania nanoparticle dispersions

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In the context of the fabrication of porous material, more specifically solid foams, from particle-stabilized liquid foams, the understanding of the physicochemical parameters and phenomena controlling the interface adsorption of these particles in the lamella is essential. In many cases, particle-based foam stabilization is obtained by adding a surfactant to a dispersion, to render the particles partially hydrophobic. This facilitates the migration towards the interface of the surfactant-coated particles, forming a viscoelastic layer.

In this work, the properties of the interfacial layer of TiO₂ concentrate (up to 5% wt) nanoparticle (NP) dispersions containing cetyltrimethylammonium bromide (CTAB) are addressed. More specifically, both the effect of the concentration of CTAB, adsorbed on the NPs, and the concentration of coated NPs in the dispersion are analysed.

The properties of the interfacial layer are measured by the Pendant Drop technique. The experiments were performed at 20°C in a temperature-controlled cuvette. In addition to dynamic surface tension, dilatational rheology was investigated at different frequencies, obtaining the values for surface elasticity and viscosity. After the spontaneous formation of an interfacial layer, an increase of the adsorption rate was observed, during the imposed drop area oscillation. This phenomenon depends on the CTAB concentration and seems to be related to a particle rearrangement in the adsorption layer induced by the area perturbation. In addition, an evident minimum in the modulus of the dilatational viscoelasticity is observed as a function of the concentration of coated NPs, that could also be related to rearrangements in the layer.

Keywords: TiO₂ dispersion, surface rheology, CTAB, water-air interface

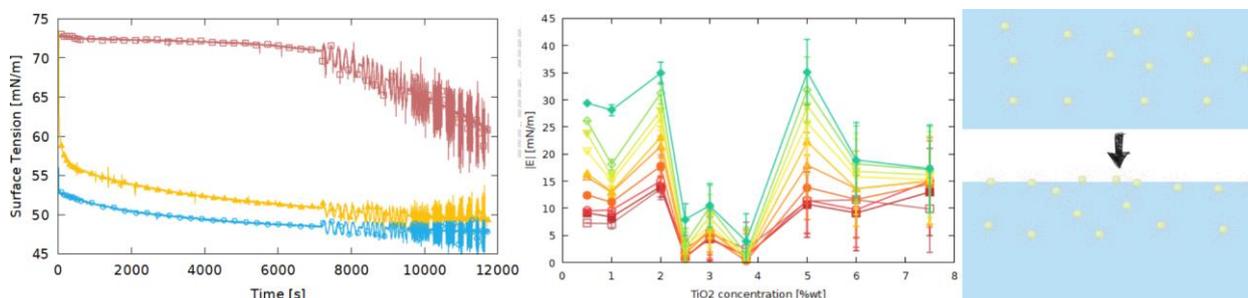


Figure 1. Effect of particle adsorption on the measured surface tension (left), on the measured viscoelasticity (center) and schematic of the migration of CTAB-coated particles to the interface.

Acknowledgements: This work is framed within the ITN nanoPaInt Action (EU-MSCA ITN-2020, grant agreement 955612), that Iván Navarro Arrebola gratefully thanks for supporting his PhD.

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Translational and rotational diffusion coefficients of hematite-silica core-shell colloidal ellipsoids and the effect of polydispersity

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Probing the translational and rotational diffusion (D_t and D_r) of anisotropic colloids is of significant fundamental interest with implications for many different applications. However, for colloids made up of inorganic materials it is quite challenging because of multiple scattering and high opacity of the samples. In the present work, using the recently implemented depolarized measurements on 3D-DLS (dynamic light scattering) (doi.org/10.48550/arXiv.2203.07097) [1], we have measured the D_t and D_r for hematite core ellipsoids over a wide range of aspect ratio and size and the results are compared with the theoretical predictions. Further, we have also used binary mixtures of ellipsoidal colloids of different aspect ratios with a known proportion to introduce polydispersity in a controlled manner and investigated the effect of polydispersity on D_t and D_r .

Keywords: Diffusion, Colloids, 3D-DLS

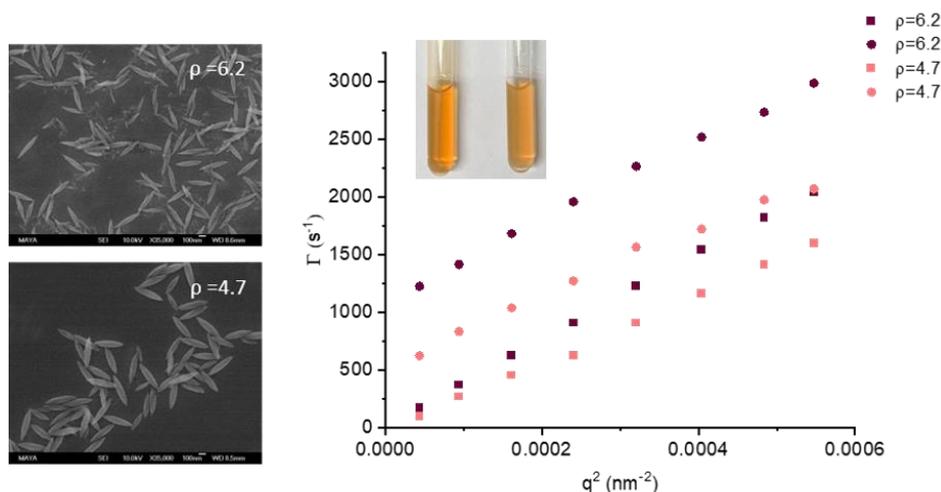


Figure 1. The left panel shows the SEM images for hematite ellipsoids having two different aspect ratios. The right panel shows the extracted relaxation rate, Γ , as a function of q^2 for VV (square) and VH (circle) measurements for the two different aspect ratios, $\rho_1=6.2$ and $\rho_2=4.7$. Inset on the right panel shows the physical appearance of the sample.

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Epitaxial Growth of Binary Colloidal Systems

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Binary colloidal crystals present unique material properties in industries such as semiconductors and photonics[1] where by the tuning of interaction potentials between the large and small species, one can obtain a plethora of binary superlattice structures[2]. However, binary crystals pose more complications to form compared to the one-component system, and thereby rarer in occurrence. In this work we aim to increase the probability of crystallisation while simultaneously influencing the crystal type via a patterned template for epitaxial growth. It is well known that heterogeneous nucleation occurs at the walls of a sedimenting colloidal system, and naturally, the introduction of a pattern forces these particles to order themselves in a way that minimizes their entropy[3]. Whilst patterning has been achieved through methods involving lithography[4] or optical tweezers[5], both have limitations to key features of shape or relative positioning. With the advancement of 3D computer-aided design and two-photon lithography (TPP) by instruments such as the Nanoscribe[6], we take a bottom-up approach to fabricate precise templates representing the negative replica of the binary crystal in question. We observe and characterise the interactions of the template and particles via confocal microscopy. Furthermore, tuning of the template lattice spacing and dimensions of its constituent structures, helps define the effectiveness of crystal growth and determine the long-ranged ordering of sedimenting layers into the bulk.

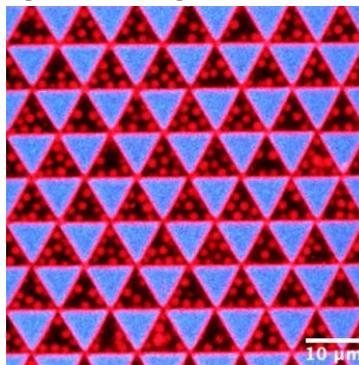


Figure 1. Confocal Microscopy XY-image of $8.3\mu\text{m}$ side length tetrahedra array (blue) with a suspension of $2.2\mu\text{m}$ PMMA spheres sedimenting on top (red).

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Interparticle forces in presence of polycarboxylate ethers under basic conditions

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For the workability of concrete and cement as highly abundant construction materials the flow behaviour in the early stages of these materials is of special interest. This can be influenced using additives such as polycarboxylate ether (PCE) type super plasticizers to decrease the viscosity of cement pastes, yielding an enhanced workability. A better understanding of the interactions on the nanoscopic level and the impact on the macroscopic rheology is of great importance for the development of higher performing additives.

The interaction between model particles is measured via colloidal-probe atomic force microscopy (CP-AFM) in sphere-sphere geometry. Combining CP-AFM with optical microscopy allows to arrange colloidal particles coaxially and determine the interaction forces between these particles upon approach. Silica beads with diameters in the micrometer range serve as model cement grains, due to the restriction of the AFM technique to either spherical particles or particles with a defined roughness. The influence on the interaction forces of these model grains in presence of basic pH and different salts such as KCl and CaCl₂ and their concentrations is investigated, showing electrostatic and steric interaction for low ion concentration and high PCE concentration, respectively.

Keywords: CP-AFM, PCE, silica

Acknowledgements: The authors would like to thank the Deutsche Forschungsgemeinschaft for funding of the Project under the project number 387092747, KL1165/24-1 and -2.

Interactions and Structure of Foam Films stabilized by Proteins and Microgels

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Foams appear in many applications such as in personal care products, firefighting and food technology. For understanding macroscopic foam properties, it is important to investigate its single building blocks – the so-called foam films, which separate the air bubbles from each other. A widely known foam-stabilizing protein is β -lactoglobulin (BLG) which appears naturally in milk and is responsible for milk froth. For novel technical applications, temperature responsive foams stabilized poly(N-isopropylacryl amide) (PNIPAM) microgels are of high interest. The crosslinker content has an impact on the deformability of the microgels and this is represented also in the foam film properties [1]. Also restructuring of the occupancy of microgels on single surfaces in comparison to free standing foam films is an important link towards macroscopic foams. A challenge for testing protein and microgel stabilized foam films are often their massive inhomogeneities, which makes it difficult to measure the respective foam film thickness.

To get insights into foam film properties, we use a camera based thin film pressure balance to study protein and particle stabilized foam films in terms of disjoining pressure inside the foam films, drainage kinetics, and foam film stability. Therefore, we use two different methods: an intensity measurement for grey (colorless) thin films and a color assignment method for colorful thick films, where the color is compared to the expected color of a thin water film. Film thickness profiles give insights into particle bridging, agglomeration and network formation in the foam films.

In case of BLG-stabilized foam films, the comparison with hydrophobized silica nano particle stabilized foam films helps to distinguish protein specific effects, such as deformation due to proteins soft character, from regular colloidal interaction.

For a complete picture, SANS measurements on macroscopic foams provide additional insights into the link between foams and single foam films.

Keywords: foam films, microgel, β Lactoglobulin, disjoining pressure

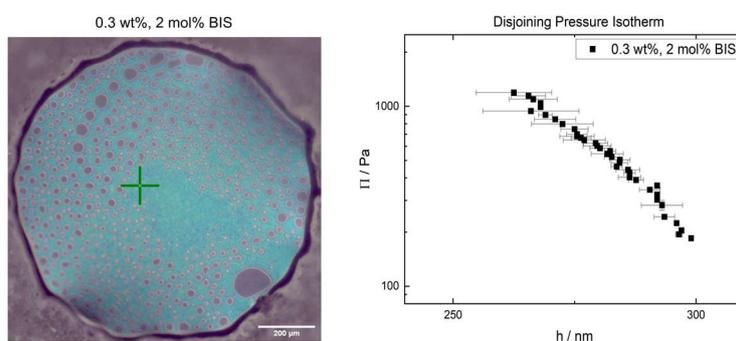


Figure 1. Left: Real color image of a PNIPAM microgel foam film with a tracker marker in green. Right: Disjoining pressure isotherm resulting from multiple color-to-thickness calculations from multiple measurements.

Acknowledgements: The authors acknowledge funding from the DFG Project 54.012 – 09/14 and thank A. Völp for fruitful discussions and providing β -lactoglobulin.

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Refractive-index and density matching for a model colloidal system to capture gel collapse

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One of the most intriguing problem in colloidal gels is collapse under gravity or external loading [1-2]. This is affecting the shelf-life of products from agrichemicals to foods [3-4]. The failure can be triggered by local phenomena, to capture such behavior requires real-space monitoring down to the single-particle level. Moreover, imaging colloids at the microscopic level has always been confined by the limited imaging depth from light refraction.

Here we address this challenge via confocal microscopy. To improve refractive-index matching within the PDMS-xanthan gel system, we fitted the decay of the image intensity at different sample composition. The optimal matching formulation has been found by the least decay. To avoid colloids creaming or sedimenting quickly (within a few hours), we mixed a dense oil component—pentafluorotoluene with PDMS to increase the droplet density [5]. The resulting gels are so close to density and refractive-index matching. Furthermore, combined with a solvatochromic dye, droplet centers and contacts can be tracked by a composite filter [6-7], as seen in *Figure 1*. Contacts are then linked to compressive forces and stresses within the gel network, we show the potential of this model system to reveal the role of stress and detect the trigger of gel failure.

Keywords: Refractive-index matching, density matching, gel collapse, emulsions.

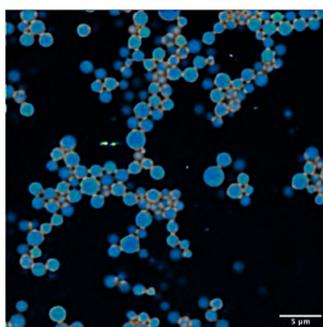


Figure 1. A confocal image of colloidal gels with separate droplets and contacts.

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Rheology of mixed solutions of sulfonated methyl esters and betaine in relation to the growth of giant micelles

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The rheological properties of mixed solutions of sulfonated methyl esters (SME) and cocamidopropyl betaine (CAPB) are related to the synergistic growth of giant micelles. Effects of additives, such as fatty alcohols, cocamide monoethanolamine (CMEA) and salt, which are expected to boost the growth of wormlike micelles, are studied. We report and systematize the most significant observed effects with an emphasis on the interpretation at molecular level and understanding the rheological behavior of these systems [1].

The experiments show that the mixing of SME and CAPB produces a significant rise of viscosity, which is greater than in the mixed solutions of sodium dodecyl sulfate and CAPB. The addition of fatty alcohols, CMEA and cationic polymer, leads to broadening of the synergistic peak in viscosity without any pronounced effect on its height. The addition of NaCl leads to a typical salt curve with a high maximum, but in the presence of dodecanol this maximum is much lower. At lower salt concentrations, the fatty alcohol acts as a thickener, whereas at higher salt concentrations – as a thinning agent. The frequency dependences of the measured storage and loss moduli, G' and G'' , for investigated micellar solutions show standard or nonstandard viscoelastic rheological behavior.

The systems with standard behavior obey the Maxwell viscoelastic model (at least) up to the crossover point ($G' = G''$) and can be analyzed in terms of the Cates reptation-reaction model. The systems with nonstandard rheological behavior obey the Maxwell model only in a restricted domain below the crossover frequency; they can be analyzed in the framework of an augmented version of the Maxwell model.

Keywords: Rheology of micellar solutions; wormlike micelles; sulfonated methyl esters; reptation-reaction model; shampoo formulations

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Competitive effect of oil viscosity and interparticle interactions between carbon particles using polymer dispersant

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Polymeric-based dispersant has inherent importance as lubricants in engine oil formulation. The dispersant concentration and oil viscosity play a key role in determining the fate of engine wear and environmental pollution by controlling the soot aggregation and release. In this work, a model system containing carbon particles in oil of different viscosities was used to simulate carbon particles interactions in oil. Polyisobutylene succinimide (PIBSI) was used as a dispersant to provide stabilization of carbon particles in oil.

The influence of solvent viscosity and PIBSI concentration on carbon particle surface charges and aggregation behaviour were examined. The model systems using dodecane and hexane were prepared by making carbon dispersions, added with varied PIBSI dosages. The surface charges of the carbon particles were calculated from the electrophoretic mobility measurement, and the aggregation behaviour was evaluated using hydrodynamic particle size measurement and UV absorption. Comparatively, the magnitude of carbon effective surface charge in the decane solvent system was higher than in hexane without any PIBSI.

The trend reached an agreement at high PIBSI concentrations, with decane systems having larger charge magnitude, and particles in hexane were leaning toward the zero charges. DLS measurements revealed that large carbon aggregates formed at low PIBSI concentration for the hexane system, whereas a contrasting finding was reported for the decane system. The UV absorption spectra of carbon particles in the decane system revealed that the system with 5 wt.% of PIBSI had the highest absorption, where the peak of absorption spectra in hexane increases with PIBSI concentration.

Keywords: Dispersant, Oil, Surface Charge

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Dynamics of melting chocolate studied by X-ray photon correlation spectroscopy (XPCS)

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Dynamics of soft matter systems on the length scale of sub-micrometer and above-second time scales are very important for their functional properties including mechanics, rheology, and stability. The physics behind this type of dynamics is typically related to structural reorganization, aging, as well as transitions between different states. In the case of chocolate, the wonderful taste and the melting experience in the mouth are closely related not only to the fine structure but also dynamics. XPCS is a powerful tool for research in these fields, and has been applied to biological systems in terms of protein thermal gel [1] and phase transitions [2,3]

In this context, we have recently performed an XPCS study on the melting of a dark chocolate in the ultra-small-angle X-ray scattering (USAXS) mode [1-3]. Measurements were performed at different temperatures, below and above the melting point. The static USAXS profiles at different temperatures overlap each other indicating no significant structural changes during heating and melting on the length-scale of a few hundreds of nanometers. At 22°C, when the chocolate is in the solid state, XPCS measurements show equilibrium dynamics. Heating the sample from 25 to 33°C, non-equilibrium dynamics similar to aging occurs, i.e. dynamics slows down with time, and the overall dynamics becomes faster with higher temperatures as expected. Quantitative analysis using the Kolhrausch-Williams-Watts equation demonstrates that the dynamics is hyper-diffusive [4]. Such a hyper-diffusive dynamics in chocolate during melting is most likely due to the relaxation of the internal stress formed during manufacturing and is typical in soft matter systems.

Keywords: XPCS, Chocolate, Melting

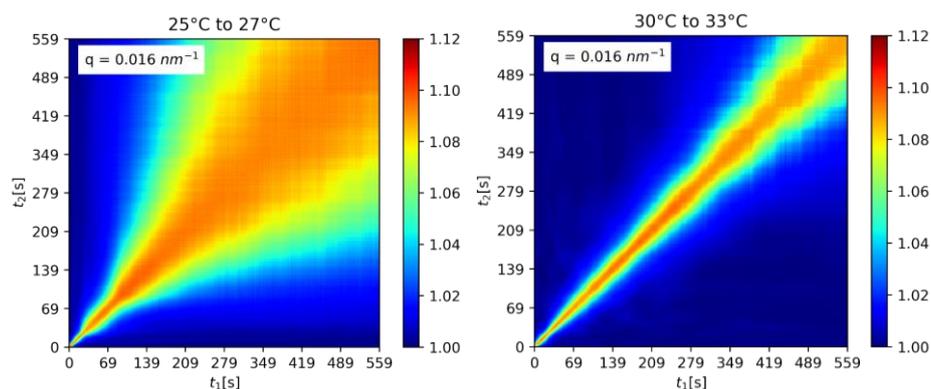


Figure 1. Two-time correlation functions from USAXS-XPCS for a dark chocolate during heating (L) and melting (R).

Acknowledgements: This work was supported by BMBF.

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Colloidal Stability of Apolar Nanoparticles in Solvent Mixtures and Solutions of Intercalants

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Ligand-stabilized gold nanoparticles (AuNPs) are promising building blocks for materials with well-defined structures and properties. Tuning their colloidal stability is essential for a wide range of applications. Previous work has shown that the temperature-dependent agglomeration of AuNPs is strongly influenced by the disorder-to-order transition of the ligand shell determined by both ligand-ligand and ligand-solvent interactions.^[1] For example, cyclohexane promotes disordered ligands, while hexadecane promotes the ordered state, leading to a lower AuNP agglomeration temperature (T_{aggl}) in cyclohexane. This study investigates the dispersion stability in mixtures of these solvents and the effect of intercalant molecules.^[2,3]

We used Small-Angle X-ray Scattering to study the non-linear relationship between the ratio hexadecane:cyclohexane and T_{aggl} . Agglomeration always occurred at lower temperatures than expected for linear mixing. Small-Angle Neutron Scattering experiments showed that irrespective of the solvent composition, 30-40 vol% of the shells' volume was occupied by solvent molecules, indicating good solvation. At intermediate compositions, the fraction of cyclohexane inside the shell was larger than in the bulk. Furthermore, no enrichment of either solvent around the ligand shell was observed at any composition. We hypothesize that the enrichment of cyclohexane inside the ligand shell stabilizes the disordered state of the ligands, which, consequently, leads to a non-linear trend of T_{aggl} .^[4]

We investigated the role of small molecules at low concentrations that can intercalate the ligand shells. Bicyclohexyl was added to find whether it interacts with the alkyl particle shell and causes stabilizing entropic effects. We varied the intercalant concentration and solvent composition to assess whether small molecules may affect the disorder-to-order transition of the ligand shell. Complementary molecular dynamics simulations provide information on the structure of the ligand shell at atomic length scales.

Keywords: dispersion, non-polar nanoparticles, colloidal stability, solvent mixture, intercalants

Acknowledgements: The authors acknowledge Institute Laue-Langevin for allocation of beamtime at instrument D11 (doi:10.5291/ILL-DATA.9-10-1690)

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Exploring anisotropic growth of hydrophilic gold nanorods and their self-assembly in view of biotechnological applications

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In the past 20 years gold nanorods (AuNRs) gained popularity within the nanomaterials field also thanks, among the several valuable properties, to the tunability they provide with a two-component surface plasmon resonance (SPR), associated respectively to the Transversal and Longitudinal components of the plasmon. Their biotechnological applications vary from sensors to biomedicine and the control of synthesis parameters is always fundamental to ensure reproducibility [1,2]. The AuNRs seed-mediated synthesis relies on a complex and delicate equilibrium of reactants to achieve anisotropic growth conditions: silver ions and surfactant agent show preferential adsorption onto specific facets of gold and hinder reduction in these directions in presence of a weak enough reducing agent [3].

In this framework, AuNRs were prepared using silver nitrate and cetyltrimethylammoniumbromide (CTAB) with the aim to study how different reaction conditions impact the AuNRs aspect ratio and optical properties. The AuNRs were investigated combining complementary techniques such as Uv-Vis-NIR, FTIR, XPS and XAFS spectroscopies, DLS and TEM/SEM microscopies. Particular emphasis has been placed on understanding the silver and CTAB role within AuNRs synthesis and self-assembly, in view of biotechnological applications.

Keywords: Gold Nanorods, Seed-mediated synthesis, Extended X-Ray Absorption Fine Structure

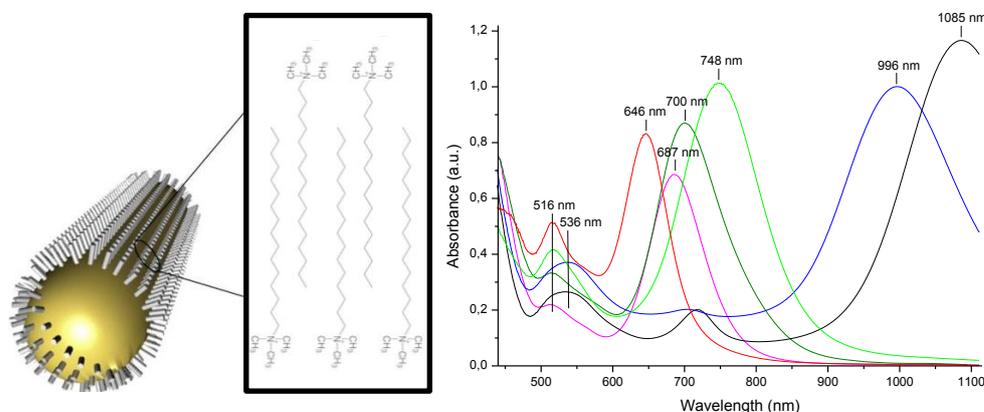


Figure 1. (left) Scheme of AuNRs, (right) Uv-Vis-NIR spectra of different aspect ratio AuNRs.

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Effect of alkylphenol ethoxylated non-ionic surfactants free on the colloidal behavior of acrylic dispersions

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Acrylic latex particles are largely applied in the paint industry. Alkylphenol ethoxylated non-ionic surfactant (APEO) was often used in industrial synthesis of acrylic latex dispersions due to its low cost and high performance. However, the toxicity of APEO [1] motivated the search for alkylphenol ethoxylated non-ionic surfactants free (APEO-free). The present work evaluated the effect of three commercial APEO-free surfactants on the colloidal behavior of latex particles composed of styrene (50%): n-butyl acrylate (50%), styrene (30%): n-butyl acrylate (70%) or methyl methacrylate (30%): n-butyl acrylate (70%). All latex particles were synthesized by emulsion polymerization using sodium persulfate as initiator.

The effect of the type of surfactant on the colloidal stability of acrylic dispersions was evaluated by ζ -potential measurements, dynamic light scattering (DLS) and phase separation analyser LUMiReader. The results indicated that the presence of non-ionic surfactant plays a key role in the colloidal stability, mainly when the medium ionic strength was increased. Meanwhile, there was no substantial influence on the hydrodynamic radius and zeta-potential values of the colloidal particles.

The type of surfactant affected the properties of films prepared by drying the acrylic dispersions, namely, the surface free energy, glass transition temperature and morphology. The present study demonstrated that it is possible to replace APEO surfactant by others APEO-free without affecting the colloidal stability of acrylic latex dispersions.

Keywords: Acrylic latex dispersion, emulsion polymerization, colloidal stability, non-ionic surfactant

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Evaporation driven instability in tear film: 3D dynamics

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The study of tear film instability and its consequent rupture is an extended application of evaporation in thin films. A uniform thickness of tear film over corneal surface is critical for clear vision and hence is often seen as a measure of good eye health in ophthalmology. We study the origin of instabilities in a tear film that leads to its consequent rupture during prolonged inter blink.

We try to develop a mathematical model to provide a rigorous explanation to experimental observation of tear film break up [1][2]. Till date, there is no one comprehensive theory that lucidly defines the phenomena of rupture in a tear film. We validate our numerical simulation techniques using a 2 -D Model of non-linearized and coupled equations based on locally elevated rate of evaporation [4]. We then use this numerical technique to translate the model to a 3 -D domain to add another dimension of understanding to the phenomena.

The simulation results from experimental observations are compared and reasonable correlation is found between the two [3]. The model efficiently captures and employs the theory of evaporation driven instability in a tear film that originates upon a rupture in lipid layer. The study also incorporates a thorough analysis on several key parameters including the surface tension at tear film interface, water permeability through corneal surface and thin-film disjoining forces [5].

Keywords: Thin Film, Surface Intermolecular Forces, Tear Film Lipid Layer, Dye Eye, Tear Film Stability, Rupture Dynamics

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Kinetics of transfer of volatile amphiphiles from vapors to surfactant solution drops

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Subject of this work is to investigate the kinetics of transfer of volatile surface-active amphiphiles from their vapors to low molecular weight surfactant solution drops. The amphiphiles, which were used in our study, were benzyl acetate, linalool, and citronellol. All of them have low saturated vapor pressures, limited (non-negligible) solubility in water, and well pronounced surface activity. The used surfactant was sodium dodecyl sulfate (SDS) in the presence of small amount of NaCl.

The parameters of the adsorption isotherms, the adsorption and desorption rate constants of the individual volatile amphiphiles from saturated vapors to aqueous drops are reported in Ref. [1]. First, the equilibrium surface tension isotherms of mixed SDS and volatile amphiphile solutions at different molecular ratios of components and concentrations were measured. The results were processed using an appropriate theoretical model for mixtures to obtain the interaction parameters between molecules at interfaces, adsorption energies and the respective areas per molecule. Second, the dynamic of adsorption of the surface active volatile amphiphiles from their vapors to the SDS solution drops were studied using the pendant drop method (Fig. 1). Using the surface tension isotherm parameters, the kinetics of surface tension gives adequate information on the dynamics of adsorption at different times. The theoretical analysis of kinetic data in the case of adsorption from vapor to the surfactant solution drop describes excellently the experimental data and gives information for the effect of SDS on the mechanism of adsorption of amphiphilic molecules from their vapors to the drops.

Keywords: Volatile amphiphiles adsorption and desorption rates, kinetics of adsorption

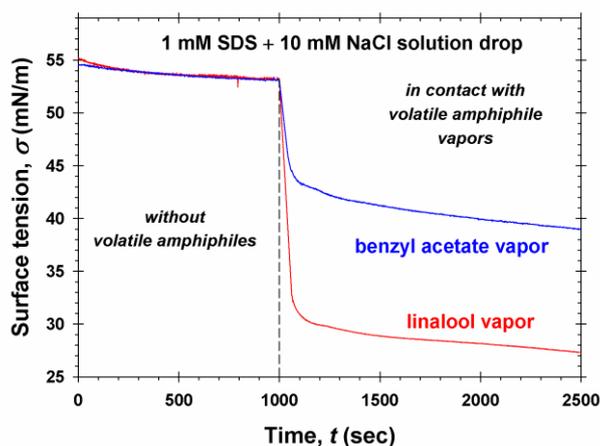


Figure 1. Kinetics of surface tension of SDS solution drop in contact with volatile amphiphile vapors.

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Anisotropic rod-like and spherical particles with temperature-driven tunable interactions

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Colloidal particles grafted with stimuli-responsive polymers constitute an important class of colloidal systems. Anisotropic rod-like colloids have attracted particular attention due to their unique behavior, as a result of their higher excluded volume and the additional rotational degree of freedom, which lead to interesting rheological properties [1-2].

In the present study, we have prepared high aspect ratio silica microrods and silica spheres grafted with dense temperature-responsive polymer chains, and investigated their responsive behavior and rheological properties in aqueous media. In-house synthesized silica rods [3] and commercial silica spheres were surface grafted with well-defined homopolymer and amphiphilic diblock copolymer brushes grown by atom transfer radical polymerization (ATRP) [4-5]. The pH- and temperature-responsive homopolymer, poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA), was employed in the synthesis of the homopolymer grafted particles, while for the diblock copolymer functionalized particles, poly(methyl methacrylate) (PMMA) was chosen as the first block followed by chain-extension with PDMAEMA.

The de-grafting kinetics of the polymer chains from the surface of the silica rods and spheres were investigated under varying solution pH as a function of the polymer molecular weight. We showed that the presence of the hydrophobic PMMA inner layer in the diblock copolymer grafted silica colloids resulted in a chain length-dependent suppression of the degrafting process from the inorganic surface. Next, the temperature-responsive behavior and rheological properties of the diblock copolymer grafted colloids were investigated. An irreversible interparticle aggregation was found during the heating and cooling cycle for the rod-like colloids, in contrast to the diblock copolymer grafted silica spheres which exhibited complete thermal reversibility. Finally, a dense rod suspension was shown to change from a weak solid at low temperatures to a strong solid at higher temperatures as a result of the temperature-driven tunable particle interactions.

Keywords: Silica rods; block copolymer brushes; temperature-driven interactions

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Brownian suspension with inertia Lamm simulation

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Suspensions of solid particles (both Brownian and non-Brownian) in liquid present intriguing flow properties, and understanding their rheology is a subject of both fundamental and technological interest [1]. Particle-based simulations can offer a useful means of scrutinising the relationship between microstructure and bulk rheology, and are also a helpful tool for predicting the viscosity of dense suspensions with prescribed particle-level physics. However, existing models that treat Brownian and lubrication forces are constrained by the need to invert the resistance matrix for the system, limiting their use to rather small systems.

In this work we explore alternative models, considering pairwise interactions to calculate force and torque derived from lubrication, Brownian and contact forces. No longer constrained by expensive matrix inversion, our model can simulate large particle numbers, opening the door to simulations with broad polydispersity. Our model also includes direct particle contacts which may have a lubrication breakdown and thereafter rolling and sliding friction [2].

Overall our model offers a new framework in which to explore the rheology of a vast range of suspensions from Brownian, nanometer particles, through shear-thickening micron particles up to wet granular materials.

Keywords: Brownian suspension simulation.

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Effect of dilution agents, fat globules and temperature on the size measurement of casein micelles via dynamic light scattering

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Casein micelles are largely hydrated and polydisperse protein aggregates that are composed of four casein fractions (α_{s1} , α_{s2} , β , and κ -casein) and calcium phosphate clusters. This study examined the hydrodynamic size of casein micelles using dynamic light scattering (DLS). To avoid multiple light scattering, the samples have to be sufficiently diluted. Four types of dilution agents (i.e. ultrafiltration permeate, simulated milk ultrafiltrate (SMUF), calcium imidazole buffer, deionized water) that may affect the stability of casein micelles were compared. The suitable dilution degree was evaluated through power-law fitting and linear regression, whereby the optical density served as a quick guide to determine the appropriate degree of dilution. The corrected autocorrelation function (ACF) was employed to estimate the size of casein micelles by subtracting the contribution of residual fat globules for skim milk and semi-skimmed milk samples. Moreover, the effect of temperature on the size of casein micelles was investigated. Results of dilution series and kinetic size measurements revealed that both UF permeate and SMUF can stabilize the structure of casein micelles in a diluted system. In contrast, dilution in calcium imidazole buffer or deionized water caused a loss of micelle integrity, depending on the incubation time. The contribution of residual fat globules to the size estimation of casein micelles was negligible in skim milk when the dilution degree reached 2^8 at a scattering angle of 150° . For semi-skimmed milk, the raw DLS data could be used to estimate the size of the casein micelles by subtracting the contribution of the fat droplets (as obtained upon dilution in a casein dissociating solution). Regarding the temperature effect, an increase in incubation temperature from 5 to 45 °C reduced the hydrodynamic size of the casein micelles and increased the count rate.

Keywords: Casein micelles; Particle size distribution ; Dynamic light scattering ; Autocorrelation function

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Novel investigations on the ion-specific effects on sulfate-functionalized cellulose nanocrystals

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Sulfate-functionalized cellulose nanocrystals (SCNCs) are considered stable and well-dispersed in dilute aqueous suspensions due to negatively charged sulfate groups on the nanocellulose surface. The dimensions of the nanocrystals are approximately 7*200 nm, making them rod-like and prone to aggregation at higher mass concentration and ionic strength. For future applications of nanocellulose, such as sensors, adsorbents, and catalysts, it is vital to understand the surface charge behavior in various environments, and this information is also crucial in any subsequent functionalization step of the SCNC surface.

For the surface charge characterization of SCNC, conductometric titrations with a base are typically performed, with the local minima giving information on the material's sulfate content. On the other hand, potentiometric titrations yield the surface charge density (SCD) as a function of pH. These titrations also reveal any effect of the ions present in the dispersion, i.e., the ion-specific effects on the surface charge behavior.

This study performed simultaneous conductometric and potentiometric titrations of SCNC from pH 2.5 to 12. From this data, we could obtain novel information on how the SCD of SCNC depends on both pH and the type of counter-ion (Li⁺, Na⁺, K⁺). We also looked into the potential presence of more than one type of surface sulfate group, the second one being less reactive and becoming deprotonated at higher pH.

Our findings reveal a significant ion-specific effect of the surface on sulfate-functionalized nanocellulose, which should be further investigated in order to understand its reactivity and suitability for various applications.

Keywords: Nanocellulose, counter-ion effects, surface charge.

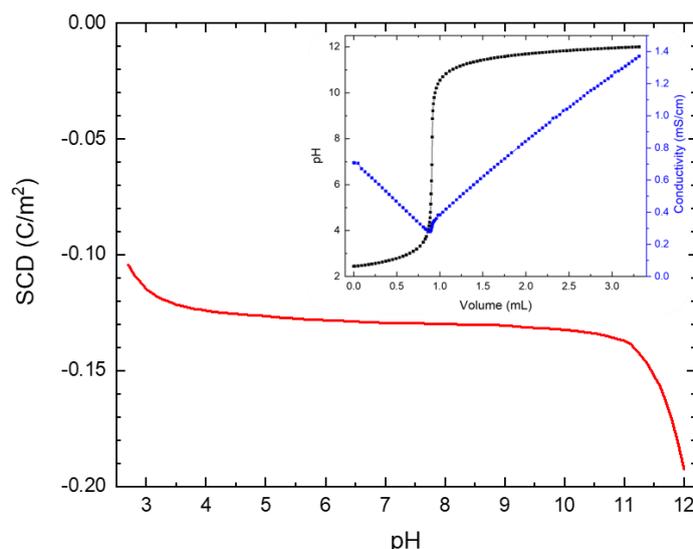


Figure 1. Surface charge density as a function of pH of 0.6 wt% SCNC containing 1 mM NaCl. Inset: The raw data from the corresponding titration.

The Effect of rGO Addition on the Tribological Performance of a Commercialized Fully Synthetic Engine Oil

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Tribological behavior of a commercialized, fully synthetic engine oil was investigated upon the incorporation of reduced graphene oxide (rGO) in various concentrations between 0.01 and 0.2 wt%. In practice, stability of the prepared oil-based rGO dispersions was assessed by turbidimetry and dynamic light scattering measurements, while a reciprocating tribometer consisting of a steel ball on special cut steel blocks was used to evaluate the tribological properties.

It was proved that the addition of rGO (0.02 wt%) led to an improvement of the tribological behavior compared to the pristine engine oil, since the friction coefficient (COF) was significantly decreased by 5% in the boundary lubrication regime. Both the surfaces and the rGO additive were thoroughly characterized by microscopic and optical spectroscopy techniques. Our findings confirmed that a protective layer was formed between the worn surfaces, due to the presence of rGO. Therefore, carbon accumulation and various additive elements such as Ca, Zn, S and P were detected on the rubbing surfaces of both the steel ball and block through energy-dispersive X-ray spectroscopy. Finally, it was shown that the wear scar diameter on the surface of the steel ball was lower by 3%, upon testing the engine oil sample containing rGO the optimum concentration (0.02 wt%), compared to the control sample.

Technology transfer concerning on the preparation and characterization techniques of stable oil-based rGO dispersions to waterborne polyurethane/rGO ones will be accomplished.

Keywords: Tribological performance; rGO additive; Engine oil; Hansen Solubility Parameters



Figure 1. Oil-based dispersions incorporating rGO in various concentrations.

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Microalgae as soft permeable particles

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One of the major bottlenecks for microalgae production is the harvesting process because of the colloidal stability of unicellular algae in suspension [1, 2]. Interaction forces between particles in an electrolyte solution govern the colloidal stability of a suspension. Therefore, the comprehension of these interactions is fundamental for optimizing the harvesting of microalgae suspensions. It is well known that the electric double layer plays a fundamental role in the electrostatic stabilization of colloids. Soft particle theory developed mainly by Ohshima [3, 4] describes the electric properties of particles covered by an ion-permeable polyelectrolyte layer, which is usually the case for biological particles [5]. In this study, the influence of extracellular permeable layer on the electrokinetic properties was examined for one freshwater microalga, *Chlorella vulgaris*, and two seawater microalgae species, *Nannochloropsis oculata* and *Tetraselmis suecica*. The soft particle model was used to interpret the electrophoretic mobility measurements at different ionic strengths. This allowed us to estimate two parameters that define the characteristics of the polyelectrolyte layer of each microalga: volume charge density and the characteristic penetration length. These parameters were determined from the fitting of the measured electrophoretic mobilities to Ohshima's theory and then evaluated by a sensitivity analysis. Furthermore, transmission electron microscopy (TEM) was performed to observe the cells' surface and analyze the polyelectrolyte layer of microalgae. The results showed that all three microalgae have a soft particle character. Additionally, the surface potential of microalgae was estimated from electrophoretic mobility measurements using the soft particle theory, showing that the algae surface potential is less negative than the apparent zeta potential. This finding indicates that the energy barrier due to the electrostatic repulsion between cells is much smaller than that usually expected [6].

Keywords: Microalgae; Soft Particle; Electrophoretic mobility; Biocolloid

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Drying of a thin film of complex fluid under an evaporation mask

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Wet coating consists in spreading a liquid film containing particles or polymers on a substrate and letting the solvent evaporate. It is of great interest for industry as it is cost effective and allows the functionalization of substrates with a broad range of materials. However, whilst drying, evaporation flux heterogeneities spontaneously appear at the edges. This can deform the surface and generate flows in the film, leading to a non-flat deposit in the end.

These evaporation flux heterogeneities being difficult to quantify, we use an evaporation mask located just above the film to impose a controlled heterogeneity of the evaporation flux. Experimental studies have shown that a marked depression appears in the dried film below the mask location [1,2]. Qualitatively, the solvent evaporates faster in the unmasked area, which deforms the surface and generates flows. These outward flows carry solute away from the mask, which explains the observed depression. This mechanism has been exploited in the last decade in order to obtain deposits of given shapes but is not quantitatively described in the literature [3].

We study both experimentally and theoretically the effect of an evaporation mask placed above a drying film of polymer / solvent solutions. We find analytical solutions for the final shape of the polymer layer considering that either gravity or capillarity drives the flows. We demonstrate that gravity can play a role in these deformations even for films with an initial thickness that is smaller than the capillary length. Our predictions are in good agreement with experimental results obtained with polystyrene/toluene. A typical experimental profile of the dried film is shown on Figure 1(a). The analysis we have conducted therefore offers the first quantitative prediction of the shaping of a deposit with an evaporation mask.

Keywords: wet coating, evaporation, polymers

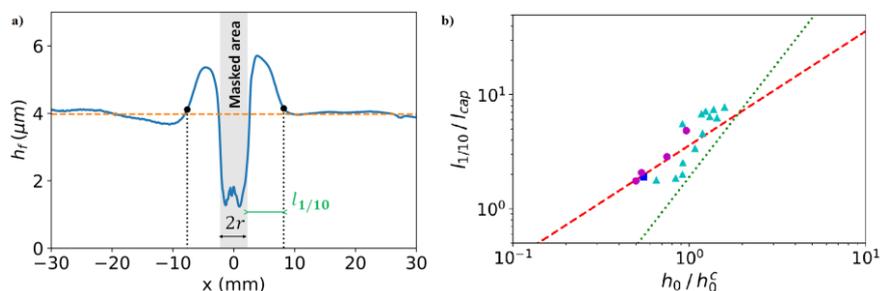


Figure 1. (a) Height profile of a film obtained by drying film of polystyrene/toluene solution under a rectangular mask. (b) Evolution of the lateral extent $l_{1/10}$ with the initial thickness h_0 . Theory if gravity (green) or capillarity (red) dominates and experimental points for different initial volume fractions in polystyrene.

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Design of experiments to model the size of AgNPs in microfluidic synthesis

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Silver nanoparticles (AgNPs) possess unique optical, antibacterial and catalytic characteristics which facilitate their application in multiple industrial fields. Therefore, the determination of fabrication and synthesis routes is a very critical step to fulfil application requirements. Microfluidics has been demonstrated as a useful platform for AgNP synthesis which allows the manipulation of small volumes of reagents and the precise control of operational parameters [1]. If used together with powerful tools such as design of experiments, regression analysis and response surface methodology it can further increase the synthesis effectiveness in terms of size and sustainability.

This study is concerned with the development of a predictive response surface model for AgNP size, based upon experimental data obtained in a T-junction microfluidic device, as a function of hydrodynamic and reaction conditions. The continuous flows of silver nitrate and tannic acid/trisodium citrate were supplied by two tubes meeting at T-junction, whereas the reaction was performed in the outlet tube. The particle size distributions obtained were measured by dynamic light scattering (Z-sizer) and transmission electron microscopy (TEM). Both techniques were in very good agreement as shown in Fig.1.

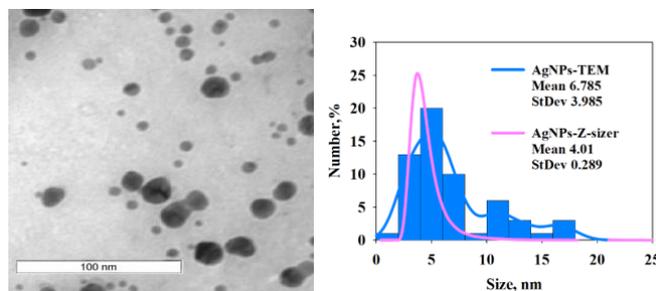


Figure 1: AgNPs size distributions at optimal conditions measured by TEM and light scattering.

The effects and interactions of pH of the solution, relative concentration of trisodium citrate, curvature of the outlet channel, flow rates of reagents and storage temperature on the size of the AgNPs were examined at two/three levels through a D-optimal design (162 runs).

The experimental data of the size of AgNPs were fitted to a second-order polynomial function with average prediction error around 12.68 %. The obtained model was validated by subsequent experiments (12 runs) within the limits of the experimental factors with average prediction error around 8%. The response surface methodology revealed the optimum combination of parameters for minimum size of particles with prediction error around 7.0%.

Keywords: silver-nanoparticles, microfluidics, design-of-experiments, regression

Acknowledgements: This work was funded by the EPSRC Programme Grant PREMIERE EP/T000414/1. KN is funded by a PhD studentship from the School of Chemical Engineering, University of Birmingham, UK.

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PBM-CFD simulations of microfluidic synthesis of AgNPs

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The development of reliable predictive models based on and validated by precisely tailored experiments is a rapidly growing area of research enabling reduction of material and energy consumption. The implementation of efficient fabrication routes such as microfluidic synthesis [1] along with the use of computational techniques is valuable in providing new insights into formulation engineering and reduction of environmental impact.

This interconnected numerical and experimental study aims to predict the size distribution of silver nanoparticles (AgNPs) synthesized in a T-junction microfluidic device as a function of the process variables. The numerical approach used is a combination of population balance model and computational fluid dynamics (PBM-CFD) examining three steps in the formation of AgNPs including reduction, nucleation, and growth.

The nucleation and growth rate constants were obtained from experimental data based on the Finke-Watzky two step mechanism [2] which assumes a slow continuous nucleation followed by an autocatalytic growth step. The operating conditions, such as flow rates and species concentrations, were the same in both experimental and numerical studies, whereas PBM parameters including critical nucleus size and aggregation efficiency on the final particle size distribution were taken from literature and evaluated in the development of the model.

Experimental validation of CFD and PBM results was performed by comparison of silver ion concentration and particle size distribution at different outlet channel lengths. Good agreement was found.

Keywords: CFD, PBM, reaction-kinetics, microfluidics, silver-nanoparticles

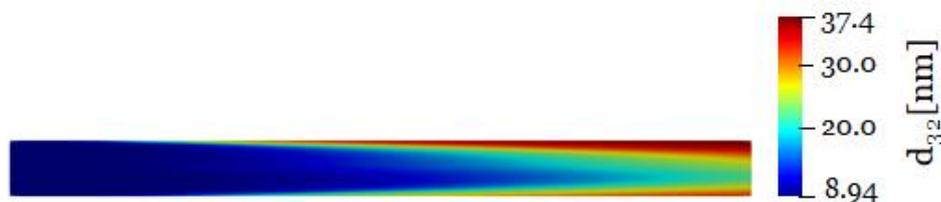


Figure 1. Contour plot of d_{32} which corresponds to the Sauter mean diameter of the distribution across the channel

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Giant third-harmonic generation and quantum coherent effects in ultrasmall Au₆ nanoclusters

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The combinations of optical linearities and nonlinearities are the basis of all-optical devices employing self-phase modulation, optical bistability, regenerative oscillations and four-wave mixing.¹ Due to their application in imaging, medicine, communication and industries, the demand for miniaturized devices motivates the assessment of the nonlinear optical properties of nano-scaled layered materials in visible and near infrared region.² Atomically precise gold nanoclusters (GNCs) are foreseen to display photoluminescence (PL) with excellent photostability and high biocompatibility. Understanding their structure-property relationship is fundamentally important for emerging applications in photonics, devices, imaging, spectroscopy, laser science and catalysis. Although the existing experimental and computational studies on GNCs have focused on clusters with a few tens to hundreds of atoms, however, a limited number of studies have focused on the photophysics of ultra-small GNCs containing less than ten atoms. Herein we demonstrate a new type of thermo- and photostable ultra-small Au₆ nanoclusters with centrosymmetric octahedral core displaying both linear and nonlinear optical properties along with quantum coherent effect in the photocycle. The particles emit intense PL upon 400 nm excitation (~35% quantum yield) and produce giant third harmonic generation by infrared (1300 -1550 nm) excitations. Most interestingly, the value of third order non-linear susceptibility ($\chi^{(3)}$) is ~6-9 orders of magnitude larger than routinely studied 2D nanomaterials, including graphene and metal dichalcogenides. The experimental and DFT calculations suggest that all Au atoms in this NC are in the Au(I) state. This induces ultrafast ligand-to-metal charge transfer without the involvement of semiring states. Femtosecond transient absorption spectra revealed an ultra-efficient (150 fs) intersystem crossing and the role of quantum coherent effects in the photocycle. Such Au₆ NCs also behave as efficient electron acceptors in the excited- and ground-state and validate their application as p-type dopants in field-effect transistors.

Keywords: Gold nanoclusters, Third harmonic generation, Photoluminescence, Quantum coherent effect

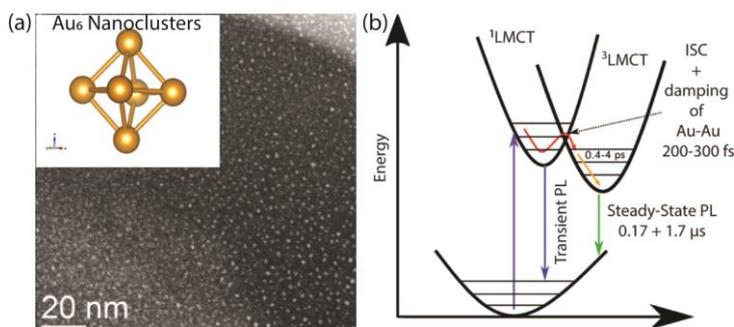


Figure 1. (a) HR-TEM image of the GNCs. Inset displays its octahedral geometry. (b) Photocycle of GNCs.

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Exploring the glassy behaviour of the Gaussian Core Model by random pinning

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The Gaussian core model (GCM) introduced by Stillinger [1] describes point particles interacting by means of a Gaussian-shaped potential. This model is one of the most common and simplest models for the description of ultrasoft systems, yet a clear picture of its glassy behaviour is still missing [2-3].

In this talk I will present results from Molecular Dynamics simulations of the GCM with random pinning. Thanks to the pinning procedure one can avoid crystallisation and thus explore the glassy behaviour of the system. In particular, I will discuss the observation of a reentrant glass formation that follows the well-known behaviour for equilibrium crystallisation. Moreover, structural and dynamical properties of the glassy state will be addressed, in relation to the concept of cluster formation.

Keywords: Gaussian core model, molecular dynamics simulations, random pinning, glassy behaviour.

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Are Colloidal Trimers Governed by Fickian yet Non Gaussian Dynamics?

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In recent years, the conventional dynamics of colloidal particles have been called into question. Many studies of colloidal behaviour have found that even during Fickian diffusion colloids may exhibit non-Gaussian displacements, called Fickian yet Non-Gaussian dynamics[1-2]. By performing molecular simulations, we investigated the dynamics of isotropic fluids of colloidal trimers interacting via the Mie potential, the hardness of which can be tuned by changing the attractive and repulsive terms. We obtained the critical points for each of the systems, which allows for consistent comparison between the potentials, studying their dynamical properties at a reduced temperature and density. We found that the dynamics of the trimers were complex, consisting of fast and slow trimers, which results in deviations from Gaussianity at intermediate timescales. These deviations are temporary and vanish as the system enters Fickian diffusion.

Keywords: Dynamics, Mie potential, Fickian yet Non Gaussian, Molecular Simulations

Acknowledgements: This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC) via an Industrial Cooperative Award in Science & Technology (ICASE) co-funded by IBM. The authors would like to acknowledge the assistance given by Research IT and the use of the Computational Shared Facility at The University of Manchester.

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Predicting Self-Diffusion Coefficients of Mie Spheres Using Machine Learning

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While estimating the self-diffusion coefficient of colloidal and molecular species using molecular simulation techniques is relatively straightforward, predicting its dependence on temperature and density is substantially more complex. Many empirical and semi-empirical theories have been formulated to predict the behaviour of the self-diffusion coefficient of a single system at different state points [1]. Recently, several groups have attempted to predict the self-diffusion coefficients of single systems using machine learning methods, rather than the empirical methods used previously. With the large amounts of self-diffusion coefficient data published in the literature, there was enough data to train the models that outperformed previous equations for singular systems [2-3]. In this work we looked at a family of related systems, namely spherical particles interacting with different Mie potentials, to obtain a machine learning method that would be able to predict the self-diffusion coefficients of each system, depending on temperature, density and the attractive and repulsive contributions to the interaction potential. In addition, we also use our methodology for reverse engineering, i.e., from experimental information of the self-diffusion coefficient, temperature and density, we can find the corresponding Mie potential that represents the system with good accuracy. This approach can be used to include dynamic properties in the development of coarse-grained force fields in a similar way as it has been done for thermodynamic properties [4].

Keywords: Machine Learning, Diffusion Coefficient, Mie potential

Acknowledgements: This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC) via an Industrial Cooperative Award in Science & Technology (ICASE) co-funded by IBM. The authors would like to acknowledge the assistance given by Research IT and the use of the Computational Shared Facility at The University of Manchester.

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A Computational Model for Interpolyelectrolyte Complexes

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Advances in modern polymer science allow to create evermore complex self-assembled structures, which are driven mostly by using electrostatic and hydrophobic forces. An example of such a system are multicompartiment interpolyelectrolyte complexes (MIPECs) to be obtained by combining appropriate copolymers of opposite charge and which are stabilized by a hydrophilic corona [1]. These water-soluble colloids of 50-200 nm size combine different solubilisation properties, functionalities, and variable mesoscopic structure that make them interesting for example in the field of drug delivery. The structure of the MIPECs have been already studied e.g. by Small Angle Neutron Scattering (SANS) [2]. However, a detailed description of the architecture and appropriate modeling of the data is still missing. In this talk, we will present a computational model which can describe the existing SANS data and offer further structural insights from the model parameters.

This top-down, coarse-grained model presents micelles of hydrophobic chains as spherical particles confined into a spherical region composed of the IPEC. This simplistic model allowed us to use Molecular Dynamics (MD) simulations to rapidly sample the configurations of the system. The obtained scattering intensities revealed the lack of a fractal behavior [3] and the confinement shape. Moreover, we will show that by considering a third different Scattering Length Density (SLD) we can realistically model the scattering contribution of the confined region and obtain a realistic model of our system. This structural model then was tested on experimental SANS data obtained from complexes of oppositely charged microemulsion droplets and polyelectrolytes.

Keywords: Coarse-Graining, Polymers, SANS, Molecular Modeling

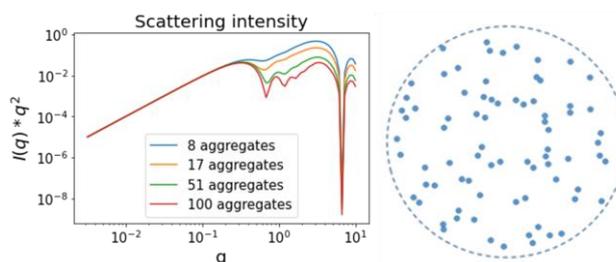


Figure 1. At left, the scattering intensity is plotted (normalized with $I(q=0) = 1$). At right, a 2D representation of the system is depicted.

Acknowledgements: An important contribution on the routine to calculate the scattering intensity is given by Dr. Sergei Grudinin, which we deeply acknowledge. The funding of the PhD project support “Structure and Dynamics of MIPECs of Dual Polarity” by the ILL and TU Berlin is also gratefully acknowledged (Project no. : 191_24).

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Self-diffusion and sedimentation of shape-anisotropic colloids

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Recent scientific advancements have enabled the synthesis of nanoparticles with complex shapes, which have the potential to become primary building blocks for future materials [1]. Understanding the transport properties of such non-spherical particles is not only important for many applications, e.g., their self-assembly into (hierarchical) suprastructures, but also interesting from a scientific point of view, as little is known about their dynamics. Computer simulations play a central role for studying these systems, but the majority of existing methods have been optimized for, or are even limited to, spherical particles. To address these challenges, we employ multiparticle collision dynamics (MPCD) simulations of a discrete particle model [2] to study dispersions consisting of shape-anisotropic colloids. Specifically, we investigate the self-diffusion and sedimentation of cubes, sphero-cylinders (with varying aspect ratios), tetrahedra, and octahedra, and we cover both dilute and concentrated colloid volume fractions. Our computational approach can be used to study the transport properties of complex colloids, and we plan to extend our methodology to investigate systems out of equilibrium and/or in confinement.

Keywords: colloids, shape-anisotropy, MPCD, diffusion, sedimentation

Acknowledgements: This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) (Project Nos. 274340645, 405552959 and 470113688) with additional support from an Auburn University Center for Polymers and Advanced Composites Undergraduate Research Fellowship (PGK). This work was completed, in part, with HPC resources provided by the Texas Advanced Computing Center (TACC) at the University of Texas at Austin and the Auburn University Easley Cluster.

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On the role of polydispersity on the phase diagram of low-density colloidal solutions

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The low-density phase diagram of nanometric colloidal particles has a widespread range of application, spanning from material science up to biomedical systems. Colloids of various shapes have been developed over the last decades either for creating novel devices with peculiar and tunable properties, such as liquid crystals, self-assembling materials with particular optical properties, as well as for realising innovative drug delivery carriers [1]. When synthesised, such nanocomposites are always characterised by a non-negligible polydispersity, that might have a non-trivial effect on the properties and clustering of the complex fluids made by such nanomaterials in solution.

In this work we will address the role played by polydispersity on the low volume fraction equation of state of hard colloidal nanoparticles of various elongations (aspect ratio $A = L/D = [1, 5]$) to predict the compressibility of a solution of a drug delivery vessel candidate, namely Au/Ag CTAB coated nanorods [2]. By means of Monte Carlo NPT simulations we demonstrate that polydispersity on diameter or length of elongated nanoparticles play a diverse role on equation of state (EOS): while a polydispersity in elongation leads to an EOS comparable with the monodisperse case, a polydispersity in diameter renders the system overall more compressible with a dependency on the distribution of the diameters (Figure 1). This result is quite general for anisotropic systems. Moreover, simulation data have then been strengthened by a theoretical approach based on a Parson-Lee approximation of the Onsager theory, that demonstrated to predict quantitatively how the EOS changes with polydispersity with respect to the monodisperse case (Figure 2). Such a result implies that the EOS of a system with a known polydispersity can be quantitatively predicted through a simple theory starting from the EOS of the corresponding monodisperse case, thus becoming a powerful tool for both computational and experimental purposes [3].

Keywords: Anisotropic colloids, polydispersity, low density equation of state, theory, simulations

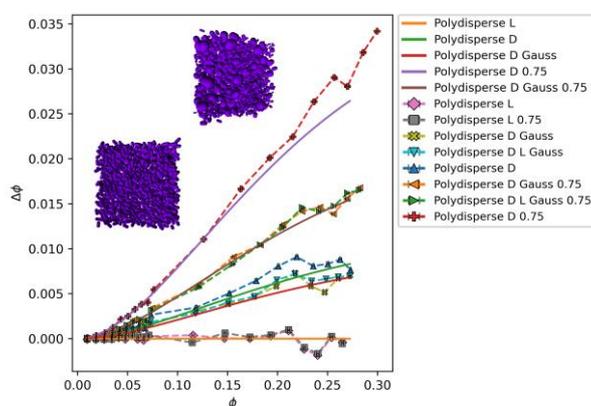


Figure: EOS computed for various polydispersities with respect to the monodisperse case.

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A Model for Bubble-Particle Collision Frequency in a Turbulent Flow Field

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Process modeling is a valuable tool for process design and optimization. Nonetheless, the extent of its use depends on the physical complexity of each particular application. Dispersed air flotation is one of the most complex processes to model. In particular, in mechanical flotation cells, turbulent flow prevails and promotes bubble-particle collisions. Many size and time scales of both hydrodynamic and physicochemical nature have to be resolved to model the process. The only way to achieve this is a combination of co-current (pulp and froth) and sequential multiscale modeling. A generalized framework for modeling the pulp phase from the device scale to thin film scale separating bubbles and particles is discussed here. The core of the model is the term describing the collision frequency between bubbles and particles. Existing approaches to derive this term are reviewed and critically commented demonstrating several inconsistencies.

A unified and consistent approach for deriving this collision frequency term is described overcoming all the inconsistencies of previous approaches. The schematic of the steps leading to an expression for this frequency is shown in Figure 1. Specific results are presented for the case of flotation of fine particles, being practically the only case for which a simplified collision frequency expression of algebraic complexity can be derived.

Keywords: Mathematical model; Turbulent flow field; Fine particles

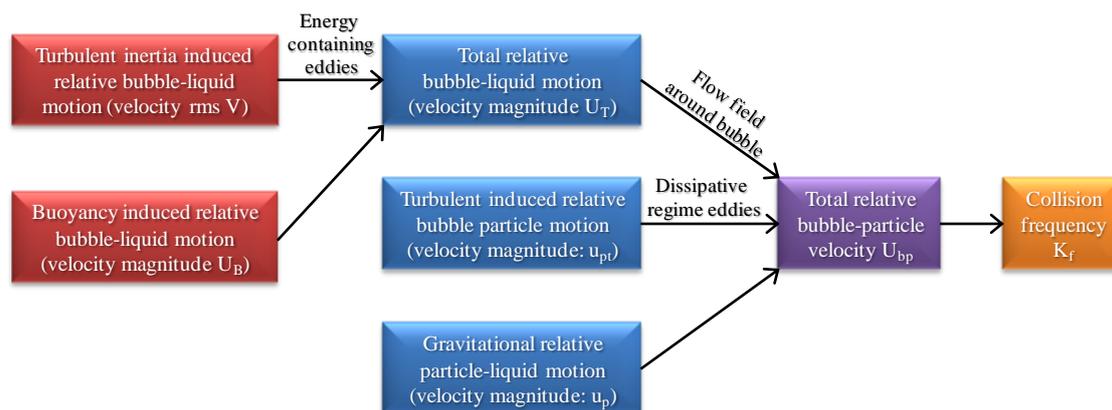


Figure 1. Internal structure of the proposed modeling framework for bubble-particle collision frequency in turbulent flow.

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Ionization Equilibria and Swelling Behaviour of Weak Polyampholyte Core-shell Microgels - A Monte Carlo Study

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The charge of polyampholyte microgels can be tuned by varying the pH, and a charge reversal from a positively charged microgel at low pH to a negatively charged microgel at high pH can be achieved. A swelling transition from a collapsed to a swollen state occurs when the pH is increased or decreased, starting from an intermediate value. While the ionization and swelling behaviour of microgels depend on many parameters coupled in experiments, simulations can systematically provide information about the influence of one particular parameter. Building on our earlier work on alternating polyampholyte microgels, we now investigated the pH-dependent ionization and the swelling behaviour of polyampholyte core-shell microgels using Monte Carlo simulations with the constant-pH method for a bead-spring polymer model[1,2]. While in many studies, the degree of ionization is a predefined input parameter, in our work, it is a direct result of the simulation.

In principle, the width of the U-shaped transition of the microgel swelling depends on the relative dissociation constants of acid and base[1]. Due to the spatial separation of acidic and basic monomers, the ionization is enhanced less compared to a microgel with an alternating distribution of the two species. Furthermore, we saw a shift of the isoelectric point caused by an increased charge density in the core. Added salt screens the charges within the network, and the U-shape transition becomes more narrow. Radial distribution functions show a clear core-shell structure both at low and high pH and a microgel collapse accompanied by a complete interpenetration of the shell and the core at intermediate pH values.

Keywords: polyampholyte microgels, Monte Carlo simulations

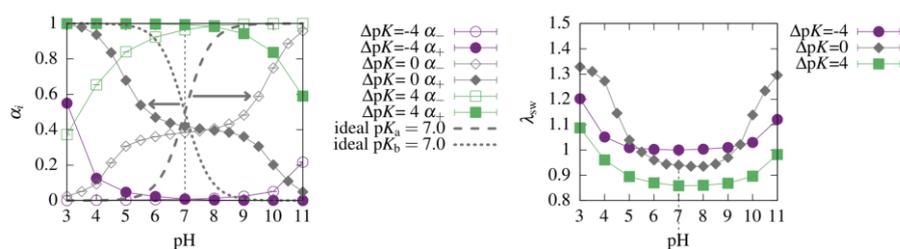


Figure 1. Degree of ionization as a function of pH and different ΔpK ($\Delta pK = -4$: $pK_a = 9.0$, $pK_b = 5.0$; $\Delta pK = 0$: $pK_a = 7.0$, $pK_b = 7.0$; $\Delta pK = +4$: $pK_a = 5.0$, $pK_b = 9.0$). Dotted lines represent the ionization of a system without interactions for $pK_a = 7.0$ and $pK_b = 7.0$ (left). Degree of swelling as a function of pH (right).

Acknowledgements: Financial support from the Deutsche Forschungsgemeinschaft within the SFB 985 - Functional Microgels and Microgel Systems is acknowledged.

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Polymers at Interphases via Simulations Across Scales: from Atoms to Macroscopic Properties

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Nowadays, computational approaches can be used in order to provide a direct insight at the properties of complex polymer-based materials across multiple spatiotemporal scales. Molecular simulations in particular have the advantage of accurately describing the chemistry of the systems under study, and of predicting their behavior at the molecular level. However, the study of polymers via molecular simulations is a very challenging field, due to the broad spectrum of the underlying length and time scales. Here, we present a hierarchical multi-scale methodology for predicting the macroscopic properties of polymer-based nanostructured systems, that involves atomistic and coarse-grained simulations. The coarse-grained (CG) models are derived through a “bottom-up” data-driven strategy, using information from the detailed atomistic scale, for the given chemistry. The systematic linking between the atomistic and the chemistry-specific CG scale, allows the study of a broad range of molecular weights, for specific polymers, without any adjustable parameter [1-3]. At the same time, machine learning (ML) algorithms have been developed to re-introduce atomic detail in the CG scale, and thus obtaining atomistic configurations of high molecular weight polymers [3].

We apply the entire methodology to (a) cisPB polymer melts [4], and (b) cisPB/silica nanocomposites [5]. For both systems we provide a detailed study of their dynamical and rheological macroscopic properties. For the polymer melts, we report predictions about the self-diffusion coefficient of polymer chains, the relaxation modulus and the zero shear-rate viscosity, as a function of molecular length probing the transition from oligomers, to Rouse-like, up to the well-entangled systems.

Concerning the polymer nanocomposites, we examine the structure and the dynamics of polymer chains at the polymer/nanoparticle interphase, by probing directly the density and the conformations of polymer chains, as well as and the segmental and terminal dynamics of the adsorbed, “bound” layer. In all cases the results are compared against experimental data and theoretical predictions.

Keywords: interfaces, Keywords: Molecular simulations, polymer nanocomposites, machine learning methods

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Modelling of Polymer/Alumina Interfaces via Ab-initio Calculations and Machine-learned Molecular Dynamics Simulations

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The properties of polymeric nanostructured materials are typically determined by the presence of polymer/solid interfaces. Polymer chains in interfaces are characterized by a very broad range of characteristic time (from fs up to sec) and length (from Å up to several nm) scales [1]. The latter and the complex quantum mechanical interfacial interactions indicate that multiple spatiotemporal scales must be bridged. Here, we study such systems via a new hierarchical multi-stage simulation methodology, involving ab-initio calculations and atomistic simulations of polybutadiene (PB)/alumina interfacial systems. Initially, density functional theory (DFT) calculations of a single butadiene monomer adsorbed on alumina surface are performed. We sample the energy and configurations of the system via constraint DFT minimizations based on adsorption characteristics. In the second stage, a detailed (classical) atomistic force field is obtained for the butadiene/alumina interaction by machine learning (ML) algorithms using pairwise additive parametric functional forms, e.g. Lennard-Jones, to fit the DFT data [2]. The last stage of the proposed hierarchical simulation approach concerns the prediction of the properties of PB/Alumina interfaces at the atomic level, using the developed classical atomistic force field. We study the structure, conformations and dynamics of polymer chains as a function of distance from the alumina substrate.

Keywords: interfaces, MD, DFT

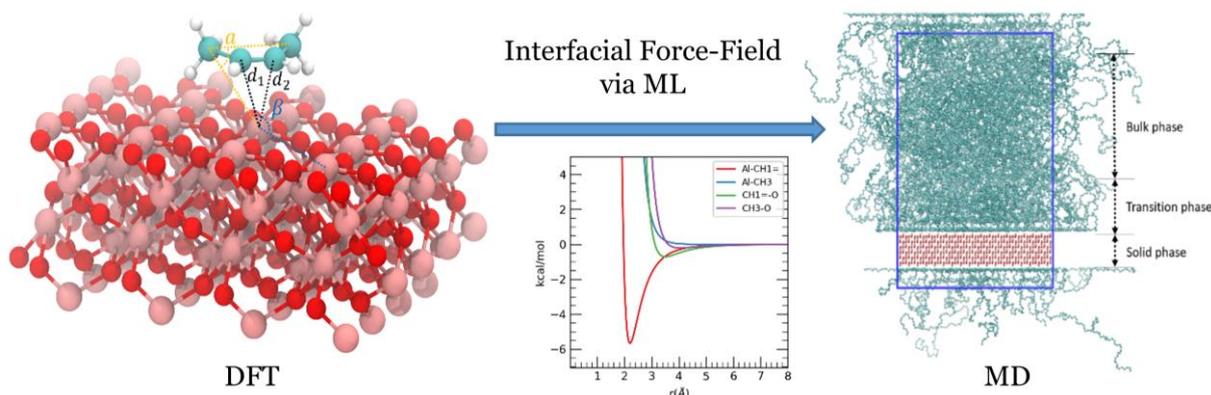


Figure 1. Schematic of the multi-scale methodology. Initially, distances d_1 , d_2 and angles α , β are constrained for many different values to sample the configurational space. We fit the DFT data by a ML algorithm and we obtain pairwise potentials that are applied in MD simulations. We calculate the gradient of properties within the transition phase.

Acknowledgements: We acknowledge funding from European Union's Horizon 2020 research and innovation programme (grant agreement no. 810660, SimEA)

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Capillary assembly of anisotropic particles at cylindrical fluid interfaces

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The unique behaviour of colloids at liquid interfaces provides exciting opportunities for engineering the assembly of colloidal particles into functional materials. The deformable nature of liquid interfaces means that we can use interfacial curvature, in addition to particle properties, to direct self-assembly. To this end, we use a finite element method (Surface Evolver) to study the self-assembly of rod-shaped particles adsorbed at a simple curved liquid interface formed by a sessile liquid drop with cylindrical geometry. Specifically, we study the self-assembly of single and multiple rods as a function of drop curvature and particle properties such as shape (ellipsoid, cylinder, spherocylinder), contact angle, aspect ratio and chemical heterogeneity (homogeneous and triblock Janus).

For chemically homogeneous rods, we can control the orientation of the rods to lie parallel, perpendicular, or obliquely with respect to the long axis of the cylindrical drop by tuning particle properties, even though the lateral dimension of the liquid drop is larger than the length of the rods in all cases studied. For triblock Janus rods, where contact line undulations are larger, we can not only control the orientation of the rods, but also achieve strong spatial confinement of the rods lateral to the cylindrical drop.

Finally, by tuning particle properties to achieve parallel alignment of the rods, we can favour tip-to-tip assembly and suppress side-to-side assembly, not just for cylindrical rods, but also for ellipsoids and triblock Janus rods. Our capillary assembly method based on cylindrical drops therefore provides a facile method for organising micro and nanoscale objects into complex cluster structures.

Keywords: Self-assembly, Colloids at fluid interfaces

Competing dynamics at play: self-assembly of colloidal particles with mobile DNA linkers

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Besides being a key mechanism in living systems, the specificity of DNA base-pair hybridization can be used to finely tune bonding interactions in synthetic systems, allowing the bottom-up design of sophisticated materials obtained by directed self-assembly. A powerful approach to apply this strategy is the surface functionalization of colloidal particles with complementary single DNA strands. Such DNA coated colloidal particles (DNACCs) experience a reversible self-assembly at temperatures below a specific temperature threshold, which can be tuned by selecting the length of the DNA strands.

In most early works on DNACCs, functionalization was performed by attaching the DNA strands to fixed points on the surface of solid particles. However, prescribed crystalline structures in such systems are hard to reach due to strong kinetic arrest effects arising during the self-assembly. Recent studies have explored the functionalization of particles with soft surfaces—either liquid or polymeric—that allow some significant degree of surface diffusion of the DNA strands. This alleviates kinetic arrest effects by enabling the reconfiguration of the aggregates without any disassembly. Despite the dynamic phenomena governing these systems is qualitatively understood [1], no model to date has been able to characterize the relative importance of each contribution, nor the diversity of experimental self-assembled structures observed for different parameters [2]. Here we present the first dynamic model able to predict the effective valency of DNACCs with fully mobile DNA strands, for suspensions under stable self-assembly conditions, depending on the density and diffusivity of both, colloidal particles and DNA strands on their surface. Extensive Langevin dynamics simulations performed with this model show excellent agreement with available experimental data from suspensions of functionalized microdroplets. Therefore, our model paves the way for a thorough quantitative understanding of these systems. Its application to suspensions of amphiphilic polymer micelles will be also outlined.

Keywords: DNA crosslinking, DNA coated colloids, self-assembly, dynamic modeling;

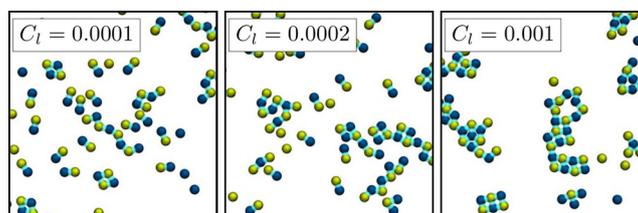


Figure 1. Self-assembled structures in a monolayer of microdroplets with different surface densities of DNA linkers.

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In silico investigation of colloidal particle deposition and surface affinity

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Deposition of colloidal particles from suspensions onto solid surfaces is a common phenomenon in a variety of natural and industrial relevant processes, such as environmental transport, water treatment and application of consumer formulations. Computational models and simulations play a significant role in designing and optimizing the colloidal particles deposition and detachment for a particular application [1] and to provide mechanistic understanding of the particle-surface affinity.

In this work, we first present a unified self-consistent model to computationally investigate the transport and deposition of colloidal nanoparticles from suspensions of different ionic strengths on cylindrical microfibers. The coupled computational model of convective-diffusive transport with hydrodynamics and Derjaguin-Landau-Verwey-Overbeek (DLVO) forces is validated on a single fiber Kuwabara flow cell. The model extends to two-fiber flow cell in vertical, horizontal and staggered orientations, and finally, to multi-fiber arrays as a demonstration of utility to practical problems. On the other hand, a mechanistic viewpoint is provided for particle deposition and detachment as a function of particle-surface affinity using Smoluchowski equation based numerical simulation framework. The mean first passage times for deposition and detachment are calculated to demonstrate the impact of surface interaction potential on deposited amount of particles. Our in-silico methods presented in this study finds potential applications in biochemical binding affinity assays, ultrafiltration, coatings and consumer care.

Keywords: colloidal deposition, *in-silico*, particle-surface affinity

Acknowledgements: We gratefully acknowledge the financial support from the Agency for Science, Technology and Research (A*STAR) of Singapore for a RIE2020 Advanced Manufacturing And Engineering (“AME”) IAF-PP Capsule Surface Affinities (Complete Life-Cycle) grant (Project Ref.: A20G1a0046)

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Liquid nucleation around charged particles in the vapor phase

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Experimental work in different fields such as polymer crystallization and atmospheric science confirmed that electrostatic interactions promote nucleation. Near charged particles, field gradients lead to coupling between the electric field and the density of the fluid. The dielectric fluid is attracted by a dielectrophoretic force to the charged surface, leading to an increase in the density. In return, the density affects the electric field through the change in the dielectric constant.

In our work, we theoretically investigate the nucleation of liquid droplets from vapor in the presence of a charged spherical particle. Due to field gradients, sufficiently close to the critical point of the vapor–gas system, the charge destabilizes the vapor phase and initiates a phase transition. The fluid's free energy is described by the van der Waals mean-field model augmented by electrostatic energy and a square-gradient term. We extremize the free energy and solve the Euler–Lagrange equations to obtain the thermodynamically stable density profiles at arbitrary temperatures, particle charges, and vapor densities.

In contrast to the classical nucleation theory, here, both liquid and vapor phases are different from the bulk phases because they are spatially nonuniform. In addition, the theory applies to both sharp and diffuse interfaces and calculates the surface tension self-consistently.

We construct a phase diagram indicating changes in the binodal, spinodal, and critical temperature. It is shown that the field gradient enlarges the range of temperature and vapor density where liquid can nucleate.

Keywords: liquid nucleation, Mathematical modeling

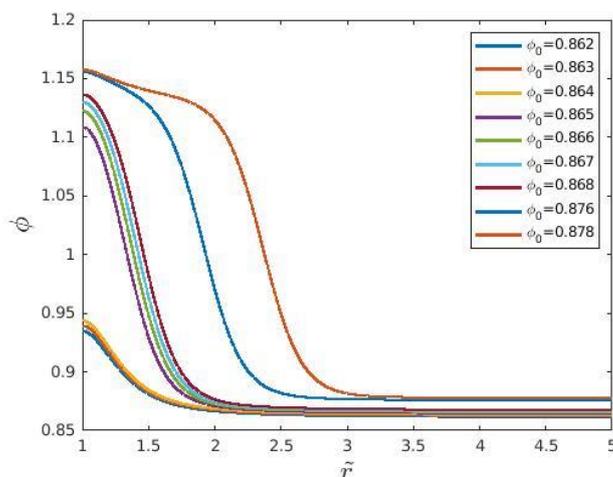


Figure 1. Density profiles for liquid-vapor coexistence around a charged sphere at different bulk vapor densities

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From wires to fractals: modeling of the metal-organic intermediates in surface-assisted Ullmann coupling of halogenated acenes

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Designing of persistent molecular structures on surfaces is an important task in the fabrication of novel low-dimensional materials with unique properties. One way to obtain such materials is the controlled on-surface covalent synthesis in which functional monomers (e.g. halogenated polyaromatic hydrocarbons, PAHs) react and form extended polymeric patterns. In this work we examine how individual properties of the monomers affect structure formation in adsorbed overlayers comprising halogenated acenes. To that end a series of Monte Carlo simulations was performed, in which the PAH monomers were coadsorbed on a catalytically active (111) surface with the bivalent metal adatoms. The main objective of these investigations was to determine the influence of the number and intramolecular distribution of halogens in the monomer on the structure of the resulting labile metal-organic precursors of covalent polymers. The calculations demonstrated that suitable tuning of the halogenation pattern of acenes enables directing the metal-organic self-assembly towards nanostructures as diverse as straight and bent wires, cyclic oligomers, ladders, Sierpiński triangle fractals, porous networks with periodic and aperiodic architectures and many others. Our studies focused also on the role of chirality of the monomers in the formation of enantiopure and racemic precursor structures. Different self-assembly scenarios were observed in this case, involving chiral resolution and racemic mixing of the adsorbed enantiomers. The obtained results indicated those halogenation patterns which can induce the aforementioned effects. The key findings of our computational studies be helpful in directing the surface-assisted polymerization reactions towards organic structures with predefined size, shape, symmetry and connectivity.

Keywords: adsorption, Ullmann coupling, metal-organic precursors, Monte Carlo simulation

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The Dominant Role of Electrostatic Forces in Supracolloidal Self-assembly of Polymer-Functionalized Gold Nanorods

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Controlled supracolloidal self-assembly of hybrid polymeric/inorganic nanorods (NRs) offers many potential applications such as imaging biological cells¹ and chiral sensing.² Solution-based assembly of these hybrid nanosystems can be achieved by tuning the balance between (attractive) solvophobic polymer-polymer interactions and (repulsive) electrostatic forces.^{3,4} However, the nanometric nature of these systems enforces limitations in characterizing them at sub-NP level and thus, limits our knowledge about their complex assembly mechanism. Using energy-filtered transmission electron microscopy (EFTEM), kelvin probe force microscopy (KPFM), and other advanced analytical methods, we obtained quantitative insights at the sub-nanoparticle level into soft-hard nanomaterials comprising inorganic gold NPs and polystyrene ligands as well as their assemblies. We revealed that polystyrene-coated gold nanorods can undergo directional tip-to-top self-assembly, even when they are uniformly coated with a polymer ligand layer. Our results suggest that directionality in the self-assembly arises from the NR's intrinsic surface charge and electrostatic forces. In addition, NPs with different size and the length of grafted polymer were assembled through new paradigm arose from our findings.⁴

Keywords: Self-assembly, Gold nanorods, Hybrid nanoparticles, ligand density, surface potential

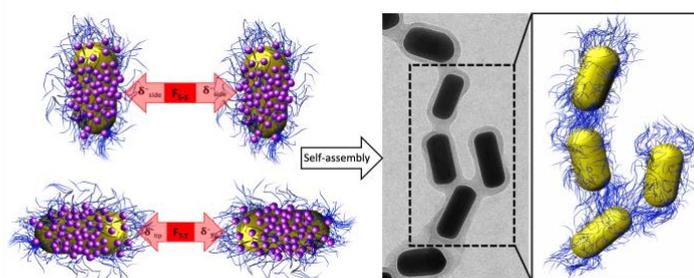


Figure 1. Self-assembly mechanism of polystyrene-grafted Gold nanorods

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Growing on membranes: next generation cell culture scaffolds - the role of the polymers

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Hierarchically organized self-assembled peptides and polysaccharides that form macroscopic membranes at liquid-liquid interfaces can serve as a platform for 3D cell culture. However, in order to create complex scaffolds that can truly mimic the natural environment, it is imperative to first be able to control their structure and mechanical properties.

We were able to form hierarchically ordered planar and spherical membranes (sacs), using amphiphilic and cationic β -sheet peptide solution that spontaneously assemble together with negatively charged polysaccharides (e.g., Hyaluronic acid, Alginate, and λ -Carrageenan). A three-stage mechanism was suggested, and key parameters affecting the membranes development process were identified (e.g., peptide aging period, membrane geometry, and membrane incubation time). Furthermore, the intrinsic properties of the polysaccharide (e.g., persistence length and charge density) were found to strongly affect the structure of the membrane. Thus, a thorough understanding of the correlation between the polysaccharide features and the membrane properties provides a manner for designing membranes with tailored properties.

Keywords: Self-assembly, Membrane, Polysaccharides, Amphiphilic-peptide

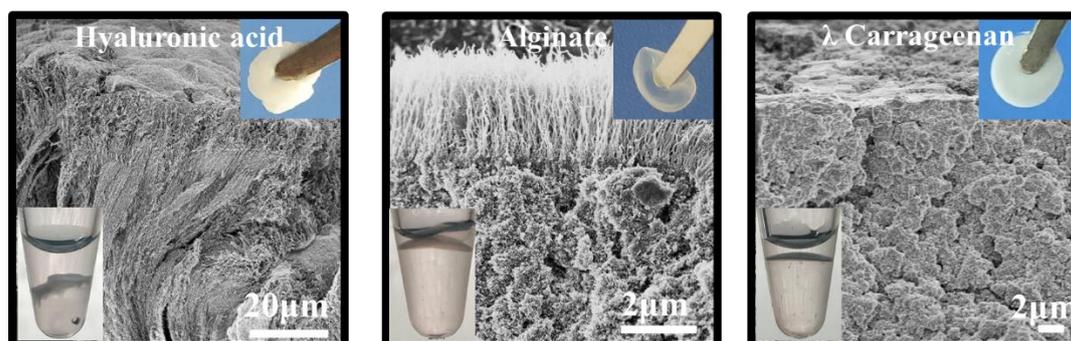


Figure 1. Membranes formed with different polysaccharides – SEM images and photos of the membranes in an Eppendorf and held by tweezers (inset).

Associative behavior of dodecaborate conjugates with alkyl tails

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The chemistry of anionic boron clusters has many facets due to their physicochemical versatility and their chemical reactivity that make them attractive choices in a wide range of fields such as ion conducting materials, a powerful anticancer agent and advanced nanodevices.

Although efforts have been made to study the self and co-assembly of these compounds but it is still not well understood and deeper investigation is strongly needed. [1-3]

In this regards, we focused on 1,4-dioxane and tetrahydrofuran oxonium-*closo*-dodecaborate(1-) derivatives. We have prepared a series of compounds by nucleophilic ring opening [4] to obtain water soluble, Na and Li salts of the *closo*-dodecaborate(2-) alkyl tail conjugates that display an amphiphilic structure with the hydrophobic tail attached via the linker to the superchaotropic dianionic head [3] and represent thus a novel class of surfactants.

The influence of the tail length, linker and counterion nature on the aggregation process, the mechanism of formation, the aggregation number, and the morphology of the multimolecular surfactant assemblies in solution were deeply investigated by isothermal titration calorimetry, NMR spectroscopy and cryogenic electron microscopy.

Keywords: Closo-dodecaborate, aggregation, self-assembly, surfactants.

Acknowledgements: 21-20008K and ARRS N1-0186.

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Formation of Metallacarborane Pentamers in Water

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Self-assembly of metallacarboranes has been extensively studied. However, the mechanism behind the aggregation process remains a subject of discussion. In our recent study, the precise calorimetric measurements (ITC) supported by NMR data analysis, quantum chemistry calculations, and molecular dynamics simulations shed light on the complex aggregation behaviour of sodium bis(1,2-dicarbollide) - NaCOSAN, one of the most studied examples of metallacarboranes [1]. The model of counterion-induced metallacarborane aggregation in water was verified leading to the formation of stable pentamers of COSAN⁻ around 2 sodium counterions via Coulombic-driven assembly.

Computer simulations show that the key prerequisite of the counterion binding to the aggregates is the strongly uneven charge distribution of COSAN⁻ clusters. Simultaneously, the size of the counterion should fit into the void between the COSAN⁻ clusters within the aggregate. Figure 1 shows some of the ITC results and the pentamer structure.

At low temperatures and/or high concentrations, the pentamers can merge into bigger nanostructures via the second aggregation mechanism which differs significantly from the pentamer formation. The second mechanism was revealed by applying the two-process model to fit ITC curves in wide temperature and concentration ranges [2].

Keywords: metallacarboranes, NaCOSAN, aggregation

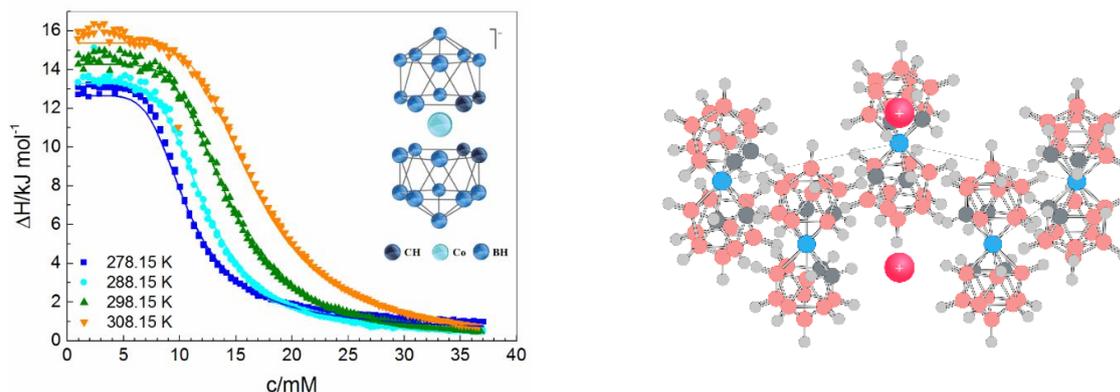


Figure 1. The enthalpograms and scheme of sodium bis(1,2-dicarbollide) - NaCOSAN - upon dilution of the 160 mM solution (left) and the pentamer structure as obtained by quantum chemistry calculations (right).

Acknowledgements: The authors would like to acknowledge LA CEUS bilateral grant of the Czech Science Foundation 21-20008K and ARRS N1-0186.

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Linking Perylene Diimides to Nanoclays: Solvent-Induced Aggregation and Energy Transfer

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Perylene Diimides (PDI) have excellent chemical, thermal, and photostability, good electron accepting character, high fluorescence quantum yields, and versatility of functionalization [1]. Self-assembly of PDI can lead to different photophysical properties [2], which can be harnessed for charge-transfer, sensing, and optoelectronic applications [3]. Synthetic discoidal nanoclays with a negatively charged surface can be organically modified with cations at the basal surface, or covalently at the silanol edge sites. Furthermore, these nanoclays have many possible aggregation states: from glasses and gels to completely exfoliated particles [4]. Control over the aggregation state of organic chromophores bound to specific inorganic interfaces is interesting for understanding charge-transfer in organic/inorganic hybrids.

Herein, novel asymmetric PDIs were grafted to the edges of nanoclays. The photophysical properties and solvent-dependent self-assembly of the nanoclay-grafted PDIs were investigated. Increased water content led to the formation of PDI H-aggregates, mainly due to π - π interactions. The anionic basal surface of the nanoclay provides the means to complex cationic chromophores to form a donor-acceptor pair with the grafted PDI. Energy transfer from donor molecules on the basal surface to the PDI was observed, and was found to be dependent on the aggregation state of the PDI.

This work showed that asymmetric PDI-based ligands can be used as a model system for linking organic semiconductors at specific nanomaterial interfaces. Further studies of how the aggregation state of the clay and the terminal functional group of PDI independently influence self-assembly and photophysical properties will lead to greater understanding of charge-transfer processes at nanomaterial interfaces, and organic-inorganic hybrids in particular.

Keywords: Layered silicates, perylene diimide, self-assembly, energy transfer

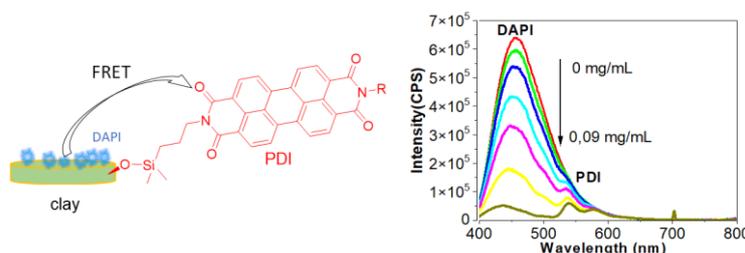


Figure 1. Structure of perylene diimide functionalized clay and fluorescence spectra of energy transfer

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Biosurfactants in green industrial formulation design: a study on Rhamnolipid-SLES mixture.

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Surfactants are key components in a plethora of industrial formulations. On the flipside, because of their scarce biodegradability and toxicity, synthetic surfactants constitute an environmental issue worldwide. Biosurfactants, amphiphiles produced by bacteria, yeast and plants, represent a valid alternative to synthetic ones, allowing a reduction of environmental and potential health problems [1]. Besides satisfactory functionality as solubilizers, emulsifiers, wetting and foaming agents, biosurfactants present good tolerance to temperature and pH changes and, above all, fast biodegradability and low toxicity.

Rhamnolipids, glycolipids electively produced by *Pseudomonas aeruginosa* as secondary metabolites, are among the most promising biosurfactants for practical applications. Specifically, rhamnolipids can be proposed as suitable candidates to totally or, at least, partially replace anionic surfactants in several industrial formulations. For this reason, the investigation of their mixtures with largely employed synthetic surfactants is strategic. In this contribution, we compare the physico-chemical and functional properties of a commercial rhamnolipid sample in aqueous solution with those of sodium lauryl ether sulfate (SLES), an anionic surfactant massively used in laundry and household cleaning detergents as well as in personal care and consumer products. The mixtures of these two anionic surfactants are also investigated, analyzing weather, and to what extent, synergistic/antagonistic interactions alter the system behavior with respect to that of the single components. Surface tension, DLS, conductometric and spin-probe EPR results, quantitatively analyzed in terms of molecular-thermodynamic models, show a weak antagonistic behavior which however does not hamper the formation of prolate mixed micelles which co-exist with vesicles. Contact angle measurements, emulsification and foaming tests demonstrate that rhamnolipids can effectively replace up to 90 wt% of SLES with negligible effects of the functional behavior. On the other hand, the ecotoxicity of these surfactant mixtures is very low, nominating rhamnolipids as key components of next-generation green formulations.

Keywords: biosurfactant, rhamnolipid, mixed micelles, surface activity, green detergents, eco-design

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Elucidation of self-assembly pathways in dilute cationic surfactant solutions using TR-SAXS

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Self-assembly of surfactants can lead to a wide variety of structures, from simple spherical micelles to cylindrical aggregates, and at higher surfactant concentrations, ordered lyotropic phases. Upon mixing cationic and anionic surfactants unilamellar vesicles (ULVs) can form spontaneously[1-3]. At intermediate states along the pathway, different structural moieties may coexist[4]. The self-assembly pathways in cationic mixtures have been studied in systems at relatively higher concentrations, where at least one of the surfactants was above the critical micelle concentration (CMC) [5, 6]. However, the pre-existing motifs, or the initial surfactant micelles, could bias the spontaneous formation to elongated aggregates. As a result, there is an interest to study these self-assembly pathways without an initial motif, in dilute concentrations well below their respective critical micelle concentrations (CMCs). Recent advances in synchrotron sources and X-ray detectors enable the investigation of such dilute solutions with millisecond time resolution.

This work studies the self-assembly of structures formed in cationic mixtures of cationic tetradecyltrimethylammonium bromide (TTAB) and anionic lithium perfluorooctanoate (LPFO) using time-resolved small-angle X-ray scattering (TR-SAXS) and rapid stopped-flow mixing. Both initial solutions were prepared at concentrations ($c_{\text{surf}} = 1.1 \text{ mM}$) well below that of the CMC (3.6 mM and 31 mM for TTAB and LPFO respectively). The behaviour is qualitatively similar to that in previously studies at higher concentrations, where the initial nonequilibrium structures observed are long wormlike structures ($l > 150 \text{ nm}$), with a shell thickness consistent for a single bilayer of the mixed surfactants ($t_b \sim 4 \text{ nm}$). Further, these long aggregates reorganise with time to form ULVs, where the final morphology observed is a mixture of the wormlike tubes and spherical ULVs. Whilst the spontaneous formation of disk-like or cylindrical aggregates in cationic mixtures is expected, the formation of long wormlike structures occurs even without an initial motif. The evolution of these structures enables discussion of self-assembly and nonequilibrium structures in dilute solutions, furthering our understanding of the kinetic pathways in self-assembly processes.

Keywords: Small-angle X-ray scattering (SAXS), time-resolved SAXS, cationic mixtures, self-assembly pathways

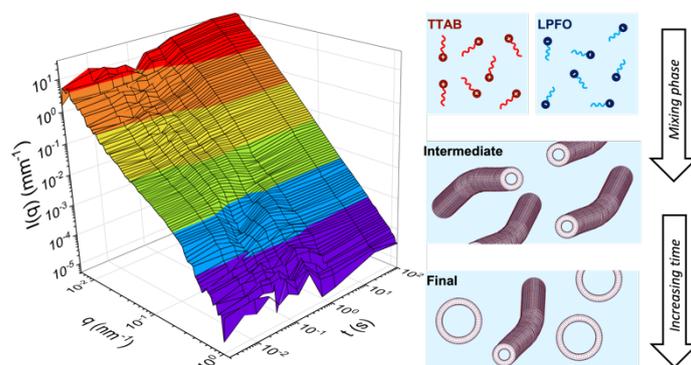


Figure 1. (left) Isometric plots of the normalized and background subtracted SAXS profiles following the rapid mixing of 1.1 mM cationic TTAB and anionic LPFO surfactants. (right) Schematic demonstrating the self-assembly process from isotropic surfactant solutions to the intermediate, and also the final structures.

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The specs of PECs

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Many biochemical reactions and processes in biological cells require a good spatio-temporal organization of components to occur efficiently. These complex reactions are mainly carried out in specific compartments known as organelles, where compartmentalization is achieved by membrane encapsulation. However, it also appears to be possible to create compartments by liquid-liquid phase separation, leading to the formation of different spatio-temporal organizers, called membrane-less organelles (MLOs). [1,2] MLOs are dynamic droplets-like condensates mainly composed of proteins, polynucleic acids, and small molecules, [3] which have developed the ability to partition and release only specific target molecules from/to the surrounding environment.

We would like to understand how this selectivity of molecule partitioning works for designing aqueous-based extraction media. Since many MLOs form by electrostatic attractions between the negatively charged polynucleic acid and proteins with a high amount of positively charged amino acids, we use polyelectrolyte complexes (PECs) as model systems. When aqueous solutions of oppositely charged polyelectrolytes are mixed, phase separation of the system will occur into a dense polymeric phase and a dilute aqueous phase, allowing the formation of condensates called polyelectrolyte complexes.

Previous studies have shown that PEC systems can extract and back extract [4] into the polymeric-rich phase proteins and small molecules, [4-6] resembling a phase behaviour similar to MLOs. However, to use PECs as extraction media or improve their applicability in industrial processes, it is necessary to understand the overall working system better. For this reason, we started to develop a method to fully characterize PEC systems. We investigated the amount of free polyelectrolytes and ions in the dilute phase, as well as the composition and amount of water in the polymer-rich phase. After these preliminary studies, the addition of a third non-polyelectrolyte component to the system will be considered.

Keywords: membrane-less organelles, polyelectrolyte complexes, PEC, extraction media

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Polymer length dependency of liquid-liquid phase separation and assembly of silk-like proteins

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Phase transitions play an essential role in the assembly of nature's protein-based materials into hierarchically organized structures, yet the underlying mechanisms and interactions remain elusive. A central question for designing proteins for materials is how the protein architecture affects the nature of the phase transitions and the resulting assembly. We examine the assembly of silk-like modular block proteins by a computational bead-spring model. We show that our model can underpin the transition from homogeneous solution to phase separation corresponding to assembly formation for various protein architectures, particularly protein chain length variation [1]. We find that in the assembly phase, a protein length- and concentration-dependent transition between two distinct assembly morphologies, one forming aggregates, and another coacervates, exists, both in the simulations and in experimental characterization of the equivalent proteins with varying lengths. We deduce that properties and internal structures of the assemblies depend on the protein size. Experimental data of silk-mimicking proteins support the model predictions.

Keywords: self-assembly, protein coacervates, liquid-liquid phase separation

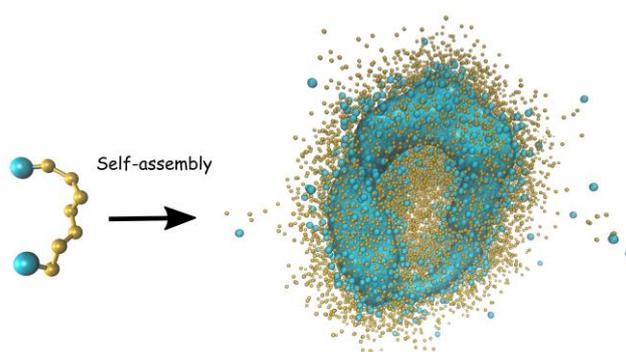


Figure 1. Bead-spring model of protein self-assembling into coacervates via liquid-liquid phase separation.

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Phase transitions in a binary system cetyl alcohol - stearyl alcohol

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A mixture of cetyl alcohol (C₁₆H₃₃OH) and stearyl alcohol (C₁₈H₃₇OH) named as cetostearyl alcohol is widely used in topical formulations. Different weight fractions of cetyl/stearyl alcohols considerably affect the formulation. In principle, storage temperature after the synthesis of products which could be 5 °C, 25 °C, or 40 °C changes the microstructure and therefore macroscopic behavior of products. Moreover, the stability and shelf-life of formulations will be affected. Therefore, the physicochemical properties of the binary system of cetyl and stearyl alcohols are important for formulations and can improve our understanding of topical and cosmetic formulations.

Here we present a small and wide-angle X-ray scattering (SWAXS) and differential scanning calorimetry (DSC) study of polymorphism in binary mixtures of C₁₆H₃₃OH and C₁₈H₃₇OH at temperatures ranging from 5 °C to above the melting point of fatty alcohols. Based on the experimental data the phase diagram of this fatty alcohols system is also proposed. The pure fatty alcohols show the same polymorphic behavior at low temperature, γ form with a monoclinic symmetry and phase transition to rotator form take place on heating close to the melting point. The binary mixtures show different polymorphism behaviors. Polymorphisms of C₁₆H₃₃OH, C₁₈H₃₇OH, or their solid solution could be found in γ form with monoclinic symmetry or β form with an orthorhombic symmetry in the phase diagram depending on the concentration of binary systems. In binary systems, we found a one-phase region of a solid solution in β form just for the 1-1 mole fraction of cetyl alcohol-stearyl alcohols. On heating, the mentioned polymorphisms transform into a rotator phase and finally melt to the liquid form.

Keywords: Fatty alcohols, DSC, SAXS, and Phase diagram

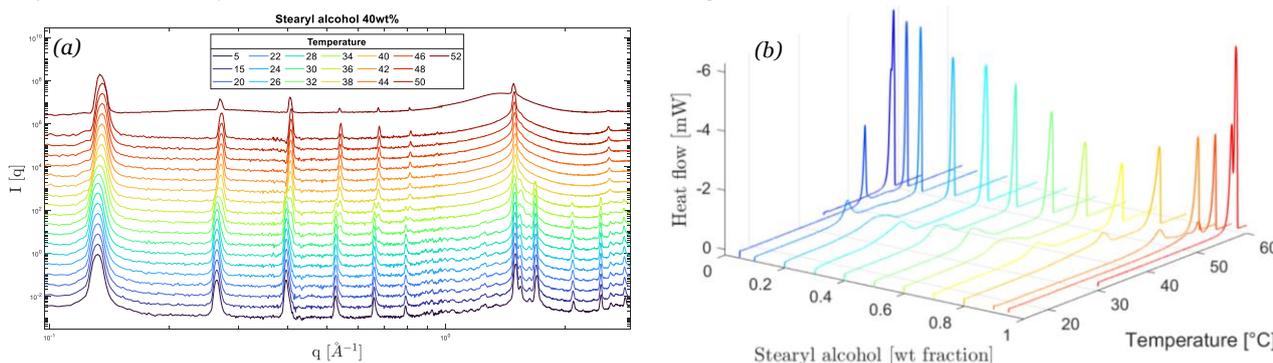


Figure 1. (a) SAXS and WAXS of the binary system with 40 wt% of stearyl alcohol and 60 wt% of cetyl alcohol at temperatures ranging from 5 °C to 52 °C (b) Heat flow curves of DSC at different weight fractions of C₁₈H₃₇OH with 0.2 °C/min heating rate.

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From cellulose model surfaces to elastic papers

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Paper is a hierarchical material based on cellulose which allows functionalization on different length scales. The resulting multilateral use is especially crucial with regard to reducing plastic use and waste and replacing it with renewable and biodegradable resources. A novelty in terms of mechanical robustness and controllable fluid mechanics are elastic papers, prepared through the functionalization of the paper fibers with elastomeric particles that concentrate at the fiber-fiber-crossing points. In order to study the particle adsorption, planar cellulose model surfaces of different roughness and porosity are prepared from trimethylsilyl cellulose (TMSC) mimicking the surface of a cellulose fiber. The elastomeric core shell particles have a pH-responsive polycation shell, and their adsorption to the negative charged cellulose surface is studied in dependence of e.g. pH-value. The question which will be addressed is how the properties of the cellulose surface and the particles affect the contact area between both, and how the contact area is influenced by defects, pores or by wedges formed with a cellulose fiber adsorbed at the planar cellulose surface. The properties can be separated into mechanical and chemical nature and measured separately by variation of the cellulose model surface.

Keywords: cellulose model surface; paper functionalization; elastic paper

Acknowledgements: The core-shell particles used in the study were provided by the group of Matthias Rehahn at the TU Darmstadt. The authors gratefully acknowledge funding by the DFG.

Tuneable interphase transitions in ionic liquids/carrier systems: voltage control

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Due to their high chemical and thermal stability, low melting points and negligible volatility, ionic liquids (ILs) have been extensively studied. Among the many areas of study, controlling the interfacial structure of ILs at charged interfaces is critical in many of their applications, such as energy storage systems, sensors, and enhanced lubrication technologies that use electric fields.^[1-3] In the latter scenario, high production costs and environmental concerns regarding fluorinated ions have largely limited the commercialization of IL lubricants.

To address these issues, a series of novel, non-halogenated ILs have been recently synthesized and developed,^[4-5] which have shown promising potential as tribological lubricants, both as neat lubricants and when added as additives.^[1, 3] However, in order to fully understand the performance of the tribological ILs, a better understanding of the effect of electrical potentials on the interphase transitions in IL/carrier, as well as the intimate relationship between such structures and their tribological properties is required.

To this end, we present results from several techniques used to study the nanoscale structuring flipping and friction of the non-halogenated ILs at an electrified gold surface when dispersed in a polar solvent (propylene carbonate). Using quartz crystal microbalance (QCM) and neutron reflectivity (NR)^[6], we demonstrate how the interfacial structure and composition of ions can be readily controlled through an applied potential, whilst using atomic force microscopy (AFM), we show how such tuneable surface layer may in turn be used mediate different surface interactions and friction. Such a multi-pronged approach provides valuable molecular insight into the electro-tunability of IL boundary layers and hopefully will help guide the development of future IL additive lubrication systems.

Keywords: interfacial layers; non-halogenated ionic liquid; quartz crystal microbalance; neutron reflectivity; atomic force microscopy

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A New Generation of Liquid Ionic Surfactants

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Most of the commonly used Ionic Liquids (ILs) contain bulky organic cations with suitable anions. With our COMPLET (Concept of Melting Point Lowering due to Ethoxylation), we follow a different approach. We use simple, low-toxic, cheap, and commercially available anions of the type $C_x(EO)_yCH_2COO^-$ to liquefy presumably any simple metal ion, independently of its charge. In the simplest case, the cation can be sodium or lithium, but synthesis of Ionic Liquids is also possible with cations of higher valences such as transition or even rare earth metals and Ti^{4+} .

Keywords: surface -active Ionic Liquids; micelles; liquid crystals; ethoxylated surfactants; Akypo™



Figure 1. Typical COMPLET-based ionic liquids containing divalent transition metal ions.

Anions with longer alkyl chains are surface-active and form surface active ionic liquids (SAILs), which combine properties of ionic and nonionic surfactants at room temperature. They show significant structuring even in their pure state, i.e., in the absence of water or any other added solvent.

In particular, we studied the octyl ether octaethyleneoxide carboxylic acid ($[H^+][C_8E_8C^-]$, Akypo™ LF2), with partial replacement of H^+ by Na^+ and Ca^{2+} in its pure state and in mixtures with water as well as with dodecane. The resulting phase diagrams are remarkable. The surfactants form spheroidal or only slightly prolate direct micelles, from the dilute aqueous solution to interdigitated micelles in the pure IL state and even when oil is added to the pure IL without water. Further, this type of surfactants (C_iE_i -carboxylates) shows a completely different lower critical separation behaviour: the dynamic equilibrium is between highly cross-linked and classical core-shell globular micelles and micellar shape-transition to cylinders is only possible at low temperatures and via ion bridging.

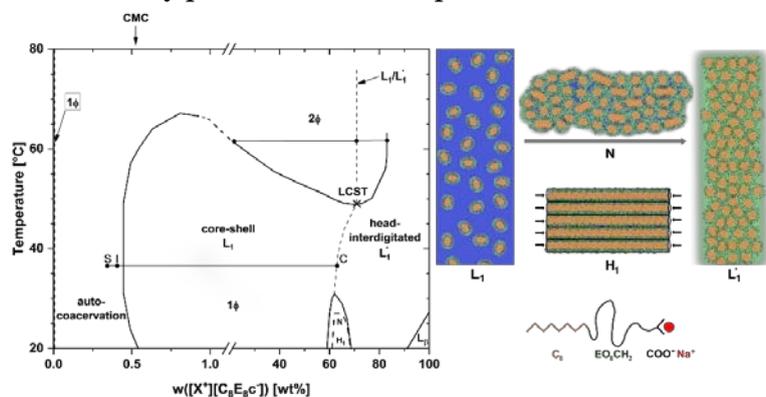


Figure 2. Typical phase diagram of a C_iE_i -carboxylate salt with a nematic phase at higher temperatures and interdigitated, approximately spherical micelles in the pure state.

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Interplay between cosurfactant and electrolyte for the rheological behavior of mixed surfactant systems

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Recently we showed that cosurfactants with 8 to 10 carbon atoms chain-length and small head-group can induce significant increase in the viscosity of SLES+CAPB solutions, due to the formation of entangled wormlike micelles (WLM) [1]. Cationic cosurfactants and nonionic ones with small head-group are most efficient in increasing the solution viscoelasticity.

In a subsequent study [2] we clarified the effect of several counterions on the rheological properties of SLES+CAPB solutions (without cosurfactants) and compared the results with those for the SLES solution. All counterions studied are able to induce WLM formation and the solution viscosity passes through a maximum as a function of salt concentration. The electrolyte concentration at viscosity maximum decreases with increase in counterion charge density, defined as the ratio of counterions charge and its hydrated radius, Z/R . The addition of CAPB to SLES increases significantly viscosity and leads to higher viscosity maximum in the presence of K^+ compared to Na^+ , which is opposite to the trend observed for SLES alone. This is attributed to the subtle interplay between the two surfactants and the electrolyte in the mixed SLES+CAPB system.

Despite the fact that both the cosurfactant and the electrolyte act in the same direction and induce WLM formation, one could not predict in advance what would be the effect of the counterions in presence of C8-C10 cosurfactants. In the current study we showed that the rheological behavior of the SLES+CAPB+cosurfactant triple mixture is mainly governed by the counterions which induce WLM formation. The cosurfactant-containing systems also confirm that the counterion efficiency is governed by the Z/R ratio, however, the viscosity is higher and the salt concentration for peak formation is lower in the presence of C8-C10 additives.

In conclusion, there is a synergy between the counterions and cosurfactants for inducing the formation of WLM in SLES+CAPB solutions.

Keywords: salt curves, counterions, co-surfactant

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Structure, molecular packing and interactions in compartmentalized algal-based nanocarriers: a spectroscopy and calorimetry study

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The delivery of poorly water-soluble drugs is a longtime challenge that has led to the development of several solubilizing and encapsulating systems, to administrate hydrophobic molecules for biomedical, pharmaceutical, food and cosmetics applications. Among the most popular soft matter nanocarriers, lipid-based vectors in dilute regimes such as dispersed liposomes and cubosomes are particularly favored, thanks to the advantageous properties of lipids as versatile and biocompatible building blocks.

Particularly, this flexibility and polymorphism allow to obtain either simpler aggregates such as unilamellar phases or complex hierarchical structures like the inverse bicontinuous cubic architectures. In excess water conditions, the obtained dispersed liposomes and cubosomes possess optimal characteristics as drug delivery vectors. Indeed their high surface-to-volume ratio that grants good encapsulation and retention capability, non-toxicity and biodegradability represent attractive attributes. Moreover, the use of natural-derived building blocks can grant additional carrier-target biocompatibility.

In this work, lipids extracted from two biomasses of the marine microalga *Nannochloropsis* sp. containing either phospholipids or triglycerides were employed for preparation of liposomes or cubosomes respectively, to be investigated as carriers for three model hydrophobic antioxidants (i.e. curcumin, tocopherol and piperine) [1,2]. The two aggregate types were characterized from the physico-chemical perspective, firstly with a focus on supramolecular structure (DLS, synchrotron SAXS) and morphology (Cryo-TEM), then the interactions at the molecular and supramolecular level were investigated with Nuclear Magnetic Resonance and Isothermal Titration Calorimetry.

Specifically, the interactions between the loaded cargo and the carrier in both liposomes and cubosomes, and the structuring and packing effect of deeply inserted molecules in the bilayer were investigated with NMR. At the same time, ITC was employed with an unconventional titration modality to study the different molecular packing at the surface, the easiness of membrane fusion and rearrangement in cubosomes and liposomes and the cargo-cargo interactions in the confined bilayer space [2].

Keywords: nanovectors, bilayer packing, interactions, calorimetry, spectroscopy

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Enhanced Solubilization of Fragrances in Solutions of Sugar Surfactants in Natural Deep Eutectic Solvents (NADES)

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Solubilization of fragrances, e.g. terpenoids, in aqueous solutions has been already studied for a long time[1]. Interestingly, such fragrances can be also solubilized in natural deep eutectic solvents (NADES), a novel class of polar solvents that has the potential to become a non-toxic and cheap alternative to conventional organic solvents, ionic liquids, or even water.

As a result of our experiments, the NADES based on choline chloride and urea, dubbed “reline”, is a good candidate for solubilizing terpenoids. Both components, choline chloride, and urea are inexpensive and widely used in agriculture[2]. We were able to widen the limited scope of reline-soluble surfactants with sugar surfactants and glycolipids. They are already being industrially produced from biomass and are readily biodegradable[3]. More specifically, we examined and characterized numerous glucosides, maltosides, and sophorolipids to dissolve terpenes and other fragrances. With certain formulations, we achieved to dissolve terpenes such as limonene, α -pinene, eucalyptol, or menthol up to 25 wt% of the total mixture mass, see Figure 1.

All components were chosen thoroughly with the emphasis on biocompatibility, biodegradability and their low price. Some fragrances, such as menthol function also as a cosurfactant, thus affecting the internal structure and viscoelastic properties of the final mixtures, see Figure 1. Such properties could find application in cosmetics and pharmaceuticals in form of creams and topical drug delivery. These mixtures were characterized using rheological measurements and small-angle neutron scattering (SANS). The latter delivers a detailed structural picture that could directly become related to the observed rheological properties.

Keywords: solubilization, fragrances, NADES, sugar surfactant, terpenes



Figure 1. Left: Chemical structures of four terpenoids (limonene, α -pinene, eucalyptol and menthol) and their sources in nature (lemons, pines, eucalyptus, mint). Centre: Images of a solution of dodecyl glucoside (10 wt%) and menthol (10 wt%) in reline in unpolarized and in circularly polarized light. Right: Viscosity of the same solution at different shear rates and temperatures (25°C - 50°C). Inset: Upside-down image of the solution demonstrating the non-zero yield stress.

Acknowledgments: We thank for funding by BMBF, project: 05K19KT2 and DFG: GR1030/27-1.

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Aggregation Behaviour of Therapeutic Peptides – A Scattering Approach

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Self-assembly of peptides into larger, insoluble aggregates can cause a number of problems. Aggregation of peptides is part of the pathology of many common degenerative diseases, such as type 2 diabetes mellitus, and Alzheimer's disease. The causes behind peptide aggregation and the mechanism behind their cytotoxicity are currently unknown [1-2]. Investigating aggregate structure and the mechanisms behind aggregation is the key to better understanding of diseases in which aggregation plays a major role.

Pramlintide is an analogue of an endogenous peptide hormone that regulates blood glucose levels by controlling gastric emptying and satiety [3]. The self-assembly behavior of Pramlintide in different concentrations and solvents was investigated by studying particle size and shape with static light scattering (SLS) and small angle x-ray scattering (SAXS). Combining SLS and SAXS made it possible to study a wider range of particle sizes.

SLS+SAXS scattering curves were successfully fitted with a combined model of triaxial ellipsoid and flexible elliptical cylinder. The quality of the fit was highest for intermediate peptide concentrations (7.5-10 mg/ml), and with DMSO added to the solvent.

According to the model fit, small and large Pramlintide aggregates are in co-existence. With increasing concentration, the ratio between small and large aggregates decreases. The deviation from the model for low concentrations might be explained by increased electrostatic repulsion from charged peptide side groups due to low concentration of counter ions. At higher concentrations, the inter-particle interactions get stronger due to increased influence of the hydrophobic effect.

Keywords: Pramlintide, peptides, aggregation, scattering

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Closo-dodecaborate(2-) as building block for preparation of diverse nanostructures of controlled shape and properties

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Anionic boron cluster compounds such as *closo*-dodecaborate, $[B_{12}H_{12}]^{2-}$ are nanometer-sized ions with peculiar solution behavior. [1] The polyhedral clusters consist of B-H units with slightly hydridic character of hydrogen atoms. It is closely related superchaotropicity of the symmetric clusters as compared to common inorganic ions.

We prepared nanostructures of diverse morphology by co-assembly of *closo*-dodecaborate with cationic diblock (PGEA-PEO) and triblock (PGEA-PEO-PGEA) copolymers. [2,3] The copolymers were prepared via the PEO initiated RAFT polymerization of bromomethyl acrylate, followed by attachment of guanidinium cationic groups. While the co-assembly of dodecaborate with A-B leads to formation of nanoparticles (Figure 1), A-B-A forms hydrogels. The morphology and shape of diblock copolymer nanoparticles were controlled by relative length of A and B blocks. The rheology and self-healing properties produced by co-assembly of A-B-A triblocks depend on the length of the junction-forming PGEA blocks. The character of dodecaborate/guanidine interaction is weak and reversible, and can be affected by a salt addition.

The nanoparticles based on weak interaction of dodecaborates are promising candidates for medical applications in BNCT. [2-4]

Keywords: core-shell nanoparticles, hydrogels, co-assembly, nano-ions

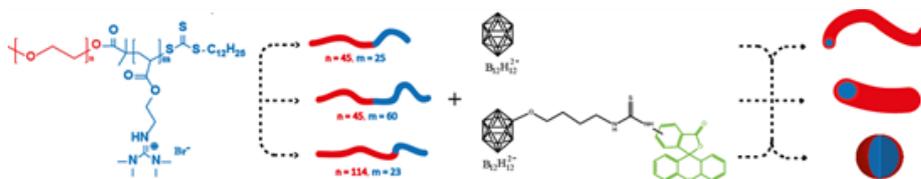


Figure 1. Schematic formation of sphere-, worm-, and rod-like nanoparticles by co-assembly of PEO-PGEA with B12.

Acknowledgements: LA CEUS bilateral grant GAČR 21-20008K and ARRS N1-0186.

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Directed assembly of surfactant-cyclodextrin building blocks in solution

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Self-assembled structures have shown a wide potential for the fabrication of functional materials in different fields. In the last years, complex building blocks involving a multi-level assembly order have raised strong interest in many scientific areas [1]. Due to their versatility and unique features, cyclodextrins (CD) play an important role in the amphiphiles assembly properties in aqueous solutions. In the present study, we investigate the supramolecular systems arising from the assembly process of surfactants and cyclodextrins into inclusion complexes. Among a variety of surfactants, polyoxyethylene alkyl ether carboxyl acids ($C_iE_jCH_2COOH$) are an attractive class of surfactants to integrate the complex systems due to their pH and thermo- responsiveness [2].

The thermodynamics of the complexation of α and β -CD inclusion complexes with $C_{12}E_5CH_2COOH$ and $C_{12}E_{10}CH_2COOH$ in aqueous solutions was studied by densitometry and isothermal titration calorimetry (ITC), and a comprehensive structural characterization was performed by small-angle neutron scattering (SANS) and differential scanning calorimetry (DSC). We demonstrate that the inclusion complexes spontaneously assemble into highly complex structures. Our investigations showed remarkably dependence of the microstructures on the mixing ratio, concentration of the components, cavity size of cyclodextrins, and the number of ethylene oxide units of the surfactants. Further, by using the pH responsiveness features of the surfactants, it was possible to fine-tune the structures and, therefore, to control the self-assembly process. For a surfactant concentration of 5% in the system, we report the formation of crystalline plates at low pH, while well-defined, multilayered hollow cylinders are formed at high pH, i.e., when the surfactant is in its ionized form.

This study delivers a comprehensive thermodynamic and structural complementary characterization approach that allows designing supramolecular aggregates of the desired properties with potential applications in a variety of formulations.

Keywords: Surfactant, cyclodextrins, inclusion complexes, self-assembly, supramolecular aggregates

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Tunable Self-Assembly of Same Size Binary Nanoparticle Mixtures Subjected to Surface Forces in Volatile Suspensions

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The capacity of nanoparticles to self-arrange to various structures and their unique physical properties has turned these building blocks essential in a broad range of applications and scientific disciplines. During the last decade, intensive research efforts were dedicated to produce 2D and 3D binary colloidal crystals. However, to our best of knowledge, the vast majority of binary 3D nanoparticle assemblies were formed using a combination of large and small nanoparticles by varying the size and the number ratios of the particles applied in the self-assembly process. In this work, the manipulation of particulate structures that appear from binary dispersions is demonstrated, comprising same size particles of two different chemistries, following the evaporation of an electrolyte solution carrier.

By varying the ionic strength and pH in the colloidal dispersions, the balance between attractive and repulsive surface forces is tuned, that is, electrical double layer, Van der Waals, hydrophobic, and hydrophilic forces, in the binary particle mixtures. Hence, the corresponding potential energy barriers are tuned to particle attachments to each other and to the underlying substrate and alter the nanoscopic arrangement of the different types of particles in the microscopic particulate structures, which appear by convective pattern formation.

Hence, by realizing the physical mechanisms which govern the potential energy contributions to the pattern formation of particulate structures at the nanometer scale, the 3D morphology of binary mixtures of same size particles is rendered homogeneous, layered, or phases separated. This is an advantageous approach toward the top-down fabrication of nonhomogeneous colloidal structures, which play an important role in optical communications, computing systems, high-density magnetic data storage devices, and chemical and biochemical sensors.

Keywords: self-Assembly; Binary Colloids; Surface Forces; Evaporation; Pattern Deposition

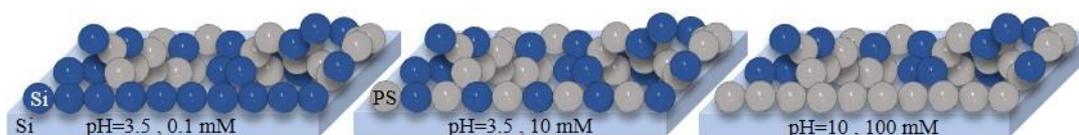


Figure 1. A sketch of three different deposited patterns resulted after the evaporation of binary colloidal suspensions of polystyrene and silica same size nanoparticles under different ionic strengths and pH values.

Experimental and theoretical study of adsorption of amino acid surfactants at air/water interface

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In this paper, the adsorption behaviour of synthesized amino acid surfactants (AASs) at the liquid/gas interface was analyzed experimentally as well as theoretically by means of an elaborate model, considering the volume of the surfactant hydrophilic “head” and its ionization degree. The AASs, based on alanine (ALA), valine (VAL), proline (PRO), phenylalanine (PHE) and leucine (LEU), were synthesized by condensation of proper amino acid with dodecanoyl (lauroyl) chloride (C12). The adsorption behaviour of synthesized compounds were determined by surface tension measurements using Wilhelmy plate and submerged bubble shape methods. In addition, the AASs solutions were characterized by pH and conductivity measurements, what allow for calculation of acid dissociation constants for each tested compound. It was shown that the adsorption behavior of the synthesized AASs can be successfully described by the proposed model (see Fig. 1), including the Helfand–Frisch–Lebowitz (HFL) isotherm based on the equation of state of 2D hard disk-like particles, with molecular properties of surfactant particles obtained using molecular dynamics simulations (MDS). It was shown, moreover, that the elaborated model allow for direct comparison of physicochemical properties of AASs with other ionic and non-ionic surface-active substances. The obtained results revealed that (as could be expected) the surfactants' surface activity increases with the hydrophobicity of the amino acid side group. Moreover, the surface activity of AASs follows the gradation of hydrophobicity of amino acids PRO < ALA < VAL < LEU < PHE and it is much higher than the one of a typical cationic surfactant with twelve carbon atoms in the alkyl chain (dodecyltrimethylammonium bromide - DTAB). Furthermore, it was revealed that intermolecular hydrogen bonds allow the formation of surfactant dimers with high surface activity.

Keywords: amino acid, adsorption, simulations

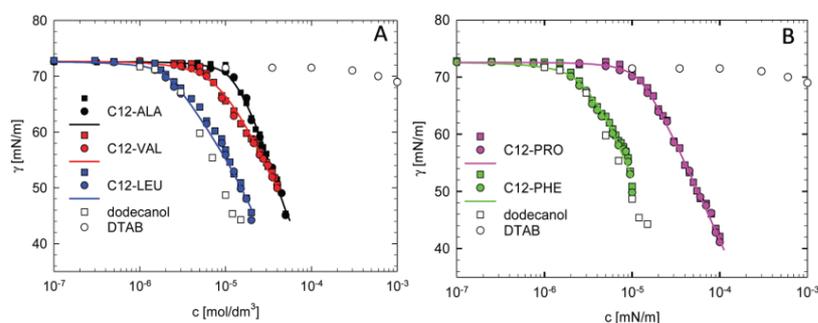


Figure 1. Surface tension isotherms of the AASs (Wilhelmy plate method – squares, bubble shape analysis – circles). Solid lines – best fits of the theoretical model to experimental points obtained using bubble shape analysis method.

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Macro- and mesoscopic gradients in self-assembled colloidal systems

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Structures prepared via self-assembly of monodisperse, spherical colloids have been of great interest in a multitude of research areas for a long time. [1] These systems, ranging from highly ordered colloidal crystals to isotropic glasses, show photonic properties that enable applications in e.g. autonomous sensors and advanced optical components.

An emerging new aspect in this field of research is the fabrication of colloidal assemblies with a gradient of a specific physical property along one axis. This position dependency opens up entirely new ways of enhancing the functionality far beyond that of the single-component, homogeneous structure. We focus on the fabrication of gradients comprising densely packed colloids via novel synthesis and assembly methods. One recent example is the use of infusion-withdrawal coating to prepare binary colloidal crystals with a composition gradient along the coating axis. [2] The gradual transition from primarily high to low thermal stability allowed us to showcase this material as a temperature sensor with an extremely simple readout.

Here we present the first steps towards a toolbox of methods for the preparation of gradient photonic materials. Strategic combination with concepts previously developed with homogeneous systems will open the path towards creative new ways of preparing functional materials from simple, nano- and mesoscopic building blocks.

Keywords: Colloidal Crystals, Gradients, Photonics

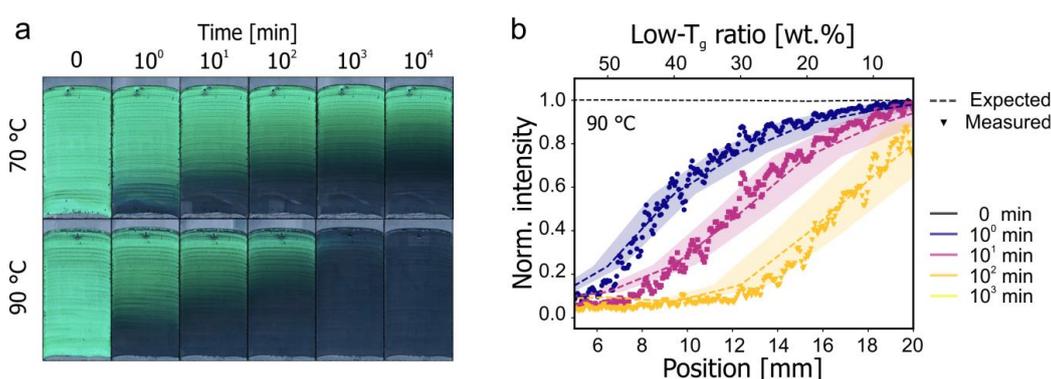


Figure 1. Gradient colloidal crystals as time-temperature integrators. a) Binary colloidal crystals with a composition gradient of particles with a high and low glass transition temperature. Ex-situ light microscopy shows how the structural color vanishes from one side to the other, with kinetics that depend on the applied temperature. b) Position-dependent μ -UV-Vis spectra at different stages of degradation, illustrating the receding stop-band intensity. [2]

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Salt-response of anionic/zwitterionic mixtures: Rheological scaling rules

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The shear rheology of anionic/zwitterionic mixtures depends mainly on the total surfactant concentration c_{tot} , the total counter-ion concentration c_{Na} , and the weight fraction w_S of the anionic surfactant. These factors are interrelated and thus difficult to decouple.

Experiments: We prepared surfactant mixtures, containing sodium lauryl ether sulfate (SLES-1EO; anionic), cocamidopropyl betaine (CAPB; zwitterionic), and NaCl, and characterized them by steady-shear and oscillatory measurements, and by polarized-light microscopy.

Findings: We found that the zero-shear viscosity η_0 grows with $c_{\text{tot}}^{1.80}$, the elasticity G_0 grows with $c_{\text{tot}}^{1.55}$, and the relaxation time τ_R grows with $c_{\text{tot}}^{0.25}$. Also, η_0 and τ_R have peaks as functions of c_{Na} , whose positions do not depend on c_{tot} . In contrast, G_0 increases with c_{Na} and levels off after the viscosity peak. Additionally, when w_S goes up, η_0 and τ_R diminish because of the stronger repulsion within the micelles, whereas G_0 increases because of the stronger repulsion between the micelles. We used these scaling rules to build master curves, which can help with formulation optimization.

Keywords: wormlike micelles; viscoelasticity; viscosity peak; relaxation time; breaking time

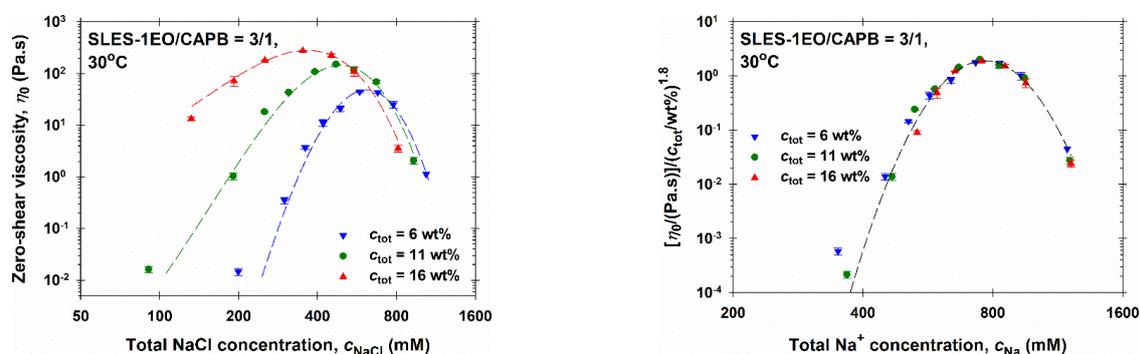


Figure 1. Plots of η_0 vs c_{NaCl} (left) and $\eta_0/c_{\text{tot}}^{1.80}$ vs c_{Na} (right) for 3/1 SLES-1EO/CAPB solutions at $c_{\text{tot}} = 6, 11$ & 16 wt%.

Acknowledgements: The authors gratefully acknowledge the funding from Unilever R&D and the partial funding from the Bulgarian Operational Programme “Science and Education for Smart Growth” 2014-2020, co-funded by the ERDF, project No. BG05M2OP001-1.002-0012.

Droplet–Bijel–Droplet Transition in Aqueous Two-Phase Systems Stabilized by Oppositely Charged Nanoparticles

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In this work, we demonstrate a novel yet straightforward methodology of stabilizing aqueous two-phase systems (ATPS) using oppositely charged nanoparticles (OCNPs). We employ commercial grade, Ludox, OCNPs to induce self-assembly. This self-assembly route promotes the stronger adsorption of nanoparticles at the water– water interface by triggering the formation of 2D and 3D aggregates of varying sizes and shapes. The interplay of this size and shape promotes stability due to increased Gibbs detachment energy and modulates the resulting cluster adsorption at the interface, thereby the structural state of emulsions. We demonstrate the influence of polymers and particles' composition on the structural transformation from droplet–bijel– droplet using a phase diagram. For the first time, such a structural transition and the single pathway are reported within the domain of ATPS to produce stable bijels or colloidal capsules. It is asserted that the essential condition of three-phase contact angle (θ) = 90° to favor the formation of bijels can be established by selecting a suitable experimental condition using a phase diagram without employing any complicated surface modification procedures reported in the literature. Further, the mechanistic route favoring the formation of bijels and emulsion droplets at different experimental regimes is presented based on the empirical study using turbidity and zeta potential measurements. These studies reveal that the formation of bijels will be most favored when the parameter M (ratio of weight fraction of positively charged nanoparticles to negatively charged nanoparticles) is chosen between 0.7 and 4. It is intriguing to note the fact that, while the droplets stabilized by OCNPs have shown good resilience under high centrifugal action, the bijels produced in this way continued to remain stable for a long time, offering a facile route to prepare the bijels with a hierarchical Bicontinuous network structure.

Keywords: Aqueous two-phase system (ATPS), Bijel, water-in-water (w/w) Pickering emulsion, oppositely charged nanoparticles (OCNP's)

Chemo-enzymatically produced rhamnoxylosurfactants as new biosurfactants

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In recent years, a growing sensibility towards environmental issues is prompting the research towards the discovery and design of environmental friendly molecules able to replace those currently used in different applications, preserving or even enhancing their activities. This is particularly true for surfactants that find a very large use in many different fields, from detergency, to industry to biomedicine.

A possible green replacement of “canonical” chemical surfactants is represented by biosurfactants, since they present lower toxicity, higher biodegradability and benign interaction with the environment [1]. With the term biosurfactants we refer to very different amphiphilic molecules produced by bacteria or plants. Among them, a very important class is that of glycosurfactants, characterized by an apolar tail and a polar head composed of one or more sugar moieties [2]. However, one of the main drawbacks of glycosurfactants is related to their high heterogeneity: they are produced as complex mixtures of congeners with variations in the chain length and in the degree of unsaturation of the fatty acid chains, as well as differences in the number of sugar units [3]. The consequence is an inherent difficulty to relate chemico-physical properties to molecular structure. With the aim to overcome this trouble, we are focusing on rhamnoxylosurfactants, glycosurfactants where xylose and rhamnose constitute the polar head, produced through a new chemoenzymatic strategy.

We will present and discuss the chemico-physical and aggregation properties of these molecules and their possible biological applications.

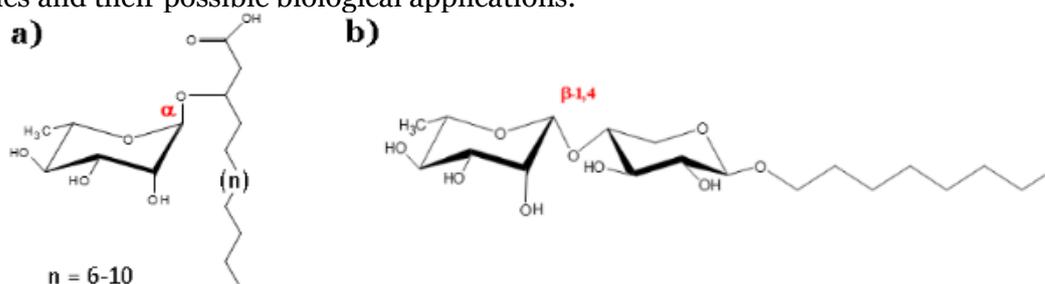


Figure 1 Comparison between molecular structure of rhamnosurfactants (a) and rhamnoxylosurfactants (b)

Keywords: biosurfactants, glycosurfactants, aggregation, rhamnoxylosurfactants

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Heteroprotein complex coacervation: β -conglycinin and lysozyme

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Complex coacervates usually follow from the combination of molecules with flexible chains, such as polyelectrolytes or intrinsically disordered proteins. Recently, it has been found that different globular proteins can also form complex coacervates through associative, liquid-liquid phase separation, which are usually called heteroprotein complex coacervates (HPCC). Although it has been reported that HPCCs are usually formed between animal proteins, we found that the β -conglycinin (β -CG) fraction in soy proteins can interact with lysozyme (LYS) to form coacervate droplets. When reaching or approaching electrostatic neutralization, the specific balance between the interaction forces at a wide array of length scales allows the proteins to assemble and rearrange into equilibrium coacervates through dynamic protein exchange, similar to the dynamic exchange and rearrangement between the ion pairs in polyelectrolyte chains. This dynamic equilibrium makes the heteroprotein complexes appear as regular spherical droplets. By contrast, when the dynamic exchange is hindered due to kinetic trapping and thus cannot reach an equilibrium (in an observable time scale), the heteroprotein complexes appear as a solid amorphous precipitate.

Considering the remarkable role of complex coacervates in encapsulation and the different physical states of electrostatic complexes, we investigated the effects of physical states on the encapsulation and protection of natural active compounds. Both β -CG-LYS coacervates and solid precipitates exhibited a very high curcumin encapsulation efficiency (> 95%) and loading capacity (> 410 $\mu\text{g}/\text{mg}$). However, different from precipitates, coacervates endowed the curcumin with long-term storage stability through its compartmental structure and concentrating effect. In addition, the underwater adhesion ability and compartmental structure of the protein-based coacervates prevented the loss of curcumin caused by water rinse and greatly reduced the loss upon rinsing with ethanol. Therefore, β -CG-LYS coacervates are not only good encapsulation vehicles, but also have potential as functional dressings and coatings.

Keywords: Heteroprotein complex coacervate; physical states; encapsulation

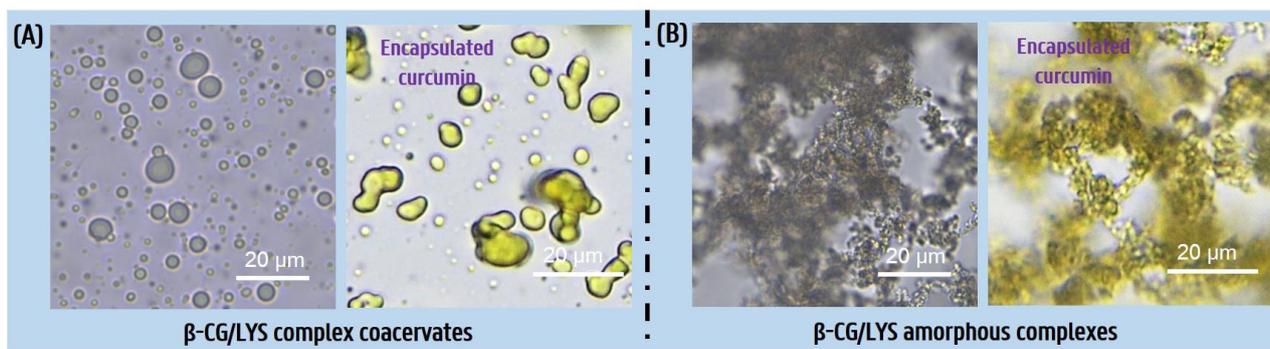


Figure 1. The morphologies of β -conglycinin-LYS complex coacervates (A) and amorphous complexes (B).

Effects of salt and fragrances on formulation rheology

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Many personal-care formulations contain sodium lauryl ether sulfate (SLES; anionic) and cocoamidopropyl betaine (CAPB; zwitterionic) as main components. Here, we studied how NaCl and fragrance-like molecules (FLMs) affect SLES-CAPB solution rheology.

By varying the salt concentration, we constructed the salt-response curves and observed viscosity peaks at ca. 400 mM NaCl; see Figure 1. The peak position, if presented as total Na⁺ concentration, does not depend on the total surfactant concentration or SLES weight fraction. Also, we found that the zero-shear viscosity η_0 and the relaxation time τ_R pass through maxima, whereas the elasticity G_0 increases monotonically with the salt (or counter-ion) concentration.

We also studied how small FLMs affect SLES-CAPB solution rheology. We demonstrated that such FLMs can act as thickeners or thinners, depending on their structure and hydrophobicity; see Figure 1 and Ref. [1]. With hydrophilic FLMs ($\log P < 1.5$) added, η_0 and G_0 are nearly constant. In the presence of FLMs with intermediate $\log P$ ($1.5 < \log P < 5.5$), η_0 and G_0 increase. In contrast, hydrophobic FLMs ($\log P > 5.5$) act as thinning agents; hence, η_0 and G_0 decrease. These rules might be useful for the design of personal-care products with perfumes.

Keywords: salt; fragrances; viscosity; elasticity; relaxation time

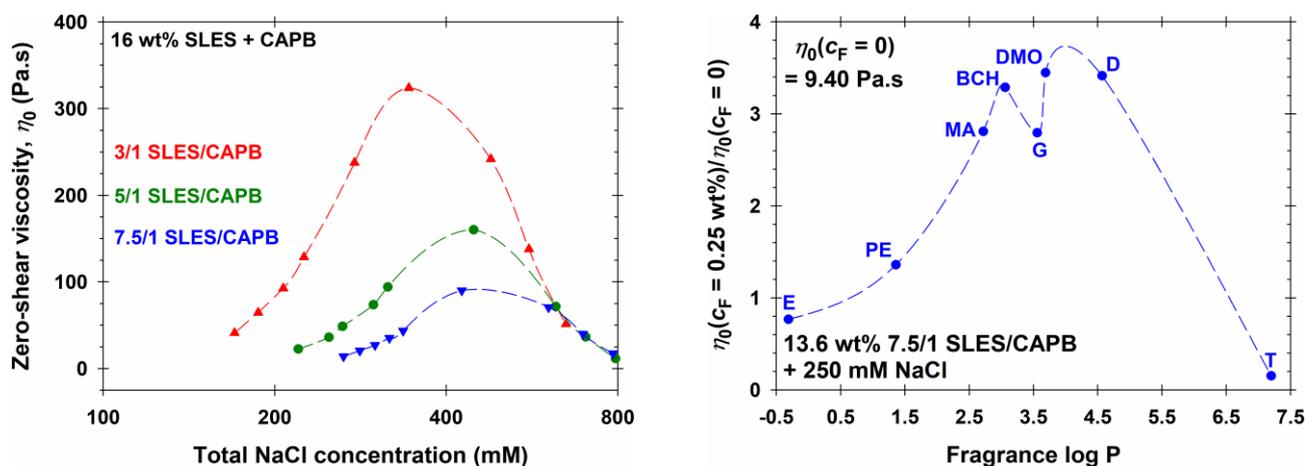


Figure 1. Effects of NaCl (left) and FLMs (right) on the viscosity of SLES-CAPB-based formulations.

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Rheology of anionic/zwitterionic mixtures: Co-ion effects

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The rheology of anionic/zwitterionic mixtures depends strongly on the counter-ion (e.g., Na⁺, K⁺) concentration but the inorganic co-ions also play a role as they affect the mean ion activity.

Experiments: We prepared surfactant mixtures, composed of sodium lauryl ether sulfate (SLES-1EO; anionic) and cocamidopropyl betaine (CAPB; zwitterionic), with a total surfactant concentration of 12 wt% and at a fixed 3/1 SLES-1EO/CAPB weight ratio. We studied how Na⁺ and K⁺ salts with different co-ions affect the solution rheology and structure, by conducting steady-shear and oscillatory deformation experiments, and polarized-light microscopy.

Findings: The zero-shear viscosity η_0 and the relaxation time τ_R have peaks as functions of c_{Na} or c_K , whose positions depend on the co-ion type. The counter-ion concentration, c_{Na} or c_K , at the peak grows in the series: Cl⁻ \approx Br⁻ \approx I⁻ \approx H₂PO₄⁻ < NO₃⁻ < ClO₄⁻ < SO₄²⁻. In this co-ion series, the mean activity coefficient decreases; hence, we need higher c_{Na} or c_K to reach the same activity. The elasticity G_0 increases with c_{Na} or c_K and weakly depends on the co-ion type. Also, the micellar breaking time τ_{br} decreases with c_{Na} or c_K as the micelles become longer (before the peak) or branched (beyond the peak). Using polarized-light microscopy, we did not detect any birefringence, proving that all solutions are isotropic rather than liquid-crystalline. The co-ions weakly affect the micellar rheology but they can impact sample solubility or minimize equipment corrosion.

Keywords: wormlike micelles; counter-ion; co-ion; viscoelasticity; viscosity peak.

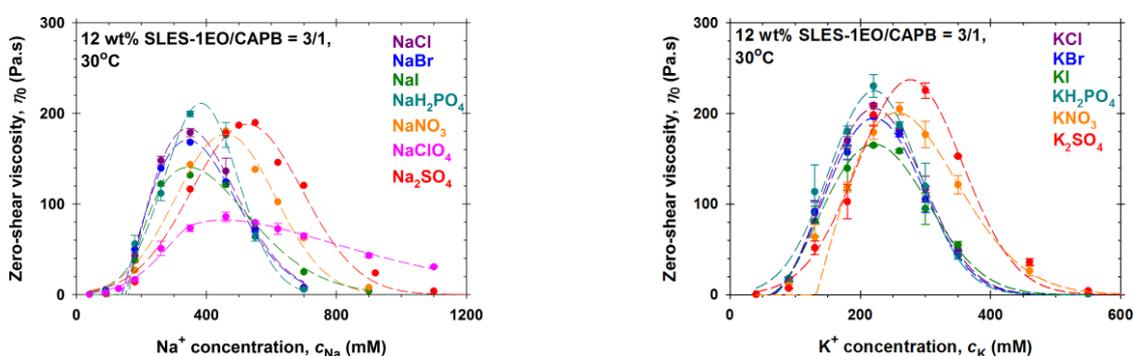


Figure 1. Plots of η_0 vs c_{Na} (left) and c_K (right) for 3/1 SLES-1EO/CAPB mixtures with different co-ions.

Acknowledgements: The authors gratefully acknowledge the financial support from the Bulgarian Operational Programme “Science and Education for Smart Growth” 2014-2020, co-funded by the ERDF, project No. BG05M2OP001-1.002-0012.

Effects of the Structure of Lipid-based Agents in their Complexation with a Single Stranded mRNA fragment as studied by Molecular Dynamics Simulations

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Fully atomistic molecular dynamics simulations are employed to compare the propensity of two groups of lipid-based agents to form structurally and energetically stable complexes with an mRNA fragment in an aqueous environment. The first group is comprised of cationic ionizable agents while the second includes amphoteric phosphatidylcholine lipids. The effects of various factors on the kinetics of their self-assembly as well as on their complexation with RNA are examined. Characteristic timescales for the realization of each process are provided. The role of the structural details and of the charge of the lipid-based agents on the morphology and the composition of the clusters formed, as well as on the preferential conformation of the mRNA chain with respect to the clusters are explored. The energetic affinity of the examined agents with mRNA is assessed and the role of the different kinds of interactions in the complexation process is determined. By combining information from the analysis of static, dynamic, and thermodynamic properties of the formed complexes, attributes that are mostly relevant to each stage of the lipid-lipid and the mRNA-lipid association are highlighted, providing thus new insight towards the efficient design of lipid-based formulations for RNA delivery.

Keywords: mRNA; cationic lipids; phospholipids; complexation; kinetics; Molecular Dynamics Simulations

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Phase Behaviour of a Biocompatible Microemulsion based on Tween 20, Ethylhexylglycerin and Isopropyl Palmitate

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A novel biocompatible microemulsion system based on Tween 20 (Tw20), ethylhexylglycerin (EHG) and isopropyl palmitate (IPP) as surfactant/co-surfactant, and oil is introduced. We show that a high solubilization capacity can be obtained by employing EHG as co-surfactant, a glycerol ether frequently used in cosmetic applications [1].

EHG is presented as a viable alternative to commonly used short- to medium-chain alcohols. The solubilization capacity is maximized for a Tw20:EHG ratio of 1:5, i.e., for large excess of the co-surfactant. The phase behavior is discussed as a function of co-surfactant and oil concentration. The phases were characterized by means of static and dynamic light scattering (SLS/DLS), small-angle neutron scattering (SANS), rheology and conductivity measurements. For ternary Tw20/EHG/water samples, with increasing EHG concentration, we report a sphere to rod transition (L_1), followed by a lamellar phase (L_α) and a sponge phase (L_3). For quaternary Tw20/EHG/IPP/water samples, spherical oil-in-water (O/W) droplets are retained up to the EHG concentration with the highest solubilization capacity. Beyond this point, oil-filled bilayers are found. The structural evolution could be followed in detail by the scattering experiments. Within the L_1 regime, the scattering data of the ternary samples attest a prolate ellipsoidal shape with increasing elongation upon addition of EHG. In the L_α regime, we report a rather weak degree of ordering indicative of a very swollen lamellar phase.

This is a system that can be structurally controlled over a wide range, possesses a high solubilization capacity for a polar oil, and has potential for applications in the field of cosmetic or pharmaceutical formulations.

Keywords: microemulsion, SANS, phase diagram, liquid crystal

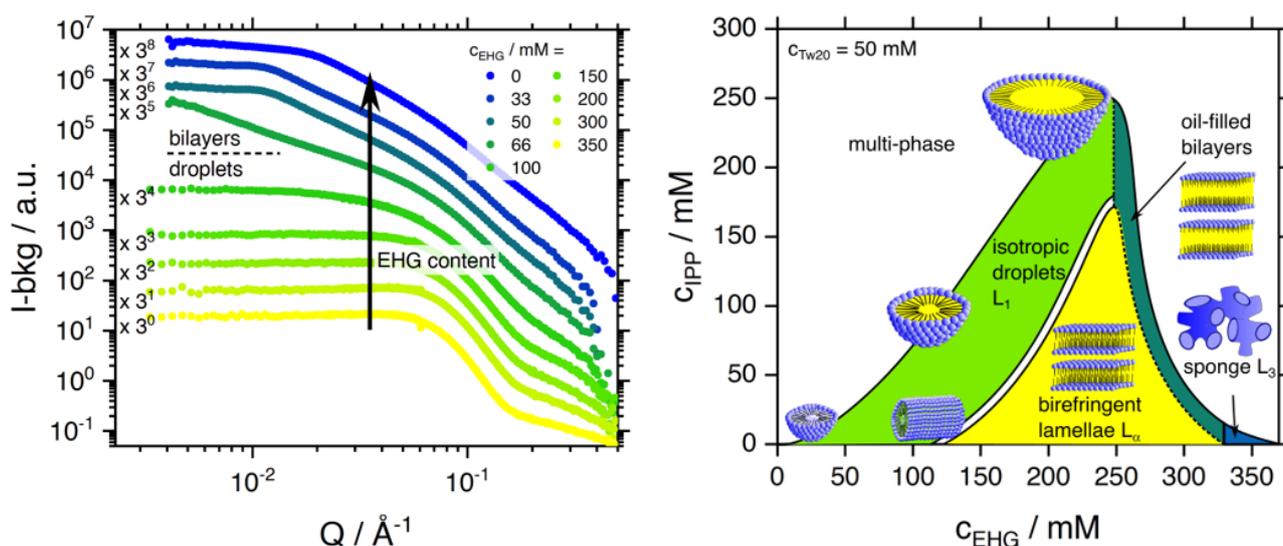


Figure 1. Left: SANS intensities of ternary samples. Right: Section of the phase diagram and proposed structures.

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Complexation between starch and single/binary aroma compounds: Formation and structure

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Starch/amylose-guest inclusion complexes (ICs) are a class of promising supramolecular host-guest assemblies in the fields of biomedical, agriculture, and food science. The primary amylose and some of the unbranched segments of amylopectin can form a left-handed single helical structure and accommodate many unstable hydrophobic aroma molecules to protect the aroma from degradation and achieve slow release. Recently, it has been found that complexing ability was not strictly dependent on the chemical class or the hydrophobicity of the aroma molecules. There remains a limited understanding of the mechanism of complexation and its relationship with the structure of aroma molecules. Due to the different properties of aroma compounds, their affinity to starch matrix is also strong or weak. The competition, synergy, and antagonism phenomena may occur between starch matrix and multiple aroma compounds. The complexation with binary aroma compounds still warrants further detailed and systematic study.

Thus, we selected four groups of aroma compounds with different structures, solubility, and hydrophobicity to investigate the formation of starch-aroma ICs in a single-aroma system. In addition, we designed an approach to compare sequential complexation (two-step) with one-pot complexation to test the hypothesis that competitive and cooperative binding behaviors coexist in a binary aroma system. We found that aroma molecules with long alkyl chains, strong hydrophobic functional groups, and a small cross-section facilitated stronger interactions with the helical channel of amylose and thus contributed to the formation of starch-single aroma ICs with compact structures. In the binary aroma system, the cyclic thymol had a stronger binding affinity to starch than linear decanal, but the presence of thymol promoted the interaction between decanal and starch. The presence of both aroma compounds during complex formation resulted in a synergistic effect which increased the encapsulation efficiency of both compounds, compared with either one alone.

Keywords: Starch; amylose; inclusion complex; aroma compounds

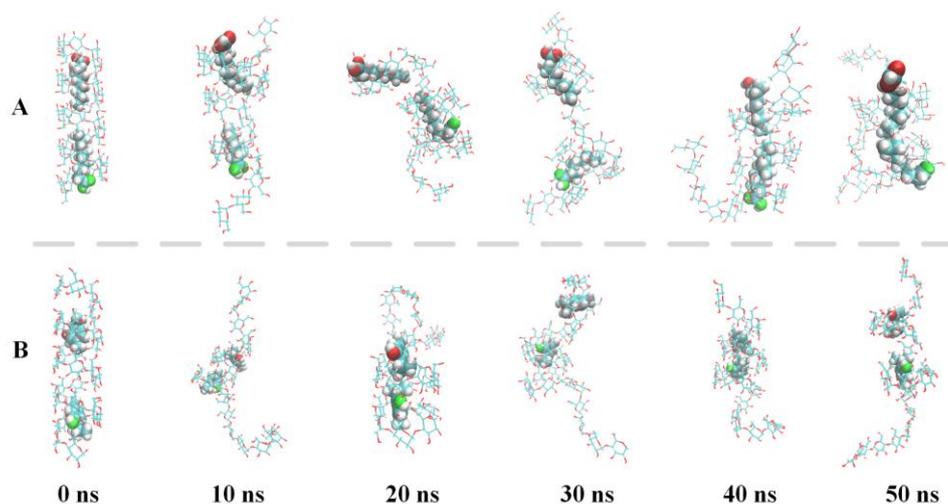


Figure 1. Conformational transitions of a mixture of the amylose and aroma molecules. Snapshots from the molecular dynamic simulations for the amylose-decanoic acid system (A) and amylose-thymol system (B).

Amphiphilic Calix[4]resorcinol-based Nanoparticles: Synthesis, Self-assembly and Biological Properties

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Particular interest among the variety of amphiphilic molecules can be caused by amphiphilic macrocycles, namely calixarenes [1]. In the calixarene family, calix[4]resorcinols are distinguished, since they can improve solubility, stability and bioavailability of different molecules. Low cytotoxicity and high biocompatibility of these macrocycles gives the prospect of their application in biomaterials and tissue engineering. Moreover, calix[4]resorcinols are easily functionalized along the upper and lower rims, after which they can bind a certain molecule, self-aggregate, enter into joint aggregation with a bound molecule and have stimulus-sensitive properties. Modification of calix[4]resorcinols can also be implemented by fragments specific to diseased cells, which is important for targeted drug delivery.

In this work, the mixed self-assembly of the sodium dodecyl sulphate and the calix[4]resorcinol with covalently linked viologen groups were investigated. A set of physicochemical methods was used to study the aggregation and encapsulating properties of the supramolecular system based on these components. The effectiveness of the mixed compositions as nanocontainers for hydrophilic doxorubicin, hydrophobic antioxidants rutin and quercetin was evaluated; and for the equimolar system a high loading efficiency of drugs and the ability to sustained release were found. This study demonstrates features of such supramolecular structures, highlighting their potential applications in drug delivery.

Keywords: calixarene, amphiphile, self-assembly, drug delivery

Acknowledgements: This research was funded by Russian Science Foundation, grant number 22-73-10050.

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Supramolecular Self-Assembly of Metallosurfactant and Porphyrin as a Drug Nanocontainer Design

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The combined method of treating malignant neoplasms using photodynamic therapy and chemotherapy is undoubtedly a promising and highly effective treatment method. The development and establishment of photodynamic cancer therapy is closely related to the creation of sensitizers based on porphyrins. The present study is devoted to the investigation of the spectroscopic, aggregation and solubilization properties of the supramolecular system based on 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TSPP) and lanthanum-containing surfactant (LaSurf) in an aqueous medium. The latter is a complex of lanthanum nitrate and two cationic amphiphilic molecules of 4-aza-1-hexadecylazoniabicyclo[2.2.2]octane bromide. The mixed TSPP–LaSurf complexes can spontaneously assemble into various nanostructures capable of binding the anticancer drug cisplatin. Morphological behavior, stability and ability to drug binding of nanostructures can be tailored by varying the molar ratio and the concentration of components. The guest binding is shown to be additional factor controlling structural rearrangements and properties of the supramolecular TSPP–LaSurf complexes. Considering the targeted effect of porphyrin to cancer cells and the synergistic anticancer effect of cisplatin and lanthanum, the revealed physicochemical and biological properties of the ternary systems based on porphyrin, lanthanum-containing surfactant and platinum drug can be useful in creating an effective anticancer therapy.

Keywords: calixarene, amphiphile, self-assembly, drug delivery

Acknowledgements: This research was funded by Russian Science Foundation, grant number 19-73-30012.

Tuning of Nanoparticles Based on Amphiphilic Calix[4]resorcinol and Octenidine for Enhanced Anticancer Activity and Selectivity

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Well-known commercial anticancer drugs do not provide sufficient selectivity of action, affecting both cancerous and healthy cells alike. The reduction of side effects in the treatment of cancer can be achieved by creating new dosage forms with a high selectivity index [1]. Incorporating drugs into nanoparticles of various nature is an effective way to reduce the side effects of anticancer drugs. The cationic gemini surfactant octenidine dihydrochloride, known as a commercial antimicrobial drug, also exhibits high anticancer activity on various cell lines [2]. In order to reduce the toxicity of octenidine on normal cells and increase the selectivity of action *in vitro*, in present work the spherical nanoparticles based on octenidine and macrocyclic acetate derivatives of calix[4]resorcinols were obtained. Nanoparticles with macrocycle containing saturated alkyl chains in the structure turned out to be more stable over time than nanoparticles with macrocycle that differs only in the presence of one double bond in the alkyl chains. The TEM images confirm the formation of particles with a diameter of ~100 nm with a vesicular shape. The study of cytotoxicity showed that these nanoparticles exhibit high activity on tumor cell lines (HuTu 80, MCF-7), while there is a sharp decrease in toxicity compared to pure octenidine on normal cells (Chang liver). Thus, the mixed surfactant–macrocyclic nanoparticles are 7 times more active and 20 times more selective than the commercial anticancer drug doxorubicin on the HuTu 80 cell line, which gives grounds to consider them as promising drug candidates.

Keywords: calixarene, amphiphile, self-assembly, drug delivery

Acknowledgements: This research was funded by Russian Science Foundation, grant number 19-73-30012.

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Application of Isothermal Titration Calorimetry for Studying Drugs Encapsulation in Beta-casein Micelles

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Isothermal Titration Calorimetry (ITC) is a very accurate experimental method for characterizing the interactions between dispersed molecules. It provides thermodynamic parameters such as enthalpy, entropy, binding constant and stoichiometry in a single titration experiment. The shape of ITC thermograms can indicate on the mechanism of the process under study, e.g., binding and micellization.

Beta-casein (β CN) is an amphiphilic protein, that is also unstructured. These structural motifs combined give rise to strong surface-active properties, and additionally drive the formation of core-shell micelles. We used ITC to study the association behavior of β CN [1] and the influence of physico-chemical conditions on the critical micellar concentration (CMC). Analysis of the micellization regions and the degree of cooperativity of micelle formation played a key role in establishing the mechanism of the protein self-association and showed that the micellization changes from a consecutive process to all-or-none micellization as a function of temperature.

Considering the dynamic nature of the assemblies and the change in the association mechanism, we developed β CN micelles as potential carriers of poorly water-soluble pharmaceuticals. The interaction between β CN and drugs remains highly intriguing, thus we employed ITC to study drug encapsulation and release, using celecoxib as a model drug [2, 3] (Figure 1). We find that the shape of the ITC thermogram of the drug-loaded micelles differs greatly from that of the empty micelles and can be characterized as a multistep exothermic process. The enthalpy changes at each step are very large compared to the enthalpy of β CN micelle formation, suggesting strong interactions between the host and the guest, which is supported by data from NMR and cryo-EM.

Keywords: ITC, Beta-casein, Encapsulation, Drugs, Interaction

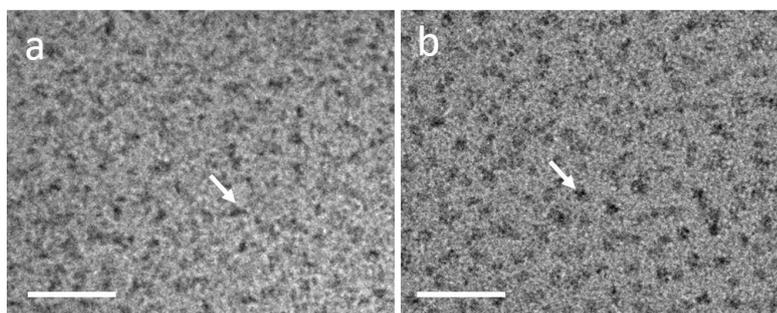


Figure 1. β CN micelles (a) empty and (b) loaded with Celecoxib at 1:16 protein: drug ratio. Bar = 100nm

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Electronic Surfactants For Use In Soap Film Based Sensors And Devices

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Conjugated oligomers and polymers are powerful advanced functional materials used in modern organic opto-electronic devices [1]. A particular area of interest is supramolecular electronics having nanoscale structural features formed from the self-assembly of molecular components [2]. In this context, the self-assembly of π -conjugated oligomers and polymers [3] at gas-water interfaces and in soap films has never been explored, despite its unique architecture, i.e. nanometrically confined water sandwiched between two functional interfaces.

In this context, we propose here to synthesize conjugated oligomers/polymers-based electronic surfactants to serve two complementary functions. I. As surfactants they can mechanically stabilize a new class of electronic soap films. II. As electronic molecules self-assembled at the gas-water interface, they can form a conducting/semiconducting optoelectronic monolayer to be exploited as functional architecture in advanced organic sensors and devices.

More specifically, the presentation will focus on the synthesis and characterization (physicochemical and ecotoxicological) of oligo/polythiophenes-based surfactants which possess conjugated structures coupled with interesting electronic properties [4]. Their surface activity (Langmuir trough characterizations), optical, and optoelectronic properties, in bulk and at interfaces, will also be presented. In addition their ecofriendly properties were tested on bacterial biological models by bacterial growth inhibition ecotoxicological assays.

This work funded by the EU FETOPEN project PROGENY (Grant agreement ID: 899205) is targeting in exploiting unique properties of soap films as advanced functional materials, to be used in fundamentally new type of biomimetic devices and sensors categorized as Proto-Opto-Electro-Mechanical Systems (POEMS).

Keywords: Surfactants, Amphiphilic Opto-electronic Molecules, Oligothiophenes, Water-Gas Interface

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From planar lamellar phases to multilamellar tubes to micelles: how a simple OHgroup can tune the structure of stearic acid based mixed systems

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Fatty acids are surfactants of particular interest in the present context of green chemistry since they can be extracted from agricultural resources. One of the main problem is their lack of solubility in water, a drawback that can be overcome by the use of specific organic counter-ions that enables their solubilization in aqueous solution at room temperature where they self-assemble into various supramolecular structures. For example, Stearic Acid (SA), one of the most common fatty acids form lamellar phases in water in presence of ethanol amine-counter ion [1]. However, the 12-Hydroxy-Stearic-Acid (12-HSA) fatty acids, which only differs chemically from SA by the addition of a unique hydroxyl group at the 12th position on the alkyl chain, self-assembles in micrometric long

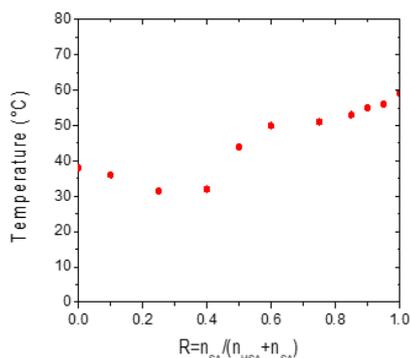


Figure 1: Temperature of transition from different self-assemble large objects at low temperature to micelles at high temperature.

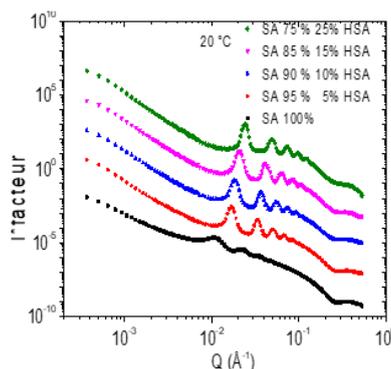


Figure 2: SANS intensity of SA/12-HSA mixtures for different ratios at 20°C.

multilamellar tubes[2] with the same counter ion, although their packing parameter at very close at first sight. Both structures are thermo-sensitive and experience a transition towards spherical micelles above a threshold temperature, which is however very different from SA to HSA.

In this context, we probe the behavior of SA/12-HSA mixtures to answer the following question: Can the

presence of one OH group on the main chain completely change the structure and the thermal response of their self-assembly? By coupling thermal and structural studies using DSC and SANS experiments, we determined the structure at different SA/12-HSA ratios. We demonstrated that a doping of SA by a few amount 12-HSA molecules induces strong structural rearrangements whereas the reverse, i.e. doping 12-HSA by SA, almost does not change the structure. Also, by playing the SA/12-HSA ratio, it is possible to tune the temperature transition threshold of solutions towards micelles over a large range of temperature solutions (figure 1).

Keywords: surfactant, thermos-sensitive solutions, self-assembly.

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Icosahedral supraparticles from titania-silica core-shell colloids

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Supraparticles (SPs) exhibiting coloration and high structural order were assembled from highly monodisperse (3%) amorphous titania-silica core-shell colloids. SPs are particles built up from smaller particles [1] and were generated by slowly drying emulsion droplets containing colloids. We successfully produced both icosahedral and onion-like SPs by assembling nanoparticles using bulk water-in-oil and oil-in-water emulsion in accordance to previous work on nanoparticles [1] and silica particles [2].

The properties of the SPs were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and confocal microscopy. As reported before and caused by the effects of a spherical confinement on the self-assembly (SA), we often found local five-fold patterns in the SPs having a diameter larger than 5 μm , indicative of an icosahedral symmetry of the photonic crystals. Because of their highly symmetric structure an icosahedral ordering of the SPs is highly desirable for strong interactions with light and for generation of structural colors without iridescence [2]. When the SA was too fast and/or the number of particles too large 'onion-structured' [2] supraballs were observed in SEM. Often these SPs contained only a monolayer of ordered colloids with the interior mainly being disordered. Clearly these particles are less suitable to generate structural colors.

In future, we plan to characterize the optical properties of individual icosahedral SPs and optimize their scattering/performance as function of the core-shell parameters. We further are exploring generating binary icosahedral SPs [3] as well which will give additional control over their photonic properties.

Keywords: Supraparticles, Silica, Titania, Core-shell, Structural colors, Self-Assembly

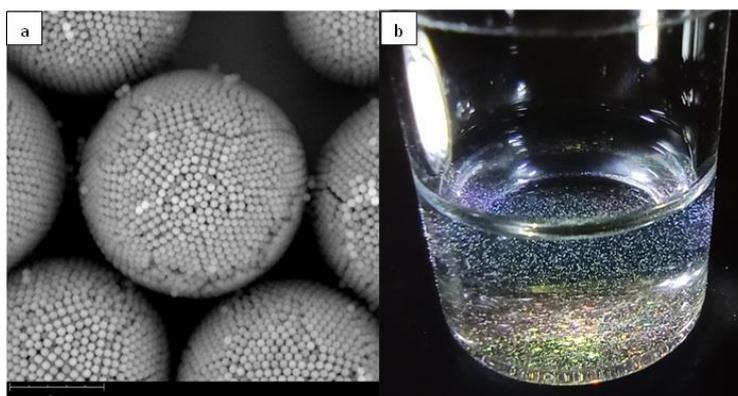


Figure 1. a) SEM image of icosahedral supraparticles (size of the middle SP= 12 μm , average size of nanoparticles: 420 nm), b) Iridescence of supraparticles after emulsion droplet evaporation.

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The Micellization of Well-defined Single Graft Copolymers in Block Copolymer/Homopolymer Blends

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A series of well-defined (polyisoprene)₂(polystyrene), I₂S, single graft copolymers with similar total molecular weights but different compositions, f_{PS} , were blended with a low molecular weight polyisoprene homopolymer matrix at a constant concentration 2 wt%, and the micellar characteristics were studied by synchrotron small-angle x-ray scattering, in the absence of a lab-based instrument. To investigate the effect of macromolecular architecture on the formation and characteristics of micelles, the results on the single graft copolymers were compared with those of the corresponding linear polystyrene-*b*-polyisoprene diblock copolymers, SI. The comparison reveals that the polystyrene core chains are more stretched in the case of graft copolymer micelles (Figure 1). Stretching turned out to be purely a result of the architecture due to the second polyisoprene block in the corona. The micellization of a (polystyrene)₂(polyisoprene), S₂I, graft copolymer was also studied, and the comparison with the results of the corresponding I₂S and SI copolymers emphasizes the need for a critical core volume rather than a critical length of the core-forming block, in order to have stable micelles. Finally, the absence of micellization in the case of the I₂S copolymer with the highest polystyrene volume fraction is discussed. For this sample, macrophase separation occurs, with polyisoprene cylinders formed in the copolymer-rich domains of the phase-separated blends.

Keywords: block copolymers, micellization, shelf assembly, graft copolymers

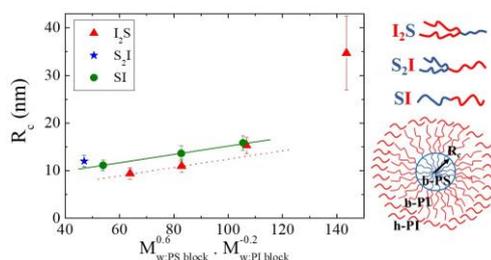


Figure 1. Core radius of the micelles formed in the 2 wt% blends of the I₂S and S₂I grafts, and the SI diblock copolymers in the polyisoprene matrix at room temperature, as a function of the particular relations to the molecular weights of the core-forming (PS) and corona-forming (PI) blocks.

Acknowledgements: The authors acknowledge Dr. J. W. Mays and K. Hong for the synthesis and kind donation of the linear diblock copolymers and the polyisoprene homopolymer. NWO and ESRF are acknowledged for allocating beam time at the Dutch-Belgian beamline. The research project was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “1st Call for H.F.R.I. Research Projects to support Faculty Members & Researchers and the Procurement of High-cost research equipment grant” (Project Number: 3401, SAXS-SOFT).

Self-assembly of Asymmetric Poly(styrene)-block-Poly(methacrylic acid) Polyelectrolyte-Neutral Diblock Copolymer in Aqueous Solution: A MD Simulation Study

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The molecular dynamics simulation study has been carried out to investigate the effect of styrene fraction (X_{PS}) on structure, solvation, and thermodynamics behavior of micelle in salt-free solution for un-ionized (acidic, $f=0$) and fully ionized (charged, $f=1$) state of PMA block. Micelle formation occurs via self-aggregation of PS_x -b- PMA_y copolymer chains with PS core and PMA corona. The clustering mechanism was tracked using the population of unimer and cluster across the simulation trajectory, which demonstrated that the micelle mechanism follows as: unimer insertion, fusion/fission among clusters and chain distribution for equilibrium micelle.

The shape of micelle transforms from spherical to ellipsoid with increase in X_{PS} and size of micelle increases with X_{PS} at both states. The ionized PMA blocks shows more favorable interactions with surrounding water molecules compare to unionized PMA blocks due to presence of carboxylate (COO^-) groups. The solvent accessible surface area (SASA) of micelle increases with X_{PS} in both states, commensurate with its shape transformation. In addition SASA per corona chain shows linear behavior with X_{PS} , has good agreement with experimental behavior of crew-cut micelle formed by polyelectrolyte-neutral block copolymer [1]. Micelle exhibits thermodynamics favorable interaction with surrounding water molecules. Electrostatics interactions has major contribution towards the formation and solvation of micelle in aqueous solution. The results of atom density profiles, solvation enthalpy and RDFs of copolymer- Na^+ ion pairs confirm that micelle exists in "Osmotic regime" in range of X_{PS} from 0.35 to 0.75, in accordance to the results of mean-field theory [2]. The aspects of micelle structure, equilibrium solvation, intermolecular structure and molecular thermodynamics are in qualitative agreement with experimental studies of PS-b-PMA in aqueous solution.

Keywords: Molecular Dynamic Simulation, Self-assembly, Polyelectrolyte.

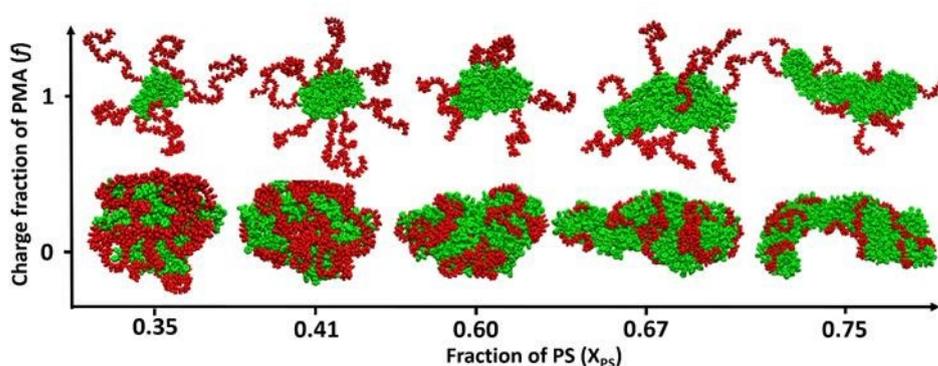


Figure 1. Structure of micelle for various X_{PS} at uncharged ($f=0$) and fully-charged ($f=1$) states.

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Interfacial Supramolecular Assembly at Air/Liquid Interfaces

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The Langmuir monolayer technique provides a unique platform for characterizing the interfacial self-assembly processes and understanding intermolecular interactions.[1] The versatility of the Langmuir technique allows for the study of intriguing systems beyond classical surfactants, including organic/inorganic hybrid composites, complex biomolecules and functional nanoparticles, among others.[2]

Given the growing relevance of self-assembled nanostructures displaying Aggregation-Induced Emission (AIE) with applications in imaging, biology and functional devices, the interfacial self-assembly of purposefully designed combination of amphiphilic block copolymers was studied. The copolymers included tunable lengths of hydrophilic polyethylene glycol and hydrophobic AIE polymer poly(tetraphenylethylene-trimethylenecarbonate). AIE fluorescence at the air/liquid interface was successfully achieved by the self-assembled nanostructures.[3]

The self-assembly of a new set of amphiphilic saddle-shaped polycyclic aromatic hydrocarbons (PAHs) into large 2D-polymers was studied at the air/water interface. Curved PAHs are able to self-assemble into remarkably large sheets up to 150 μm^2 as observed by TEM.

In this direction, the role of the hydrogen bonding in supramolecular self-assembly and the formation of supramolecular polymers was studied by a combination of supra-amphiphiles displaying exclusively aromatic stacking or including hydrogen bonds mediated by amide groups as intermolecular interactions. The directing capability of the amide group via hydrogen bonding in the self-assembly was assessed.

Keywords: Langmuir monolayers, nanoparticles, nanographene

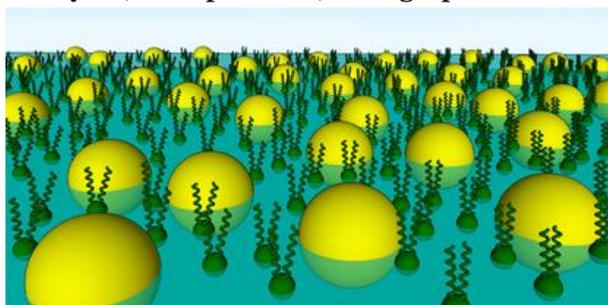


Figure 1. Sketch of inorganic nanoparticles and organic surfactants on a mixed monolayer at the air/water interface.

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Evaporative self-assembly of soft colloidal monolayers: The role of particle softness

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Self-assembly of colloids gives rise to specific patterns that are often dictated by properties of individual building blocks. We investigate the sessile drop evaporation aided self-assembly of soft microgel particles. Microgels are intramolecularly crosslinked polymeric colloidal particles that show dual polymer-colloid behavior. They possess a characteristic core-corona morphology whose relative extent dictates the softness of the particle. Evaporation of sessile drops containing amphiphilic microgel particles at suitable concentrations results in uniform monolayer deposits that span the entire drop area. At lower concentrations, the deposits are monolayer coffee rings whose width scales with particle concentration [1].

We show that tuning the internal architecture of microgels alters the microstructure of dried particulate deposits [2]. Using softer microgels synthesised with a lesser quantity of crosslinker, the monolayer coffee rings do not form at low particle concentrations. Moreover, the final deposit shows hexagonal particle arrays where the interparticle separation increases with increasing microgel softness and decreases with particle concentration in the drop.

Further insight into the role of microgel softness on the microstructure of the particulate deposits is obtained by measuring the time evolution of viscoelasticity of the particle-laden interface. Interestingly, the interface loaded with lesser crosslinked microgels exhibit viscoelastic nature even at lower particle concentrations, whereas the higher crosslinked microgels show viscous behaviour.

Keywords: self-assembly, evaporation, colloidal monolayers, microgels, tunable softness

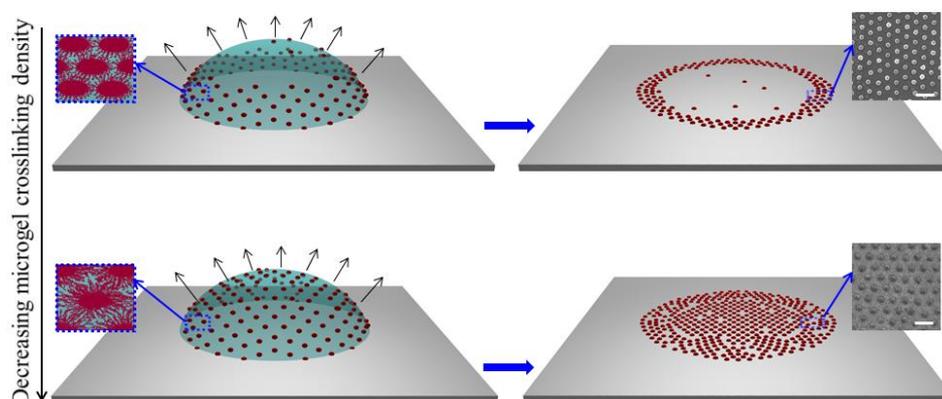


Figure 1. A transition from a coffee ring-like inhomogeneous monolayer to a uniform monolayer deposit achieved solely by tuning the softness of the microgel particles.

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How crucial is structure? Understanding how dynamics and organisation influence ionic liquid solvent effects

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Ionic liquids have been investigated as potential replacements for molecular solvents due to their particular properties and customisability.[1] Despite their merits, common application of ionic liquids remains inaccessible due to their often-unpredictable effects on reaction outcome.[2]

Recent work has investigated a simple bimolecular nucleophilic substitution (S_N2) process carried out in mixtures of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_{2n+2}C₁im][NTf₂], n = 0-5, Fig. 1a) and acetonitrile.[3] Bulk solution dynamics measured *via* ¹H Nuclear Magnetic Resonance (NMR) relaxometry as the spin-spin relaxation time, T₂, may be correlated with the rate coefficient associated with the S_N2 process, k₂. Both T₂ and k₂ are entropically influenced and show similar dependences on bulk solution dynamics, indicating they may be linked.

Although this provides surface level insight into how ionic liquids affect this reaction type, quantitative measurement of nanoscale solvent-structuring and diffusive behaviour of individual chemical species in solution can provide a more in-depth look at the microscopic interactions occurring.[4] By combining Small-Angle X-ray Scattering (SAXS) with diffusion *via* Pulsed-Field Gradient NMR spectroscopy and ¹H NMR relaxometry, partial differences in solution interactions caused specifically by varying the cation alkyl side-chain length in this homologous series can be quantified for mixtures with varying proportions of ionic liquid in acetonitrile.

Keywords: Ionic liquids, dynamics, structure, kinetics

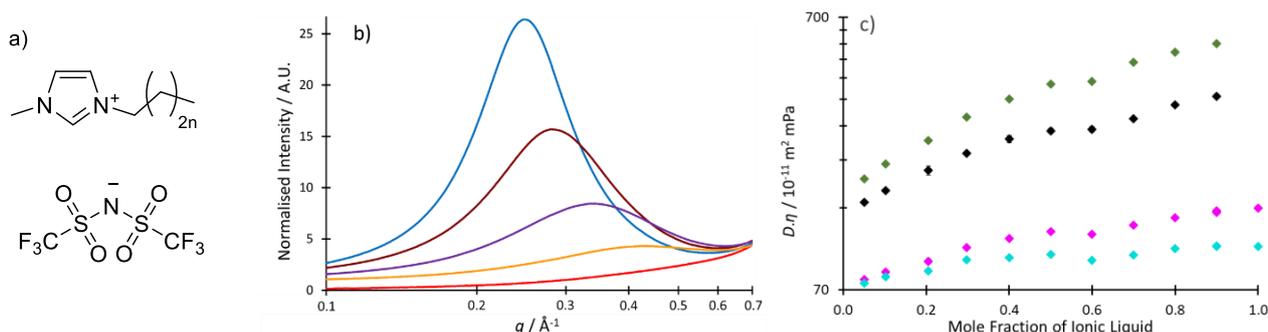


Figure 1. **a)** The [C_{2n+2}C₁im][NTf₂] homologous series of ionic liquids. **b)** Small-Angle X-ray Scattering patterns of ionic liquids [C_{2n+2}C₁im][NTf₂], n = 1 (red), 2 (orange), 3 (yellow), 4 (green), 5 (blue). **c)** Viscosity normalised diffusion coefficients associated with the cation (red diamonds), anion (cyan diamonds), pyridine (black diamonds) or acetonitrile (green diamonds) as a function of mole fraction of [C₄C₁im][NTf₂].

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Rheology of surfactant solutions: Effect of the counterion and surfactants head groups

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The rheological behavior of ionic surfactant solutions is influenced by the addition of salts, which screened the electrostatic repulsion between the surfactant head groups and change the shape of the aggregates in the solution. For ionic surfactants, in which wormlike micelles are formed with the addition of electrolyte, the viscosity of the solution passes through maximum as a function of salt concentration. It has been shown that the type of counterion affects the position and maximum of the salt curve both for SLES solutions [1] and for their mixtures with SLES + CAPB [2].

The aim of the current study is to determine the counterion effect for a series of anionic surfactants with different hydrophilic head groups. For this purpose, we studied the effect of salt concentration of NaCl, MgCl₂, MgSO₄, Na₂SO₄ on the rheological behavior of 5 ionic surfactants: PAS (sodium alkyl sulfate); SLES 1EO (sodium dodecyl ether sulfate with 1 ethoxy group); SLES 2EO (sodium dodecyl ether sulfate with 2 ethoxy groups), NaLAS (sodium dodecyl benzene sulfonate); AOS (alpha olefin sulfonate). The obtained results showed that, depending on the surfactant head, multilamellar vesicles or wormlike micelles can be formed when an electrolyte is added to the system. When multilamellar vesicles are formed, the viscosity increases slightly with the addition of side electrolyte, while with the formation of wormlike micelles the increase in viscosity is strongly expressed. The efficiency of the studied electrolytes to reach the maximum in the salt curve decreases in the order: MgCl₂ > NaCl > MgSO₄ > Na₂SO₄.

Keywords: viscosity, counterions, salt

Acknowledgements: This work is partially funded by the Operational Program "Science and Education for Smart Growth", co-financed by the European Union through the European Structural and Investment Funds, project BG05M2OP001-1.002-0012 "Sustainable utilization of bio-resources and waste from medicinal and aromatic plants for innovative bioactive products'.

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Kinetics of aggregation of amyloid β under different shearing conditions: Experimental and modelling analyses

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Amyloid β ($A\beta_{40}$) is a class of amyloidogenic proteins known to aggregate into a fibrillar network. The rate of aggregation and fibril yield is sensitive to external energy input, such as shear. In this work, simple shear and shaking experiments are performed on $A\beta_{40}$ solution using a Couette cell and an orbital shaker, respectively. Experiments show that, under uniform shear, both the mass of fibrils and aggregation rate increase with the shear rate. In the case of orbital shaking, the lag time decreases with the rotational speed of the shaker, but the final fibril mass is the same for all agitation speeds. To explain this contrasting behaviour of aggregation kinetics, a population balance model is developed to account for the effect of shear on the aggregation of $A\beta$. The kinetic model includes primary nucleation, secondary nucleation, and elongation, fragmentation, and depolymerization steps. The effect of steady uniform shear is encoded in the depolymerization rate constant (k_d), and it is shown that k_d decreases with shear rate initially and saturates at high shear rates. A competition between elongation and depolymerization rates yields different equilibrium masses of fibril at different shear rates. The model results agree quantitatively well with experimental data on the rate of aggregation and mass of fibrils as a function of shear rate [1].

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Electroferrofluids with non equilibrium voltage-controlled magnetism, diffuse interfaces and patterns

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It has been recognized that driving matter to non-equilibrium states can lead to new behaviors and functionalities. In this presentation, reporting a recently published research article [1], we show that uniform colloidal dispersions can be driven into dissipative non-uniform states with emerging behaviors. We experimentally demonstrated this with electrically driven weakly charged superparamagnetic iron oxide nanoparticles in a nonpolar solvent. The driving led to formation of non-equilibrium concentration gradients that further translated to non-equilibrium magnetism, including voltage-controlled magnetization and susceptibility.

The concentration gradients served as diffuse interfaces that respond to external magnetic fields, leading to novel dissipative patterns. We identified the closest non-dissipative analogues, discuss the differences, and highlighted the ability to directly quantify the dissipation and link it to the pattern formation. Beyond voltage-controlled magnetism, we foresee that the concept can be generalized to other functional colloids to create e.g. optical, electrical, catalytic, and mechanical responses that are not possible in thermodynamic equilibrium.

Keywords: ferrofluids, electric field, magnetic field

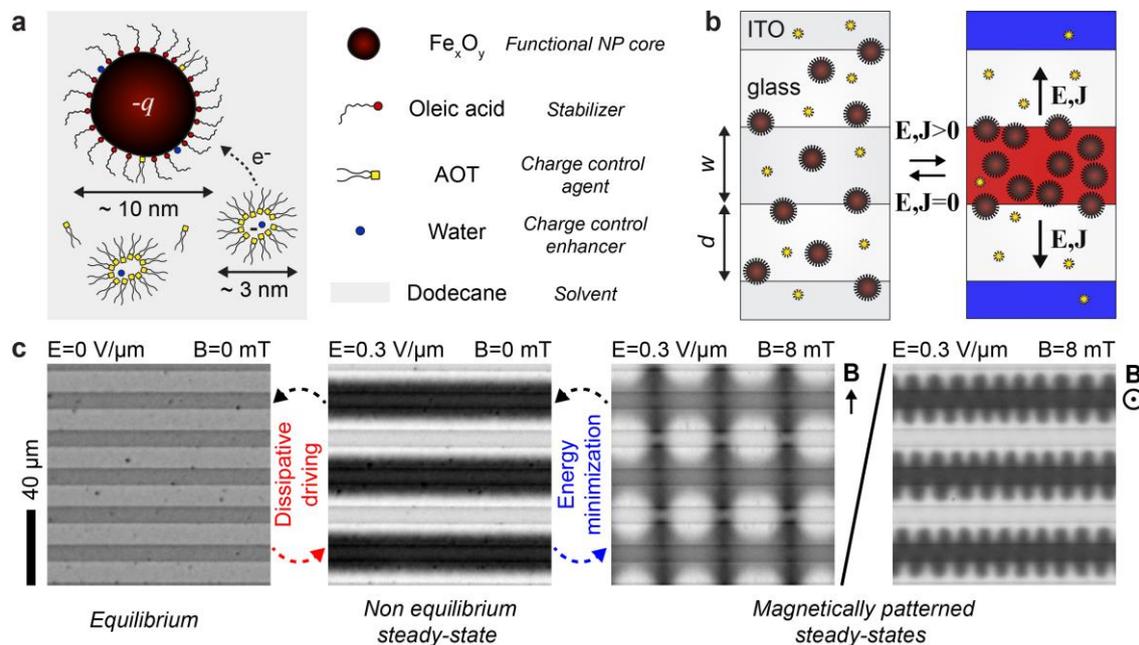


Figure 1. **a.** Composition of the electroferrofluid, **b.** Scheme of the concept of driving the nanoparticles out-of-equilibrium with E -fields, **c.** Examples of the experimental realization of the combination of dissipative driving and energy minimization to create patterns.

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Bubble Printing of MXenes for Patterning Conductive and Plasmonic Nanostructures

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MXenes are a recent addition to the family of 2D materials with many significant and unique properties such as excellent conductivity, plasmonic properties, and resistance to high temperatures. These properties have led to their use in many applications, including energy storage, electronics and sensors. Until now, inkjet printing, screen printing and 3D extrusion printing have been the main methods for printing MXenes, however, optically directed approaches have so far not been demonstrated [1].

Optically controlled microbubbles can be used to pattern colloidal particles on substrates [2]. Briefly, a microbubble is formed at the interface between the substrate and the colloidal suspension, which attracts colloidal particles due to Marangoni convection and immobilizes them on the substrate through van der Waals interactions. Previous approaches have shown printing of conductive patterns with silver nanoparticles [3] and conductive polymers [4], and recent work has demonstrated the printing of patterns with gold nanoparticles toward plasmonic sensors. A major limitation of the use of noble metal nanoparticles in bubble-printing approaches is their low melting point, which leads to melting and loss of plasmonic sensing capabilities.

Herein, bubble-printing was used to print a colloidal dispersion of MXene nanosheets on a substrate to obtain conductive and plasmonic substrates. Due to their high heat resistance, MXenes could be printed onto non-plasmonic surfaces without degradation due to heat at the bubble interface, which allowed them to retain their conductive and plasmonic properties. Overall, this work lays the foundation for future studies of optically-directed assembly of MXenes at interfaces, which will advance the fabrication MXene-based sensors and electronics, and will promote applications in which high heat resistance and conductive or plasmonic properties is essential.

Keywords: MXene, plasmonic sensors, nanofabrication, microbubbles, two-dimensional materials

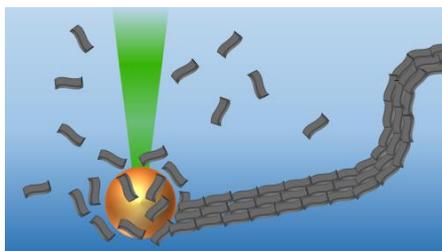


Figure 1. Schematic showing directed assembly of MXene by bubble printing.

Acknowledgements: This research was supported by the Deutsche Forschungsgemeinschaft (DFG) (project ID 447787198), and the DAAD from the funds of the BMBF (57429511). E.H.H. is supported by the Cluster of Excellence “Advanced Imaging of Matter” of the DFG—EXC 2056—project ID 390715994.

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Electrokinetic and dielectric response of a concentrated salt-free colloid. Different approaches to counterion finite size effects

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Salt-free colloids (i.e., those composed of a system of charged particles dispersed in a solution where the only ions present stem typically from the dissociation of particle surface chemical groups) have gained increasing interest [1]. One of their main characteristics is that for highly charged colloids a layer of counterions condenses onto the surface of the particles, a phenomenon that has an important influence in the behavior of these systems [2]. When the concentration of ions in solution is high (i.e., the surface charge of the particles and/or their concentration is large) the model of point-like ions must be substituted by approaches considering that the volume of ions is finite. Two models are used in this work, namely the Carnahan-Starling (C-S) and Bikerman ones (the latter for different packing options) [3]. Results on AC electrokinetics are particularized for dynamic mobility and dielectric dispersion spectra. In the former case, we observe a maximum in its real part, associated to the relaxation of two Maxwell-Wagner processes related to the diffuse (MWO) and condensed (MWC) layers, followed by a final decrease because of the inertia at the highest frequencies explored. The consideration of finite size of the ions leads to a shift to larger frequencies of the MWC relaxation frequency. The results are confirmed by dielectric dispersion, where the MW relaxations are well observable and better separated than in dynamic mobility data (Fig. 1).

Keywords: salt-free; dielectric dispersion; dynamic mobility

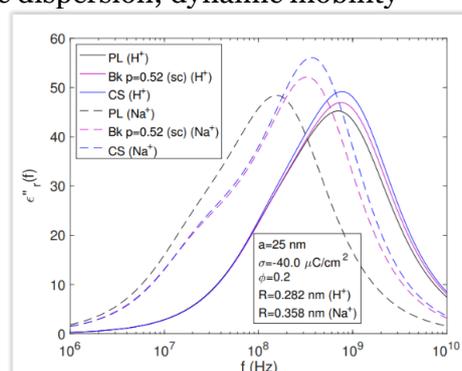


Figure 1. Imaginary part of the complex relative permittivity as a function of frequency for salt-free colloids according to the point-like (PL), Bikerman with simple cubic packing (BK), and Carnahan-Starling (C-S) approaches with different counterions: $R = 0.282$ nm (H^+) and $R = 0.358$ nm (Na^+), $a = 25$ nm, $\sigma = -40.0$ $\mu C/cm^2$, volume fraction of solids $\phi = 0.2$.

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Generation of local diffusioosmotic flow by light responsive microgels

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Our study shows that microgels trapped at a solid wall can issue liquid flow and transport over distances several times larger than the particle size. The microgel consists of crosslinked poly(*N*-isopropylacrylamide-co-acrylic acid) (PNIPAM-AA) polymer chains loaded with cationic azobenzene-containing photosensitive surfactant, which can assume either a *trans*- or a *cis*-state depending on the wavelength of the applied irradiation.

The microgel, being a selective absorber of *trans*-isomers, responds by changing its volume under irradiation with light of appropriate wavelength at which the *cis*-isomers of the surfactant molecules diffuse out of the particle interior [1]. Together with the change in particle size, the expelled *cis*-isomers form an excess of the concentration and subsequent gradient in osmotic pressure, generating a halo of local light-driven diffusioosmotic (*l*-LDDO) flow. The direction and the strength of the *l*-LDDO depends on the intensity and irradiation wavelength, as well as on amount of surfactant absorbed by the microgel. The flow pattern around a microgel is directed radially outward and can be maintained quasi-indefinitely under exposure to blue light when the *trans*-/*cis*- ratio is 2/1, establishing a photo-stationary state. (see Figure 1) Irradiation with UV light, on the other hand, generates a radially transient flow pattern, which inverts from inwards to outwards over time at low intensities. By measuring the displacement of tracer particles around neutral microgels during a temperature-induced collapse, we can exclude that a change in particle shape itself causes the flow, i.e., just by expulsion or uptake of water. Ultimately, it is its ability to selectively absorb an isomer of photo-sensitive surfactant under different irradiation conditions that leads to an effective pumping caused by a self-induced diffusioosmotic flow [2].

Keywords: microgels, photo-surfactant, azobenzene, light driven diffusioosmosis, micropump

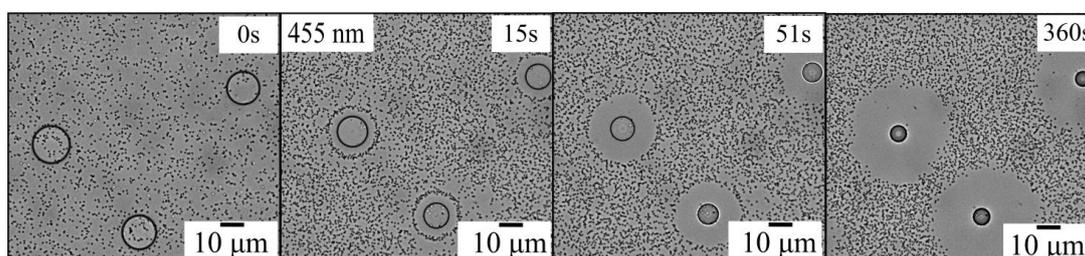


Figure 1. Optical micrographs of the microgel and the tracer particles before irradiation (at 0s) and during exposure to blue light (irradiation time is indicated on the micrographs).

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Aggregation phenomena of magnetic cubic particles in an alternating magnetic field (Brownian dynamics simulations)

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We have addressed the aggregation phenomena of a suspension composed of magnetic cubic particles in an alternating magnetic field by means of 2D Brownian dynamics simulations in order to investigate the dependence of the regime change on a variety of factors such as the magnetic particle-particle interaction strength, the magnetic particle-field interaction strength and the frequency of the alternating magnetic field. The main results obtained here are summarized as follows. In a weak alternating magnetic field and when the magnetic particle-particle interaction strength is relatively small, many single particles remain in the system and their magnetic moments significantly follow a change in the direction of the alternating magnetic field. As the magnetic particle-particle interaction strength is increased, the cubic particles aggregate to form closely-packed structures tending to an aligned face-to-face configuration. The magnetic interaction between neighbouring particles in the closely-packed aggregates restricts the orientation of the magnetic moments, and therefore they are not able to follow a change in the direction of the alternating field. As the strength of the alternating field is increased, the magnetic moments of cubic particles become more restricted to the direction of the alternating field and the closely-packed structures transform into elongated aggregates with an offset face-to-face configuration. In this situation, when the direction of the alternating field switches, the particle moments also attempt to reverse to the switched field direction, as shown in Fig. 1. Therefore, the elongated aggregates with offset surface contact temporarily collapse and then re-form.

Keywords: Brownian dynamics simulation, Magnetic cubic particles, Aggregation phenomena, Alternating magnetic field

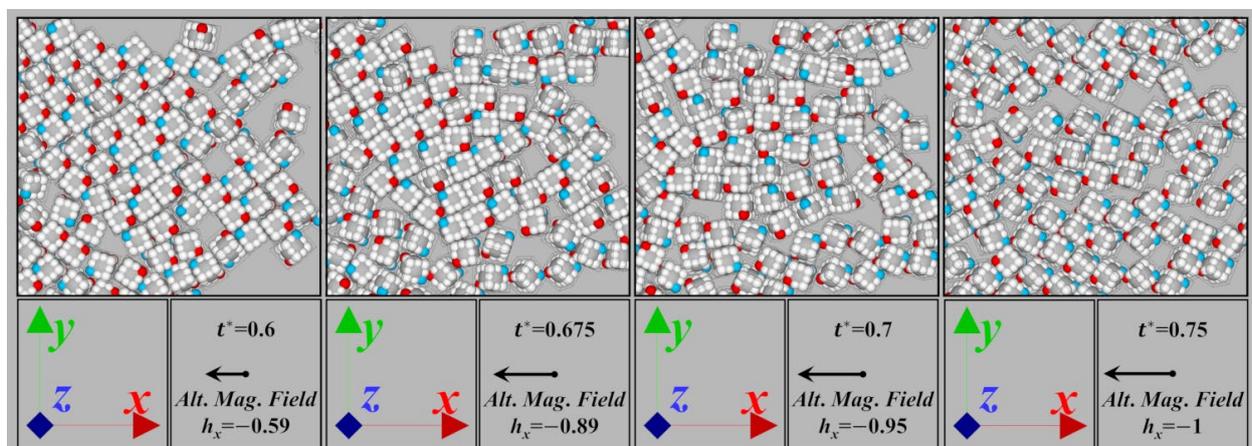


Figure 1. The transition of the local internal structure of aggregate structures responding to the change in the direction of the alternating magnetic field.

A rheo-confocal study of the rheological and structural properties of magnetorheological fluids

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Magnetorheological fluids (MRFs) are a class of smart materials whose rheological properties exhibit dramatic changes upon the application of external magnetic fields. For this reason, they are used in a wide range of momentum transfer applications. The ability of these fluids to reversibly and rapidly shift from liquid to soft yield stress solids with tunable yield stress after superimposing a magnetic field is their most notable characteristic [1, 2]. The main focus of this study is the use of rheo-confocal microscopy to visualize and understand both microstructure formation and yielding under shear in conventional magnetorheological fluids (CMRFs) under the presence of a magnetic field. Our methodology involves applying different shear rates to investigate the chain to ring transition with and without field to determine whether a steady-state can be achieved, and perform strain sweep tests in glycerol-based CMRFs to measure the yielding point and to promote structure formation both in the solid-like and liquid-like regimes for more detailed observation. Results from previous studies [3-5] have been promising, and have shown that it is possible to manipulate the rheological response of these systems by two different external stimuli: mechanical and magnetic. Here we present detailed experiments linking the microstructure acquired in-situ with the rheological measurements of linear and nonlinear material functions in an effort to provide a microscopic understanding of their yielding mechanism and flow-induced structures.

Keywords: Magnetorheological fluids, magnetic colloids, yield stress, chain and ring models.

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Analysing electrophoretic deposition using transient current measurements

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Electrophoretic deposition (EPD) is a widely used technique for coating surfaces with colloidal particles [1]. When using apolar solvents, one or more surfactants are required as charging agents. These surfactant molecules do not only adsorb to the particles, assisting in particle charging, but also aggregate into inverse micelles of which a small fraction also become charged. Since these charged inverse micelles (CIMs) are also subject to electrophoresis, they play a key role in the overall dynamics of the EPD process. Transient current analysis (TCA) is a useful technique for characterizing the dynamics of both solid particles and CIMs during EPD. In this technique a dispersion is placed between parallel electrodes, a voltage sequence is applied, and the resulting currents are measured and analyzed.

In this work we present TCA results for a model system for EPD, based on Al₂O₃ nanoparticles (Ø=140 nm) plus surfactant additives in a nonpolar solvent. Measurements are performed with and without particles. The currents are analyzed and compared to simulations based on the Poisson-Nernst-Planck equations [1], generation-recombination of CIMs [2] and Mott-Gurney-like effects at the interfaces [3]. The surfactants used in our dispersions are a cationic Cr(III) salt and a viscosity modifier based on polyalkylmethacrylate (PAMA). From the TCA and simulation the mobilities and concentrations of the particles and CIMs are obtained. Electric-field screening due to space-charge effects and long-term currents due to net CIM generation are investigated. And from currents in which the voltage is suddenly reversed information is obtained on the adsorption and desorption behavior of charges at the interfaces.

Our work provides a good understanding of the physics of EPD in the chosen model system. The TCA method can be further used to analyze other and possibly more complex EPD systems and may be useful for real-time control of the process.

Keywords: Electrophoresis, Charged Inverse Micelles, Electrophoretic deposition

Acknowledgements: This work is supported by Research Foundation-Flanders (FWO) through the Strategic Basic Research grant 1S83520N

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State diagram of soft dipolar ellipsoids

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Dispersions of anisotropic ellipsoidal particles are investigated using confocal laser scanning microscopy (CLSM). The particles were obtained by post-processing spherical particles into prolates with an aspect ratio of by mechanical stretching and consist of a polystyrene core surrounded by fluorescent microgel shell [1]. Their phase behavior is explored as function of the volume fraction across the glass transition under deionized conditions at 20 °C. We study the structure and dynamics of dispersions at various volume fractions, the influence of an external electric field on the phase diagram and the metastability of the resulting phases. Our results, supported by Monte Carlo simulations, evidence the organization of the polarized ellipsoids into columnar phases or a face center tetragonal (FCT) crystals with increasing dipolar coupling at high volume fractions with a persisting nematic ordering when the field is turned off at the highest volume fractions.

Keywords: ellipsoidal microgel, dipolar self-assembly, state diagram

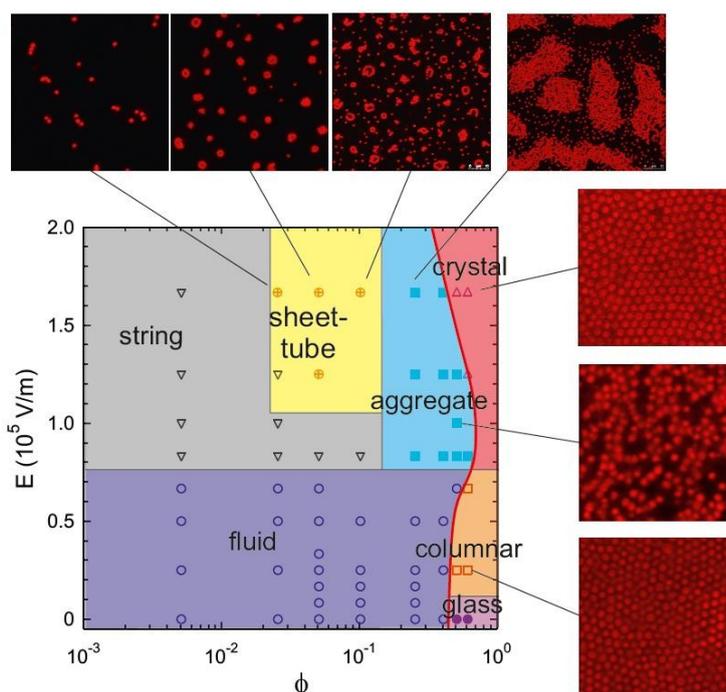


Figure 1. Experimental state diagram of dipolar ellipsoids with an aspect ratio of 3.3 polarized by an alternating electric field determined via confocal microscopy..

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NMR-Lev: A tool for contactless NMR spectroscopy

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The vast majority of Nuclear Magnetic Resonance (NMR) spectroscopic studies are carried out in an NMR tube. However, this constitutes a limitation to study phenomena such as evaporation, or studies where having a large gas-liquid interface is central. Very few attempts have been performed on surface resting droplets, which however disrupt the homogeneity of the magnetic field, due to droplet asymmetry on the xy-plane. Hence, the quality of the spectra may decrease [1]. This shortcoming can be avoided, in an ideal case where the droplet is symmetrical on the xy-plane, which is the case when a droplet is suspended in air. Acoustic levitation is a technique that employs ultrasonic transducers to generate an acoustic pressure field able to suspend in the air small droplets (volume ~2-10 μL).

In our study, based on the design by Marzo *et al.* [2] we developed a multi-transducer acoustic levitator, that can operate in the strong magnetic field inside the NMR bore. The high stability of the levitator enabled the recording of MRI images on droplets with a diameter of ~1-1.5 mm, with high signal-to-noise ratio. We could experimentally show the impact of the droplet's shape on the chemical shift, simply by varying the acoustic pressure applied on the droplet. Furthermore, time resolved experiments were demonstrated with mixtures of volatile and non-volatile solvents, which yielded insights into chemical phenomena. For instance, in the case of TEG-water mixtures we were able to observe -OH hydrogen exchange transitions during the water evaporation. The ¹H NMR spectra were acquired *via* the localized spectroscopic technique ISIS, while for the MRI images either PRESS, STEAM or FLASH pulse sequences were performed.

Keywords: Contactless NMR, Acoustic levitation, Methods

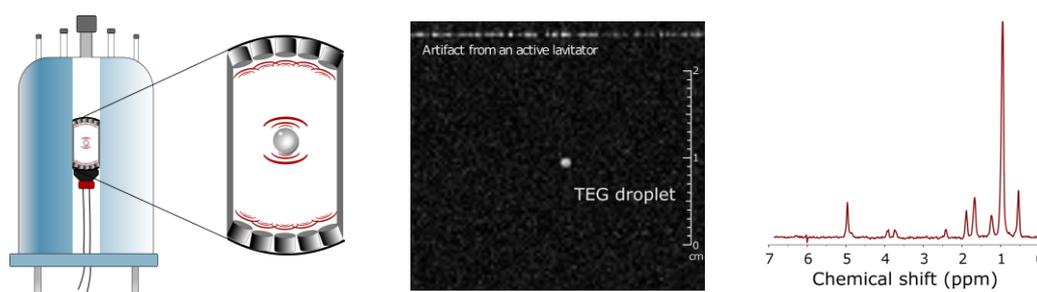


Figure 1. a) Acoustic levitator integrated in the NMR bore (not to scale). b) MRI image of a droplet of tetraethyleneglycol (TEG) levitated in the acoustic field and collected with pulse sequence FLASH. c) ¹H NMR spectrum of a levitated droplet of pure canola oil collected with pulse sequence ISIS.

Acknowledgements: The authors would like to thank the Swedish Foundation for Strategic Research (SSF) and the Swedish Research Council (VR) for financial support.

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Comparison of the frictional properties of plant and dairy proteins

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The food industry has a long-standing interest in increasing the protein content of food products. In recent times, plant proteins have increased in popularity due to the rise in veganism and awareness of sustainability issues. However, increasing protein concentration often generates an undesirable mouthfeel, which is even more prominent for **plant proteins**^{1,2}. Although the molecular mechanisms behind such adverse sensorial perception remain poorly understood, electrostatic interaction between the protein and saliva during oral processing are often hypothesized to be the cause of such adverse perception³. Therefore, the aim of this study was to compare *in vitro* mouthfeel properties of alternative cereal and legume proteins (wheat, pea and soy) with dairy proteins (whey protein isolate and sodium caseinate) at higher concentrations (5-20 wt%) using soft tribology and quartz crystal microbalance with dissipation monitoring (QCM-D). Soft **tribology** was performed using glass-polydimethylsiloxane (PDMS) contact surfaces to analyse the lubrication behaviour of proteins at 37 °C in the absence and presence of model saliva (protein: saliva ratio: 4:1 w/w). **QCM-D** was carried out using PDMS as a substrate coated with mucin to reproduce orally relevant surfaces. Preliminary results reveal effects of protein concentration and saliva-protein ratio on the lubrication performance. Solubility of plant proteins was also a key factor affecting the lubricity and adsorption behaviour. Future studies involving sensory tests are key to understand whether such *in vitro* tools are correlated with mouthfeel perception using plant proteins.

Acknowledgements: Funding from the BBSRC-Mondelez International CTP is acknowledged.

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The inhomogeneous rheological response of nematic platelets studied by spatial resolved Rheo-SAXS and XPCS

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Dispersions of colloidal platelets in the nematic phase display strong wall anchoring, which competes with the reorientational motion of the director when the system is subjected to flow. We show that the mechanical response to large amplitude oscillatory strain and stress depends on the confinement of the system due to this competition [1]. We elucidate the underlying structural response by deflecting a x-ray beam vertically along the vorticity direction of a Couette geometry, such that the structure can be probed throughout the gap with an unprecedented spatial resolution while recording in situ the mechanical response. Depending on the extent the system is yielding during an oscillation, we observe strong inhomogeneities in terms of the orientation of the nematic director, which includes a twinning where the director rotates out-of-plane in two opposite directions. Using the sequence of physical process method to analyse the response for both the mechanical and structural response, we locate the yielding in a small time-window around flow reversal and identify that the bulk is the main contributor to the mechanical response. In addition, we show that the response to stationary flow throughout the gap is strongly inhomogeneous in structure as well as in velocity. To this end we performed XPCS measurements in "tangential" scattering geometry in a Couette cell to obtain velocity profiles [2]. These findings are relevant in view of using clay as flow modifiers in industrial systems, but also when processing other platelet particles, such as graphene oxide. Moreover, we can take inspiration from these results when interpreting the flow of other yielding fluids.

Keywords: Platelets, LAOS, yielding, SAXS, rheology

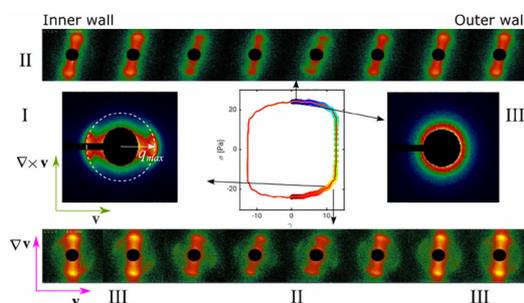


Figure 1. SAXS patterns in the flow-flow gradient plane, throughout the gap with an interval of 100 μm , and in the flow-vorticity plane. The patterns were taken at two points in the cycle as indicated in the Lissajous curve.

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Rheological investigations of thermoresponsive core-shell nanoparticles in suspension at the colloidal glass transition

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Understanding the mechanical behavior of high concentrated colloidal suspensions of hard spheres, i.e. colloidal suspensions in the glassy state, under applied mechanical fields is a long-standing problem in colloid physics. While the flow properties of colloidal suspensions in homogeneous shear flows are well understood, approaches to inhomogeneous, boundary-driven, non-shear or mixed flows remain largely phenomenological up to now. To gain more insights into the mechanical properties under those flows, comprehensive rheological investigations on a well characterized colloidal model system are crucial.

For this purpose, a polystyrene-poly(*N*-isopropylacrylamide) (PS-PNIPAm) core-shell system was synthesized in a two-step synthesis procedure. After the synthesis, the core-shell particles were purified using ultrafiltration. The size of the core-shell particles was investigated by disc centrifuge sedimentation (DCS) and dynamic light scattering (DLS). The synthesized system is thermoresponsive, i.e. the hydrodynamic radius R_H and therefore the volume fraction of the colloids is adjustable *in situ* by changing the temperature, as investigated by DLS.

With this batch of a well characterized colloidal suspension a comprehensive rheological study of the glassy state ($\phi > \phi_g$) of colloidal suspensions is feasible. In our group it could already been shown, that the intrinsic nonlinearity parameter Q_0 , which is a measure for the deviation from the linear behavior, of a colloidal suspension diverges approaching the glass transition [1]. We now plan to further investigate the mechanical behavior close to the and above the glass transition. For this purpose, we are using large amplitude oscillatory shear (LAOS) to further investigate the nonlinear behavior of the colloids, capillary rheology and elongational rheology to investigate flow instabilities and extensional flows and parallel and orthogonal superposition of shear to investigate mixed flows and the yielding behavior of the colloids.

Keywords: rheology, colloidal glass, core-shell system, thermoresponsive nanoparticles

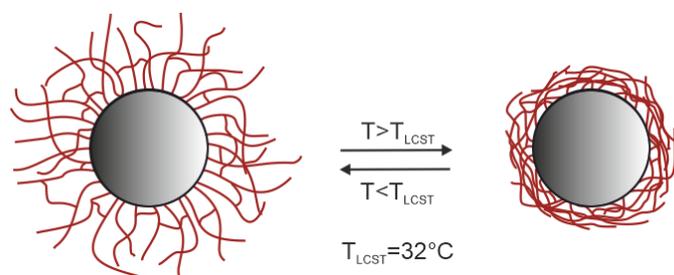


Figure 1. Volume transition of the PS-PNIPAm core-shell particles at the lower critical solution temperature.

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Design and optimization of single-node single axis levitators for contactless experiments in air

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The capacity to levitate objects using ultrasonic standing waves has been widely explored due to its scientific potential and technological applications, and is becoming a common research equipment. In comparison with other levitation techniques, this method does not require the samples to have *ad-hoc* physical properties such as an electric, a magnetic, or an optical response.

In a typical setup, a high-power Langevin transducer is coupled to mechanical amplifiers known as horns or sonotrodes to generate strong acoustic power output. Different configurations can be made, all characterized by the need to carefully calibrate the distances in the setup as function of the atmospheric conditions that influence the speed of sound (e.g., temperature, humidity). This technology is now progressively replaced by constructions that rely on multiple ultrasonic emitters that are of lower price, present good temperature stability and operate at much lower voltages. Furthermore, they allow the design of new emitter arrangements that can be rationalized towards applications, for instance if only a single levitation point is needed.

Here, we report the design principles for realizing such type of airborne single-axis acoustic levitators. Compared to previous designs, this new series of levitators provides twice the trapping force, a higher spatial stability while using a very limited number of emitters that allow a low spatial footprint. The optimized designs are made open and rely on a modeling framework that enable evaluating the levitation capacity using *in silico* designs.

Keywords: Acoustic levitation, contactless measurements, multiple transducers



Figure 1. Models of three levitator designs presenting various trapping forces and stabilities.

Acknowledgements: The authors would like to thank the Swedish Foundation for Strategic Research (SSF) and the Swedish Research Council (VR) for financial support.

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Regime change in the aggregate structure of magnetic cubic particles in a quasi-2D suspension

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We have elucidated the feasibility of multi-particle collision dynamics (MPCD) method as a simulation technique for a suspension composed of magnetic cubic particles and then have applied it to the phenomenon of a regime change in particle aggregates in a quasi-2D system. In the second issue we have considered the problem of controlling a regime change in a quasi-2D system of magnetic cubic particles via the strength and direction of an applied magnetic field.

In the first issue, from the accuracy of the MPCD simulation with respect to the normalized mean square root (NMSR) velocities and the magnetization curve, we may conclude that the random motion of the fluid particles and the Brownian motion of the magnetic particles are expected to be activated at a physically reasonable level, which leads to the feasibility of the MPCD method as a simulation tool for a magnetic cubic particle suspension.

In the second issue, the direction of an applied magnetic field gives rise to significantly different regime changes in the particle aggregates. In the case of an external magnetic field applied along the 2D plane, magnetic cubic particles significantly aggregate to form thin chain-like clusters along the magnetic field direction. If the magnetic field is changed into the direction normal to the 2D plane from this situation, these thin chain-like clusters collapse and transfer into a regime with no discernible internal structure. In the case of an external magnetic field applied in an oblique direction, more compact and rigid chain-like clusters tend to be formed along the 2D-plane in a face-to-face contact manner. From these results, we may conclude that the strength and direction of an applied magnetic field is a feasible tool for controlling a regime change in the aggregate structure in a magnetic disk-like particle suspension.

Keywords: Regime change, Magnetic cubic particle, Aggregation phenomenon, Cluster formation, Multi-particle collision dynamics, Brownian motion

Hydrodynamic correlations of trapped particles in optical tweezers

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The understanding of hydrodynamic interactions in complex fluids is of relevance in several branches of science since phenomena such as hydrodynamic synchronization in either biological systems (sperm, cilia, flagella) or active colloidal arrays, and the dynamics of microswimmers can only be explained in terms of hydrodynamic coupling [1]. Using a simple physical picture, one can understand HIs in the following way. The motion of a given colloidal particle induces a flow field in the solvent, which is felt by the surrounding colloids; when a colloid move, it displaces the fluid in its immediate vicinity, and the motion of one particle causes a solvent-mediated force on the neighboring particles. Thus, HIs are indirect interactions that affect the dynamical behavior of colloids, and such interaction is always present in colloidal systems [2].

The effects of HI on the coupling between two colloids have been experimentally analyzed using video microscopy and optical manipulation on colloids. Optical traps use the forces exerted by strongly focused beams of light to trap micron-sized objects [2]. Here we report a direct measurement of hydrodynamic interactions by studying the dynamics of two microscopic latex beads held at a fixed distance apart in separate optical tweezers. Here we show the results obtained in the correlation functions of displacements at different distances between the particles and optical stiffnesses. The computational simulation results reported by other researchers are also experimentally validated, by determining the cross-correlation function of two particles in presence of a third particle. Our experiments are compared with Brownian dynamics simulations finding a good agreement.

Keywords: optical tweezers, hydrodynamic interactions, Brownian dynamics simulation.

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Yielding of mono- and bidisperse capillary suspensions

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Capillary suspensions are created by the addition of a small amount of immiscible secondary liquid to the binary suspension, which induces or increases a yield stress due to the formation of a sample-spanning particle network. The rheological properties can be varied over multiple orders of magnitude by changing the amount of secondary liquid, thereby tuning the number and size of the liquid bridges connecting particle pairs.

In this work, we investigate capillary suspensions with spherical silica microparticles of different sizes and with varying relative volume fractions. The most significant changes compared to monodisperse networks occur if the particle polydispersity also causes a meniscus polydispersity. Hence, a small volume fraction of larger particles in a small particle network has only a minor effect, as the dominant motif is still the bridge between small particles, as shown in Figure 1a. By contrast, a low fraction of small particles in a large particle network (size ratio 1:3) can drastically weaken the network, because these bridges have a lower absolute capillary force and rupture distance, as shown on Figure 1b. Much smaller microparticles (size ratio 1:10) can be absorbed in the bridges or adsorbed on the bridge interface and reduce the bridge rupture distance. In both cases with smaller particles, changes on the single bridge length scale can be directly linked to the resulting bulk rheological response.

Moreover, using a rheometer mounted to a confocal microscope, we are able to directly investigate the yielding of a capillary suspension network subjected to an oscillatory shear deformation for the first time, illustrated on Figures 1c and 1d. The initial yielding stage is characterized by a small number of localized bridge rupture and reformation events, while the rest of the sample undergoes rigid body movement.

Keywords: Capillary suspension, capillary force, particle networks, rheology, confocal microscopy

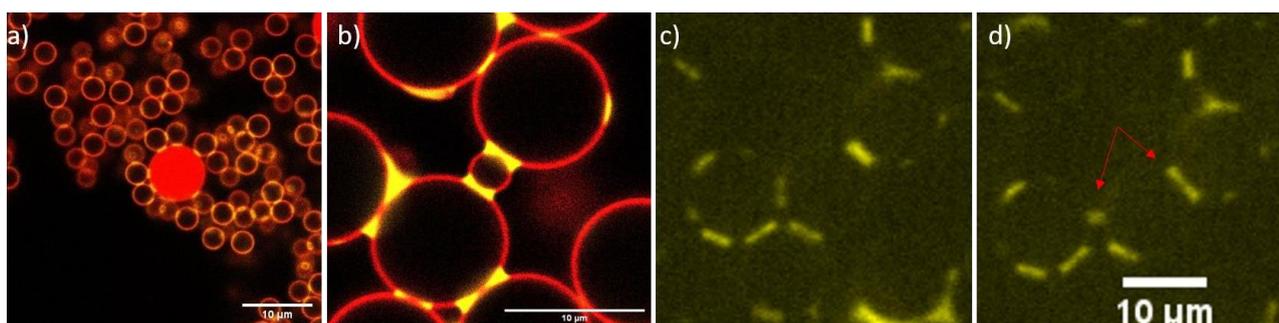


Figure 1. Confocal micrographs of (a) a larger particle incorporated in a smaller particle network, (b) a smaller particle incorporated in a larger particle network, (c-d) liquid bridges during an oscillatory shear deformation showing the localized stretching and compression, indicated by the red arrows. The liquid bridges are shown in yellow (a-d), the particles are shown in red (a-b).

Non-toxic liquid-infused slippery coating prepared by a one-pot process prevents corrosion and marine biofouling adhesion

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Wetting, or the ability of a liquid to maintain contact with a solid surface resulting from intermolecular interactions, plays a vital role in many biological and industrial processes. There are several phenomena closely related to wetting as biofouling and corrosion. The efforts to prevent degradation of surface functionality spread over several millenniums. Antifouling coatings have been developed to prevent/delay both corrosion and biofouling but the problems remain unsolved influencing the everyday life of modern society in terms of safety and tremendous expenses. Liquid-infused slippery surfaces (LISS), recently developed non-toxic omniphobic repellent technology,¹⁻³ were studied for their anti-corrosion and marine anti-biofouling properties on metallic substrates under plain and surface-damaged conditions. Low carbon and austenitic stainless steels were chosen as a model due to their wide application in marine environments. Our results demonstrate that LISSs can effectively prevent marine biofouling adhesion and decay corrosion of metallic surfaces even if severely damaged. The mechanically robust LISSs reported in this study significantly extend the slippery liquid-infused porous surfaces (SLIPS) technology prompting their utilization in marine applications owing to the synergy between rapid and facile fabrication processes, non-toxic, ecofriendly, and low-cost materials together with excellent repellent characteristics.

Keywords: lubricant-infused slippery surfaces, polydimethylsiloxane, corrosion resistance, anti-biofouling, blood-repellent coating

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Scanning Drop Adhesion Force Instrument (sDAFI)

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Contact angle goniometry is the current industry and academic standard for characterization of wetting properties of surfaces[1]. However, it may miss wetting details smaller than the foot print of the drop. Here, we present a novel approach: scanning drop adhesion force instrument (sDAFI). It is a quick and reliable technique allowing us to characterize 25x75 cm² area with the ability to detect wetting differences at μm-scale.

Lateral adhesion of a drop, also friction force, is a consequence of associated contact angle hysteresis (CAH) – difference in advancing and receding contact angles[2]. Here, we use this force as a tool to image and characterize surface wetting properties. We prepared a model surface having a defined M contour concocted from octyl tri-chloro silane (OTS) having CAH of ≈25°, and background with Perfluoro (octyl tri-chloro) silane (PFOCTS) having CAH of ≈60°. A 15μL drop of Milli-Q water is used as a scanning probe. Water drop is held in a position by a glass capillary based force sensor, equipped with a metallic ring of size ≈2mm. We record the deflection of the capillary via CCD camera, and then, convert it to force via stiffness of the capillary, and put in the form of a wetting force map. With this approach, we are able to detect inhomogeneities having dimensions order of magnitude less than the sliding drop's length, with force sensitivity down to 1μN.

Keywords: wetting, friction force, drop scanning.

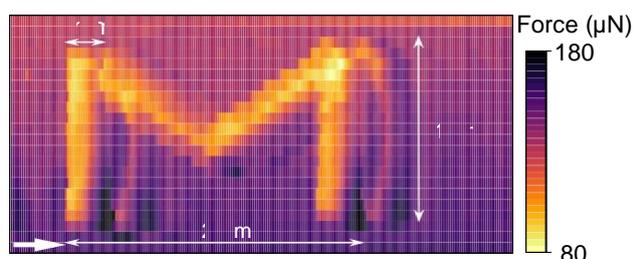


Figure 1. Wetting force map of M shape.

Acknowledgements: We acknowledge financial support by German Research Society (DFG) via the CRC 1194, project Co7 (C.H.).

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Fabrication of Stretchable Superamphiphobic Surfaces with Deformation-Induced Rearrangeable Structures

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Stretchable superamphiphobic surfaces with a high deformation resistance are in demand to achieve a good liquid-repellent performance in flexible electronics, artificial skin and textile dressings. Unfortunately, most currently existing superamphiphobic surfaces appear to lose their super-liquid-repellency to low-surface tension liquids under small deformation, in particular when being stretched. Therefore, it is still a challenge to make mechanically robust superamphiphobic coatings, which maintain their super-liquid repellency in a highly stretched state. Here, we report a stretchable superamphiphobic surface on which the microstructures rearrange during stretching to maintain a stable superamphiphobicity even in a high tensile strain. The surface is prepared by spray-coating silicone nanofilaments onto a pre-stretched substrate (e.g., cis-1,4-polyisoprene) with a polydimethylsiloxane (PDMS) layer as a binder. After subsequent fluorination, this surface keeps its superamphiphobicity to both water and n-hexadecane up to the tensile strain of at least 225%. The binding PDMS layer and the rearrangeable structures maximize the deformation resistance of the surface during the stretching process. Superamphiphobicity and morphology of the surface are maintained even after 1000 stretch-release cycles. Taking advantage of the mentioned benefits, a liquid manipulation system was designed. It has the potential for fabricating reusable and low-cost platforms for biochemical detections and lab-on-a-chip systems.

Keywords: deformation resistance, liquid manipulation, stretchable surfaces, superamphiphobicity, wetting

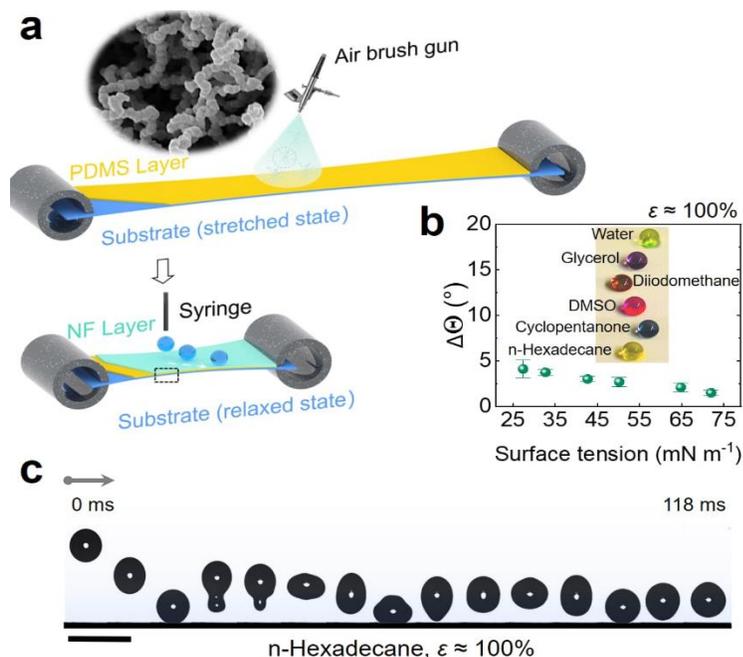


Figure 1. a) Scheme of the fabrication process of the nanofilament-based stretchable superamphiphobic (NFSS) surface. b) Contact angle hysteresis of various liquids on the stretched NFSS surface (strain $\epsilon \approx 100\%$) after 1000 cycles of test. Inset shows the image of sessile drops (10 μL) of corresponding liquids on the stretched NFSS surface. c) Image series of the impact and bouncing of a 3 μL n-hexadecane drop on the surface. Drop release height: 2 cm; scale bar: 5 mm; strain $\epsilon \approx 100\%$.

Acknowledgements: This project received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement No 883631, DYNAMO). The authors are also grateful for

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Wetting dynamics on intrinsically charged Lithium Niobate surfaces

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Knowledge of the droplet behavior on a surface is crucial in various applications like drug delivery, diagnostics, inkjet printing, spray coating, etc. Electrowetting is one of the extensively studied methods of droplet studies, where the droplet behavior in the presence of external voltage is investigated. There are materials like electrets which bear quasi-permanent surface charge, and materials like polymers, metals, and inorganic materials which can also acquire surface charge by triboelectric effect. However, there is not much knowledge is available on how the intrinsic charge of the surface will be influencing the droplet dynamics. In our study, we investigate the droplet spreading dynamics on intrinsically charged material. Lithium niobate is an intrinsically charged ferroelectric material, with very high surface charge on the z-cut surface.

Our study investigates the 1) Spreading dynamics of water droplets on intrinsically charged lithium niobate surfaces 2) Impact of polarization direction on the droplet spreading dynamics. 3) Short time influence of adsorption/pretreatment methods on the wetting behavior.

We find that the spreading dynamics can be divided into 3 regimes: linear regime, Tanner's regime, and exponential regime, in line with theoretical predictions [1,2]. While spreading studies are typically focused on Tanner's regime, the current work points out the importance of the exponential regime in the spreading dynamics of droplets placed on charged surfaces. The experiments also demonstrate significantly extended spreading times compared to theoretical predictions. Spreading times as well as the contact angles are influenced by the surface polarization and adsorption.

Keywords: Spreading, wetting, intrinsically charged, pretreatment, polarization

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Surface Acoustic Wave Mitigation of Precipitate Deposition on a Solid Surface—An Active Self-Cleaning Strategy

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Self-cleaning surfaces have been studied for a long time. Most studies emphasize passive self-cleaning surfaces, which employ hydrophobic, oleophobic as well as rough superhydrophobic and superoleophobic properties. The goal of a passive self-cleaning surface is to minimize the contact and attachment of liquids to the surface and hence the contamination of the surface by liquid and by solid deposits, to appear following the evaporation of the liquid, should it be a suspension or a solution. Here we present an active strategy to render a solid surface clean of deposits to originate from volatile liquids at its vicinity. We demonstrate that a MHz-frequency surface acoustic wave (SAW) in a solid substrate mitigates deposits of polymer from a neighboring volatile solution.

In our experiment, we confine a solution of polymethylmethacrylate (PMMA) polymer and a volatile toluene solvent between a glass cover (above) and a lithium niobate substrate (below), as in Figure 1. In the absence of a SAW, we design the surface wettabilities such that most of the polymer deposit appears on the underlying lithium niobate substrate, following the evaporation of the solution. The application of a propagating SAW in the underlying lithium niobate substrate mitigates the deposition of the polymer on its surface. Instead, we observe that the polymer precipitates on the upper glass cover. Above a SAW power threshold, the polymer appears to deposit solely on glass, leaving the surface of the lithium niobate substrate, below, devoid of polymer. Thus, employing the presence of a SAW in a substrate, we actively prevent polymer precipitates from attaching to its surface. Instead, mass conservation renders the polymer deposits appear on a nearby inert surface.

Keywords: self-cleaning surface, surface acoustic wave, coating, precipitation, liquid film, evaporation

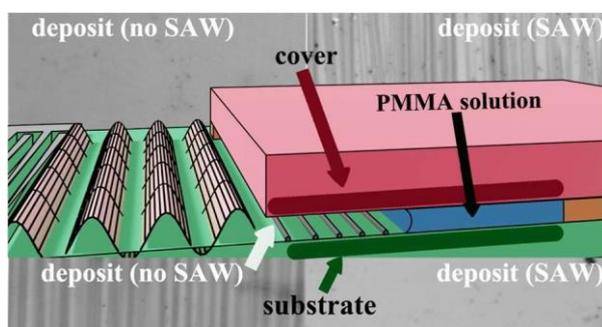


Figure 1. The presence of a surface acoustic wave (SAW) in a solid (bottom) substrate inhibits the deposition of precipitate mass on the surface of the excited substrate; the deposit appears on a nearby (upper) surface.

Acknowledgements: This study was funded by the Israel Science Foundation

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Adaptation and Recovery of a Styrene-Acrylic Acid Copolymer Surface to Water

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When a droplet is sliding on surfaces, adaptation of surfaces leads to changes of the dynamic contact angles [1, 2]. Hereby two adaptation processes play a role: (i) the adaptation of the surface upon bringing in contact to the drop (wetting) and (ii) the adaptation of the surface after the drop passed (dewetting). In order to study both processes, we investigated samples made from polystyrene (PS)/polyacrylic acid (PAA) random copolymers by using a tilted-plate method, fluorescence microscope and by sum-frequency generation spectroscopy (SFG). During wetting, water diffuse into the polymer, and the PS segments displace from the interface, while PAA segments are enriched, leading to the decrease of sliding drop velocity and contact angles. This structural adaptation of the PS/PAA random copolymer to water remains after dewetting. Annealing the adapted polymer induces reorientation of the PS segments to the surface [3].

Keywords: adaptive surface, dynamic contact angle, confocal microscopy, SFG

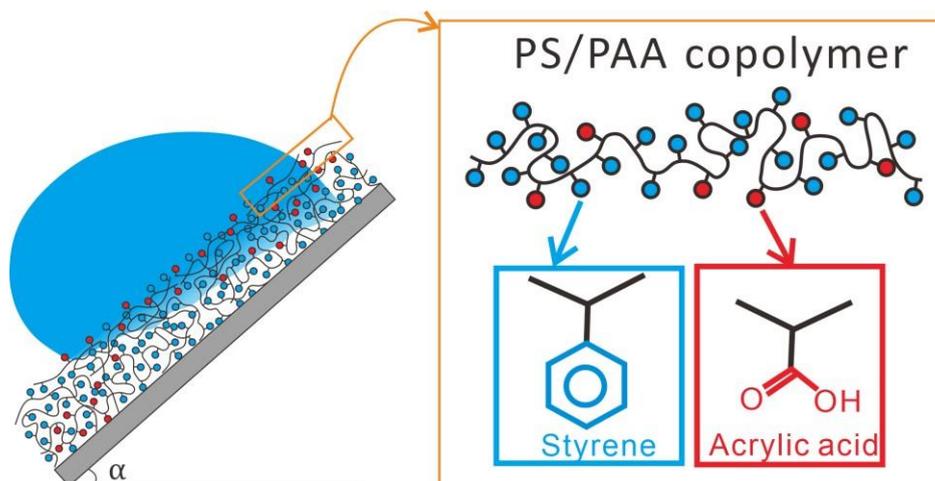


Figure 1. Adaptation of PS/PAA surfaces when contacting to sliding water drops.

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Effects of Microgel Stiffness on Droplet Bouncing

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Droplet impact on a solid surface is an important phenomenon with a wide range of applications such as spray coating and inkjet printing. In most real-life applications, solutions are being used instead of pure liquids. Therefore, the solute plays a crucial role in the interfacial dynamics of an impacting droplet by affecting its surface tension as well as its elasticity. Surfactants are often used to study the droplet impact of aqueous solutions on hydrophobic surfaces. Recently, it is shown how dynamic surface tension affects the droplet spreading with “fast” and “slow” surfactants[1]. The question is, how the mechanical properties of the solute particles can affect the surface elasticity of the droplet and consequently, the droplet impact.

Poly(N-isopropylacrylamide) (PNIPAM) microgels, as intramolecularly crosslinked nanoparticles, are water-soluble polymers below their Lower Critical Solution Temperature (LCST). The amount of cross-linker content defines their stiffness[2] and subsequently the liquid-air interfacial properties such as transient time to reach the steady-state surface tension as well as surface elasticity. In the present work, we used PNIPAM microgels in three cross-linker contents of 1, 5, and 10% in a relatively high solution concentration of 0.1wt% to exclude the dynamic surface tension (since the transient time to the steady-state surface tension is negligible in all three cases) and only study the effects of the particle stiffness on the droplet surface elasticity. A 4 μ l-droplet of these solutions was released from a syringe at different heights and bounced on a superhydrophobic surface (CA:155° \pm 3°). The center of mass of droplets w.r.t. to their radius (Y_c/r) were tracked and plotted to show their bouncing heights. Results show that the droplets with higher cross-linker content bounce more and higher.

Keywords: PNIPAM microgels, Cross-linker, Droplet bouncing

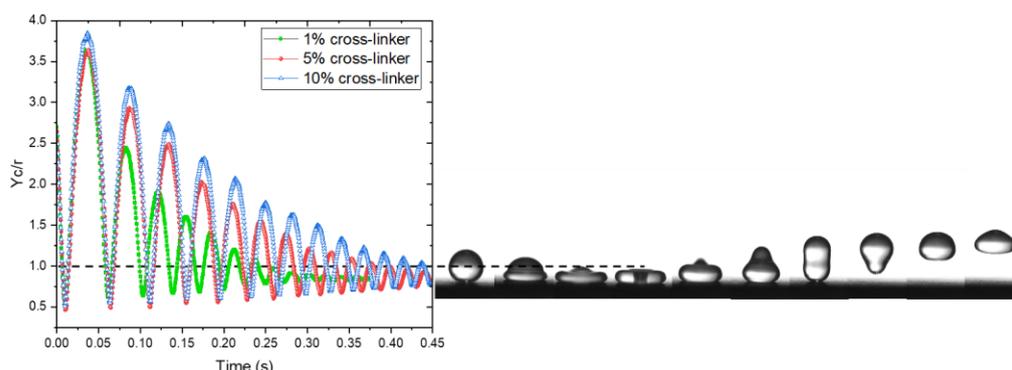


Figure 1. Droplet bouncing of PNIPAM solutions with different cross-linker contents on superhydrophobic substrate released from 5mm height.

Acknowledgements: Financial support from DFG, Project Number: 460540240, is acknowledged.

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Charging of drops impacting onto superhydrophobic surfaces

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We measure charge separation of drops rebounding from superhydrophobic surfaces. Here, we show that after a rebound, drops gain positive charge due to the interaction with these surfaces. To measure the charge, we analyzed the trajectory of rebounding drops in an external electric field by high-speed video imaging [1]. We investigate the relative importance of five parameters in the charge separation mechanism: Impact speed, drop contact area, retraction speed of the contact line, drop size and type of surface. In addition, we adapt our previous sliding drop electrification model [2] to the case of bouncing drops. The compatibility of the model suggests the same charging mechanism at the contact line for sliding and bouncing drops, revealing that the drop contact area is the dominant control parameter for charge separation. Our results indicate that, drops deposit negative charge on the surface at the rear of the receding contact line and gain the opposite net charge during the retraction phase. When the maximum contact area is large enough, drops reach a saturation point that depends on the drop capacitance and the surface chemistry of the sample.

Keywords: Bounce, charge separation

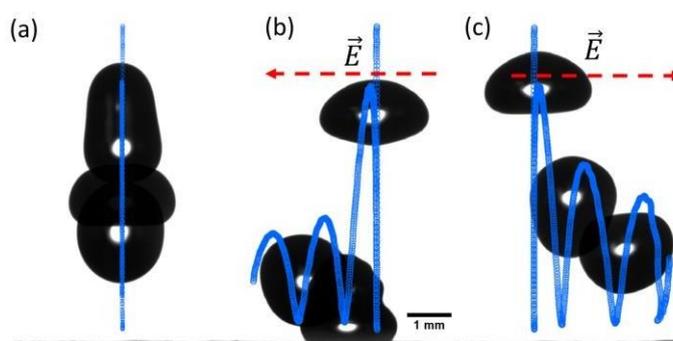


Figure 1. Drop rebounding from a superhydrophobic surface in three cases: (a) No electric field; (b) electric field oriented from right to left; (c) electric field oriented from left to right.

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Washing cycle and temperature effect on cleaning hydrophilic surfaces with purified water grades

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Nowadays, the use of detergents in washing and cleaning is a part of our daily life. However, an extensive use of detergents is a known source of water pollution and can cause a serious environmental problem.

In a previous study we have shown that the idea of using pure water in washing and cleaning can be implemented [1]. By examining the efficiency of various water grades in cleaning hydrophilic/phobic surfaces we concluded that the absence of ions from the pure water grades, helps the removal of dirt from the surfaces by increasing the electrostatic interactions.

In this work, we examine the effect of temperature and the number of washing cycles on the washing efficiency of various water grades. Using two different methods we investigate removal of thin and thick films from solid surfaces. Via Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) – a technique that was previously used to evaluate the efficiency of various water grades in detergent free cleaning [1]– we monitor removal of thin vaseline films. The first two cycles are shown to be more important for the washing process while no or little effect is found in the following cycles (figure 1A).

Results from measuring the mass of oil deposited on the surface of glass tubes before and after washing, agree with the QCM-D findings. Figure 1B shows that the amount of mass left on the surface after cleaning gradually decreasing. First two cycles are again the most efficient ones. Moreover, these results show that higher temperature improves the cleaning efficiency.

Keywords: ultra-pure water, detergency, detachment of oil from solid surfaces, washing cycles, temperature

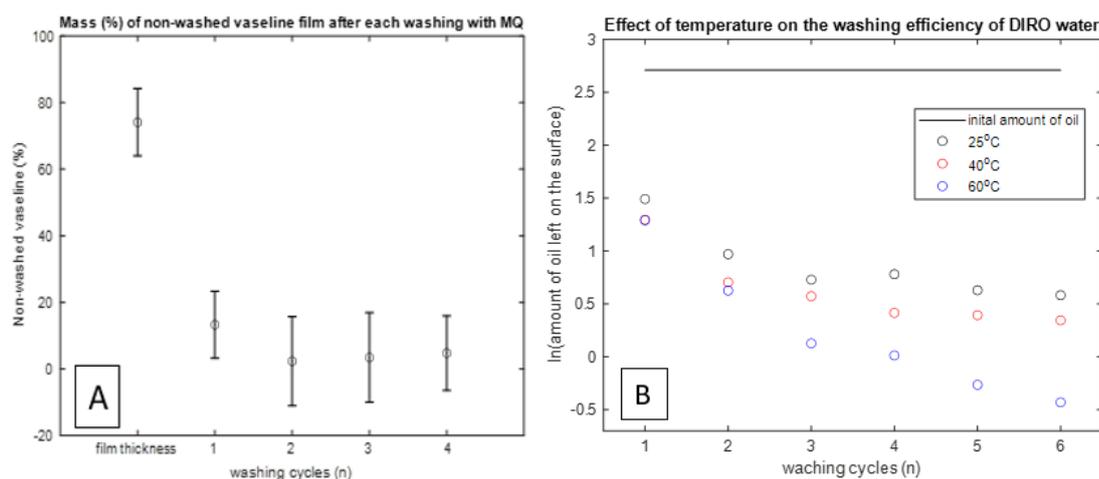


Figure 1: A: fraction of non-washed Vaseline mass after each washing cycle when MQ water was used for washing. B: Amount of non-washed oil (log) after each washing cycle (n) and at different temperatures when purified DIRO water was used.

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Hierarchical superhydrophobic composite membrane for enhanced distillation with excellent fouling resistance

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In arid regions close to the coast, seawater desalination has become a vital source of clean water. Therefore, energy-efficient desalination strategies need to be developed to avoid excessive strain on limited energy supplies. As a hybrid thermal/membrane-based desalination process that can use waste heat, membrane distillation (MD) has received increased attention for small-scale desalination applications as well as for treating high salinity brines. The challenge remains to enhance the distillation rate while simultaneously avoiding membrane wetting and fouling. In this work, composite membranes with multiscale pore sizes are developed by coating a thin layer of nanoporous nanofilaments on microporous membranes. Distillation performance and fouling resistance are studied using contaminants with low surface tension that can increase the risk of membrane wetting. Resistance against organic fouling by protein adsorption is tested as well. Our new multiscale porous membranes demonstrate high fouling resistance while achieving enhanced distillation flux as compared to commercial membranes. This work shows a promising approach for MD process optimization for the treatment of wastewater and seawater.

Keywords: Membrane distillation, Superhydrophobic, Fouling.

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Rivulets in Soft and Rigid Nanowedges

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Wetting of edges occurs in a broad variety of natural and industrial processes, since most surfaces are rough, porous, and/or fractured. The simplest element inherent to them is a wedge or a corner. According to the classical theory of capillarity, a liquid rivulet entering a wedge must propagate along its spine indefinitely long if the liquid-gas interface is concave [1]. In contrast to a liquid ascent in capillary tubes, even gravity cannot stop such a rivulet flow in wedges.

In the present work, we consider wetting statics of a wedge channel. We show that even when the liquid-gas interface is concave, the steady state of a rivulet is possible if the intermolecular (surface) forces are taken into account [2]. We show that the wedge geometry as well as the surface force parameters significantly affects the shape of a rivulet (Figure 1, a).

Since a surface or a porous material can be soft, in addition, we model a wedge with elastic walls and show how the liquid presence deforms the walls of the wedge (Figure 1, b).

Keywords: Edge Wetting, Capillary Flows, Nanofluidics, Surface Forces

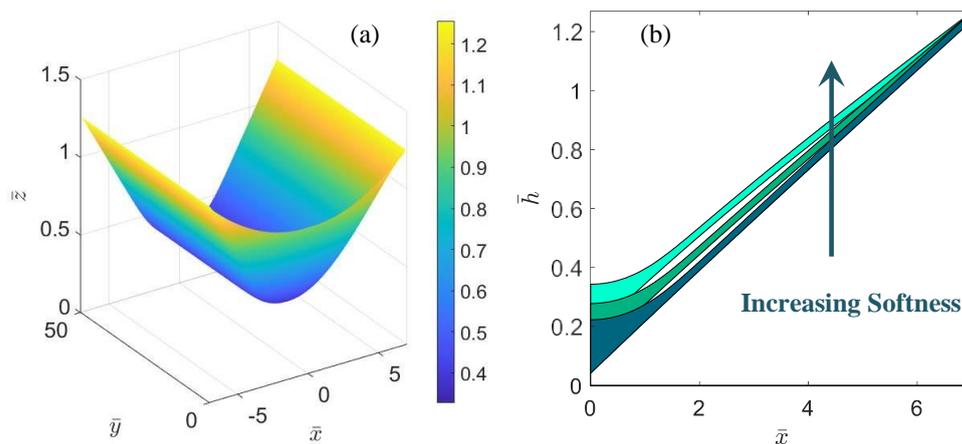


Figure 1. (a) Liquid-gas interface of a rivulet in a rigid wedge. (b) The rivulet shapes in soft wedges.

Acknowledgements: The authors gratefully acknowledge the financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Priority Program “Dynamic Wetting of Flexible, Adaptive and Switchable Surfaces” (SPP 2171), Project Number 422792679..

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Reversible chemotaxis of dynamically reconfigurable emulsion droplets

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Chemotaxis is the ability of organisms to move in response to a chemical stimuli, where an environmental signal is transduced into chemical recognition and motion. The fundamental investigation of natural out-of-equilibrium systems have utilized emulsion droplets to both better understand and mimic these behaviors. Droplets are suitable model systems to this end, and many reports have been made on the chemotactic and life-like behavior of droplets with random or uni-directional motion. Minor variations in interfacial tension result in large Marangoni convections at the fluid interface, inducing movement toward lowering the interfacial tension of the droplet. The sensitivity of droplet motion via chemotaxis can be designed and targeted, such as to a photo-switchable surfactant, or to the extracellular enzymatic cleavage of by a bacterium.

In this context, we explore a model system where chemotactic motion can be controlled and altered reversibly, using biphasic emulsion droplets. Complex emulsions with a very-low internal interfacial tension are dynamically reconfigurable, which enable droplets with uniform components to reconfigure morphology based on their environment. We utilize these biphasic emulsions to demonstrate that for competing convective flows along the oil interfaces, the surface area of the exposed morphology can be used to define speed and direction. The direction of droplet movement is therefore not only defined by the magnitude of the interfacial tension gradient, but also the exposed area of either droplet phase, which can be shown or hidden. Chemical gradients generating competitive convective flows along these interfaces, modifying the droplet morphology can thus reverse its own directionality *in situ*. This responsivity and interactivity to the environment has broad implications for the design of adaptative soft robots which can, as with this example, reverse movement based on self-reconfiguration, adapting to its own environment.

Keywords: motile droplets, chemotaxis, adaptive soft matter, microswimmers

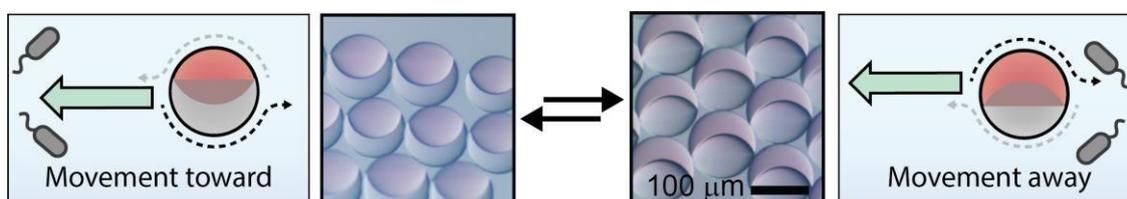


Figure 1. Morphological reconfiguration of complex emulsions enables reversible chemotactic direction.

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Development of Functional Materials Surfaces

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Superhydrophobic surfaces have attracted significant scientific interest due to their importance in both fundamental research and practical applications [1,2]. In this work, the development of a superhydrophobic and in certain cases water repellent surface is reported utilizing a simple, fast and economical way [3]. The material used was a smooth Ti6Al4V metal alloy that is widely utilized in several applications however its surface is considered hydrophilic. The surface of the material was initially irradiated by a femtosecond (fs) laser to acquire the necessary roughness. Following the irradiation, the effect of different parameters like temperature, pressure as well as residence time under heating or vacuum on the surface properties was investigated and the results were compared to the respective ones of a smooth surface. Contact angle and contact angle hysteresis measurements were performed to evaluate the wetting properties. The surface morphology was imaged by scanning electron microscopy (SEM) whereas the surface chemical composition was evaluated by energy dispersive X-Ray spectroscopy (EDS). A just-irradiated surface exhibits superhydrophilic behavior, nevertheless its residence in an oven at different temperatures results in the manifestation of a hydrophobic behavior especially for temperatures higher than 120°. A similar effect was observed in the case that an irradiated surface was placed in a vacuum chamber; after a minimum of 3 hours the surface was converted to a superhydrophobic one, which additionally possessed water repellent properties, exhibiting very high contact angle and very low contact angle hysteresis. The observed behavior can be understood if one considers the change in the surface morphology and surface chemical composition.

Keywords: superhydrophobic surfaces, water-repellence, surface roughness, water contact angle, laser irradiation.

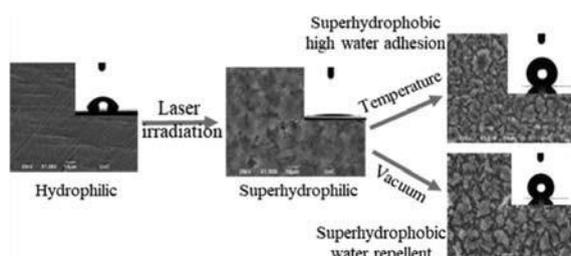


Figure 1: Schematic representation of the surface modification procedure and the respective results

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pH-Responsive Polyesters with Alkene and Carboxylic Acid Side Groups for Tissue Engineering Applications

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Main chain polyesters exhibiting excellent biodegradability and biocompatibility have been extensively studied as promising biomaterials for tissue engineering applications. However, conventional main chain polyesters lack specific functionalities, that may confer them additional physicochemical and biological properties. Herein, we present the synthesis of functional main chain polyesters bearing dual alkene/carboxylic acid pendant groups [1]. The presence of the carboxylic acid side-groups imparts pH-responsive properties to the polymers, while the polymerizable alkene pendant groups can be used to cross-link the polymer chains.

The synthesis of the pH-responsive polyesters involved the polycondensation of a vinyl functionalized diol with a diacid chloride, followed by a photo-induced thiol-ene click reaction to attach carboxylic acid side-groups along the polymer chains. Two mercaptocarboxylic acids were employed to investigate the influence of the alkyl chain length of the side groups on the physicochemical and biological properties of the polyesters. The carboxylic acid content of the polymers was adjusted to 50, 80, and 100 mol% by varying the irradiation time during the thiol-ene click reaction. The chemical structure of the polyesters was characterized by ¹H NMR and FTIR spectroscopies, while their thermal properties were investigated by TGA and DSC. The synthesized polyesters exhibited a pH-responsive behavior and pH-tunable solubility in aqueous media, attributed to the ionization of the carboxylic acid moieties.

To evaluate the cytocompatibility of the functional polyesters, cross-linked polymer films were prepared on glass slides by chemically linking the alkene side groups of the polymer chains using 2,2-dimethoxy-2-phenylacetophenone as the photo-initiator. The biocompatibility of the polyester films was evaluated using L929 fibroblast cell cultures, which showed that the cell viability and proliferation were promoted on the polymer surface bearing the shorter alkyl chain length side-groups and the higher content of carboxylic acid functionalities.

Keywords: aliphatic polyesters, responsive materials, biodegradable polymers, pH-sensitive polymers, smart polymers

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Mechanical Properties of Microgels in Dense Monolayers

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Microgels are crosslinked polymer networks that can swell in a good solvent. They can adapt their size and internal structure in response to external stimuli such as temperature, pH or ionic strength. They are highly surface active and, due to their soft and inhomogeneous structure, exhibit a rich phase behavior. Based on their interfacial properties, they can be used for applications such as, e.g., emulsion stabilization and surface coatings. However, the internal structure of microgels at interfaces is still not very well understood.

In this study, we used force spectroscopy [1] to investigate the internal structure of microgels in dense monolayers. Ordered microgel monolayers were prepared using a Langmuir-Blodgett trough [2] and investigated *ex-situ* by atomic force microscopy. The experiments resulted in data on (a) the internal structure of the microgels in the dense monolayers as well as (b) on the two-dimensional monolayer structure at the solid-liquid interface.

The results of the measurements show that the internal structure of the microgels is dependent on the monolayer. The confinement of the microgels in the monolayer leads to an increase in the polymer density in the core of the microgel with increasing compression of the monolayer.

Keywords: microgels, responsive colloids, atomic force microscopy, force spectroscopy, interfaces

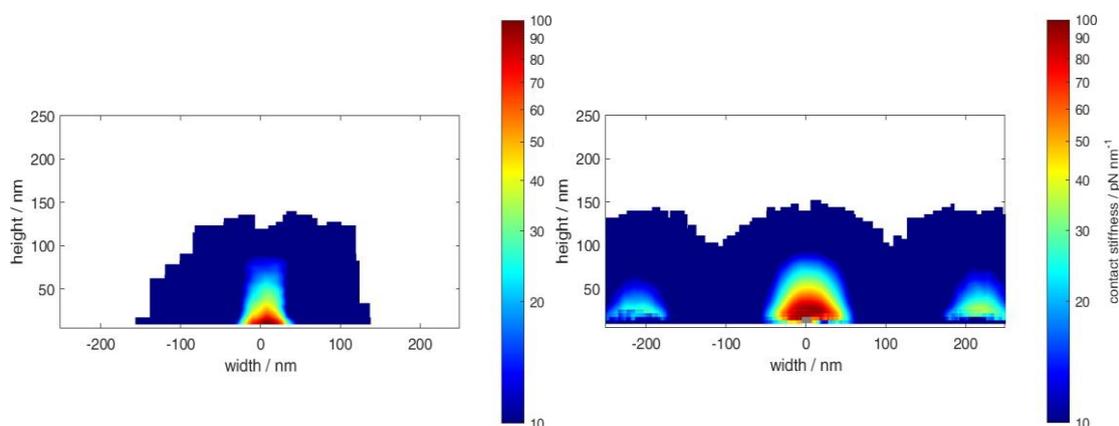


Figure 1. Averaged contact stiffness profiles of single microgels (left) and microgels in dense monolayers (right) at 27°C at the solid-water interface.

Acknowledgements: The authors gratefully acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG) within the Sonderforschungsbereich SFB 985 „Functional Microgels and Microgel Systems“ (Project B8).

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Torus, helical and circular trajectories generated by hydrodynamically coupled microswimmers

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Active matter is a substance that consumes energy from its surroundings and uses it for self-propulsion. The motion of microswimmers, flocking of birds, and swarming of fishes are examples of active matter. We study the collective motion of multiple hydrodynamically coupled microswimmers in the presence and absence of Marangoni flow. Surfactant secreting bacteria such as *Flavobacteria*, *Bacillus subtilis*, and *Pseudomonas aeruginosa* present on the seawater surface generate Marangoni flow. We observed that when a pair of two identical pushers are facing each other in a plane, in the absence of Marangoni flow, they travel along either type 1 or type 2 circular trajectories based on the Stokes dipolar strength, such that in type 1, both the microswimmers travel along the same circular trajectory with constant relative orientation angle 180° . In type 2, both the microswimmers travel along two different concentric circular trajectories. Pushers lose their stability after making certain revolutions along type 1 orbit and jump to type 2 orbit. After making certain revolutions along type 2 orbit, pushers lose their stability and run away from each other. We found that the Marangoni flow helps these microswimmers to travel along a stable circular trajectory even after the perturbation in 2D [1].

We also study the hydrodynamic coupling of a pair of non-identical pushers or pullers [2]. A stable 2D torus trajectory is observed for a pair of two-non identical pullers. We found that a pair of non-identical pushers or pullers form a co-planar rotational equilibrium (periodic or quasi-periodic) stable with respect to 2D perturbation. In the case of a collective motion of four pushers, we found that each pair of pushers travel along a helical structure.

Keywords: Marangoni flow, microswimmers, hydrodynamics

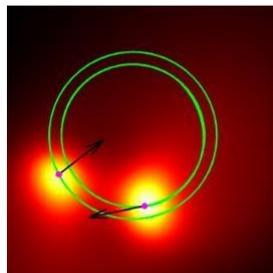


Figure 1. Type 2 trajectory generated by a pair of surfactant releasing pushers

Acknowledgements: All Soft and Active Fluids Lab members at IIT Madras.

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Physicochemical evaluation of genistein-loaded biomimetic lipid nanosystems

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Genistein is an isoflavone that belongs to phytoestrogens. Due to its anti-inflammatory and anti-oxidant activity, genistein is a promising therapeutic molecule for the treatment of many pathological conditions. Among other roles, genistein has a neuroprotective effect by down-regulating TLR4 and NK- κ B expression and reducing amyloid- β deposition and hyperphosphorylated tau filaments in the cortex and hippocampus [1,2]. However, pharmacological use of genistein has been limited by its poor solubility, bioavailability, unfavorable biodistribution and fast transformation to less active metabolites [2]. The aim of the present study was to develop biomimetic liposomal colloidal dispersions as genistein delivery systems. For this purpose, biocompatible lipids and biomaterials that are found in cell membrane such as phospholipids, sphingolipids, cholesterol and serine in different molar ratios were used. A variety of %genistein molar ratios (5-20% m.r.) were included for the loaded liposomes. The liposomal dispersions were prepared by the thin-film hydration method and probe sonication or extrusion techniques. The hydrodynamic diameter and ζ -potential of empty and loaded liposomal formulations were evaluated by dynamic and electrophoretic light scattering techniques (DLS/ELS). The cooperativity of the biomaterials was evaluated by thermal analysis of the hydrated bilayers via differential scanning calorimetry (DSC) technique. Furthermore, the encapsulation efficiency (EE%) and release studies at physiological pH values (7.4) of genistein were measured by UV-Vis spectroscopy. All the dispersions had a diameter lower than 100 nm, indicating the possibility to pass through the blood-brain barrier, while low polydispersity was measured. The above were in accordance with the thermal analysis results, proving high cooperativity of the biomaterials. The %EE showed the optimized ratio of the incorporated genistein while release studies prove the in-vitro effectiveness of the proposed liposomal delivery systems. In conclusion, the proposed biomimetic lipid nanosystems can be considered attractive genistein delivery platforms.

Keywords: Genistein, liposome, physicochemical evaluation, encapsulation efficiency, drug delivery system.

Acknowledgements: We thank Hellenic Colloid and Interface Society for the financial support.

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Development of bile salt-origin vesicles for the encapsulation of poorly soluble sea-buckthorn pulp oil

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Sea-buckthorn (*Hippophaë rhamnoides L.*) pulp oil, a nutritional oil product, has been widely used in the food, cosmetic, and medical industries due to its rich chemical composition (including fatty acids, carotenoids, flavonoids, phytosterols, or tocopherols,) and numerous health-promoting benefits, such as anticancer, antimicrobial, anti-aging, and anti-inflammatory properties [1]. Despite its many advantages, poor water solubility, susceptibility to oxidation, and low bioavailability limit its applicability, so colloidal carriers are emerging as a fundamental strategy for providing them with chemical protection and increasing their physical stability [2].

The scope of this study was the encapsulation process of sea-buckthorn pulp oil (SBPO) in a bile salt-based system and the evaluation of their physicochemical properties. The prepared dry lipid film with an amphiphilic Pluronic family triblock copolymer (P-123) containing blocks of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) was used to obtain the vesicles. In the next step, it was hydrated in an aqueous medium by entropy-promoting self-assembly of the amphiphiles into bilosomal formulation containing SBPO. The effects of different concentrations of incorporated oil on the characteristics of the resulting vesicular structures were analyzed, including particle size (dynamic light scattering), surface charge (electrophoretic light scattering), morphology (transmission electron microscopy/atomic force microscopy), and kinetic stability (multiple light scattering). To confirm the encapsulation efficiency and gain further insight into the analysis of bilosome-oil interactions, we performed an experimental study by attenuated total reflection-Fourier transform infrared spectroscopy. Our results indicated that due to hydrogen bonds with the phospholipids polar group and the hydrophobic interactions of sea buckthorn pulp oil with the acyl chains of phospholipids, efficient incorporation of the compound into the bilosomal membrane is possible. In conclusion, we described a straightforward and reliable approach to preparing highly stable bilosome-oil systems with nanoscopic sizes (< 120 nm) for versatile cosmetics and food applications.

Keywords: self-assembly, biosurfactants, colloidal system, kinetic stability

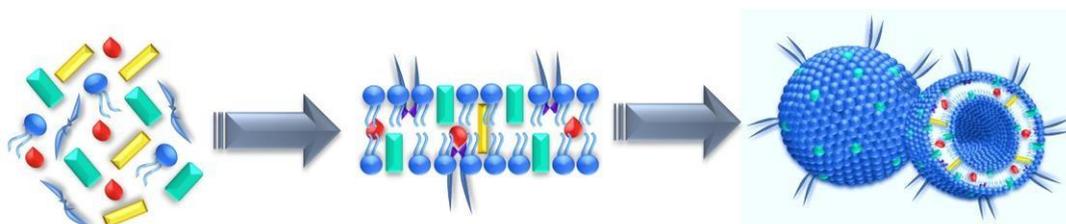


Figure 1. Schematic representation illustrating the bilosome-SBPO formation via the self-assembly process.

Acknowledgements: The support by the Department of Physical and Quantum Chemistry and Faculty of Chemistry at Wrocław University of Science and Technology is gratefully acknowledged.

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Spatial velocity order in systems of self-propelled disks

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Active Brownian particles play a fundamental role in modeling experimental self-propelled disks that undergo phase-separations [1], and many phenomena typical of active colloids [2]. We report the first evidence that pure repulsive active Brownian disks, without alignment inter-actions, spontaneously form large domains of particles with aligned velocities [3], both in dense homogeneous (Fig.1(a)-(b)) and phase-separated regimes (Fig.1(e)-(g)). The size of the velocity domains is measured through the correlation length, R , of the spatial velocity correlations, and increases with both packing fraction and persistence time, as shown in Fig.1(c). This dynamical information is included in a non-equilibrium phase diagram, packing fraction vs persistence time (Fig.1(d)), where the structural properties of the system (distinguishing active liquid, hexatic and solid phases) are superimposed with the velocity correlation lengths. The absence of translational and/or orientational orders plays a crucial role and reveals an interesting scenario involving intermittency phenomena in the time-trajectory of the kinetic energy.

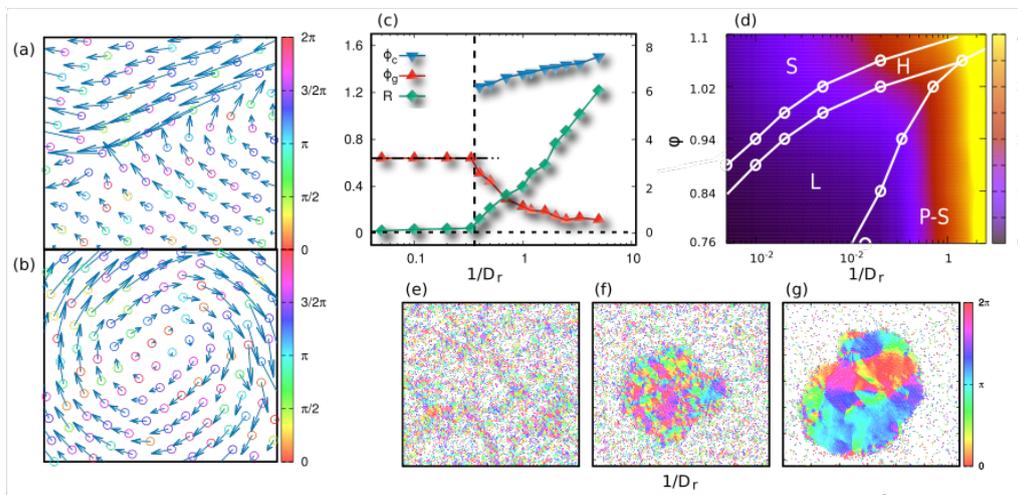


Fig. 1: Spontaneous velocity alignment. (a)-(b): Typical particle configurations where the blue arrows represent the velocities and the colors of the disks encode the orientations of the self-propulsion. (c): packing fraction, ϕ , (inside and outside the cluster) and correlation length, R , of the spatial velocity correlation, as a function τ . (d): phase-diagram showing liquid (L), hexatic (H), solid (S) and phase-separated (P-H) regimes superimposed with R (colors). (e)-(g): configurations obtained varying the persistence time where colors encode the orientations of the velocities.

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Viscoelastic patchy particle architectures as models for living matter

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Structural architectures in living cells, such as the cytoskeleton in muscle or plant tissue, are both viscoelastic and active, i.e. undergo continuous injection of energy, leading to remarkable collective non-equilibrium properties. The simulation of active systems is relatively straight forward, but the thermodynamics, kinetics and statistical mechanics of such systems are far from understood. Understanding such phenomena remains one of the grand challenges of modern statistical physics. We use patchy particles as a model system for exploring complex architectures that exhibit viscoelastic properties [1]. Patchy particles are micron-sized colloidal particles dressed with hydrophobic patches that are able to form controllable directed bonds using critical Casimir interactions [2]. Their size makes them directly observable with e.g. confocal microscopy, while having similar statistics as atoms and molecules. Their ability to make directed bonds enables self-assembled molecular or bio-inspired network-like structures [3,4]. Next, we push these self-assembled patchy particle architectures out-of-equilibrium by active Brownian particles and investigating their response. For small chainlike structures, we show that activity leads to enhanced breakage, i.e. that the time scales and the mechanisms involved are very different from equilibrium, and depends strongly on the orientation of the active force. Finally, we increase the complexity of the structures to networks and investigate the collective viscoelastic responses and structural properties affected by the active forces. Our findings clearly show how self-assembled patchy particle structures can act as a model system to study viscoelastic out-of-equilibrium materials with properties akin to living matter.

Keywords: out-of-equilibrium viscoelasticity, patchy particles, simulation

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Adhesive properties of silk-mussel foot coacervates

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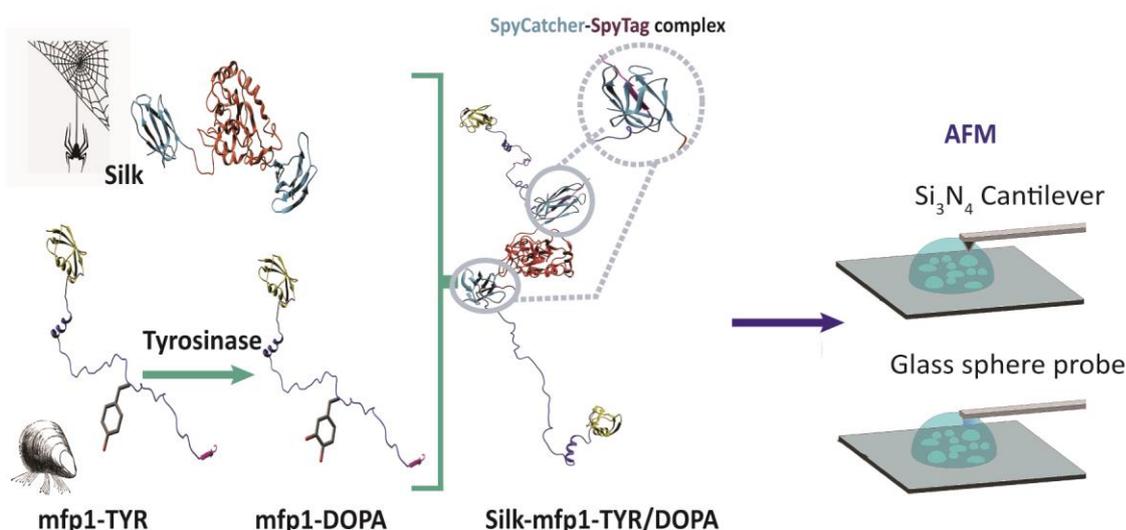
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Coacervates have been found in several biological processes and play an essential role in developing biomimetic materials. For instance, mussel-foot protein properties have been studied due to possible bio-application as an underwater adhesive [1-2]. In this research, we assemble silk-like protein and a mussel foot-inspired protein to form Silk-mussel foot coacervates (silk-mfp1). Then, their adhesive properties with different content of DOPA and Tyrosine were evaluated by an atomic force microscope (AFM). The coacervates' biophysical and adhesive properties change over time; therefore, the adhesion measurements were done using recently prepared coacervates and overnight coacervates. Thus, an increase in DOPA coacervates stiffness is observed over time.

Moreover, the adhesion characterization depends on surface contact geometry, coacervate elasticity, and protein network structure. Hence, DOPA coacervates produced a stronger adhesion than tyrosine coacervates, and the recently prepared coacervates' adhesion showed a higher dependence on DOPA content. In contrast, the intertwining of viscosity, interfacial tension, and stiffness properties plays a major role in the overnight coacervates adhesion. These findings show that the presence of DOPA is not a sufficient condition to generate an optimal underwater adhesion.

Keywords: Silk-mfp1 coacervates, adhesion, DOPA, tyrosine, viscosity, stiffness.

Strategy for assembling silk-mfp1-TYR/DOPA protein



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Water-in-water emulsions in presence of ssDNA, as synthetic models of membraneless organelles

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Water-in-water (W/W) emulsions are colloidal dispersions of one aqueous solution in another aqueous solution, forming liquid droplets in the absence of oil and surfactant [1]. W/W emulsions can be formed in biphasic aqueous systems, commonly denoted as Aqueous Two-Phase Systems (ATPS), which can be observed in mixtures of two water-soluble polymers. Thus, W/W emulsions are fully aqueous liquid dispersions that can be prepared using the thermodynamic incompatibility between two hydrophilic solutes [2].

W/W emulsions are present in cells, as globules floating inside the cytoplasm or cell nucleus. These cellular globules, called membraneless organelles (MLOs), appear due to liquid-liquid phase separation within the cells. MLOs are rich in proteins, often incorporate single-stranded DNA or RNA, and are cellular compartments where specific cellular functions take place.

We have studied the phase behavior of simplified MLO models, mixing fish gelatin or BSA (proteins) with dextran (a polysaccharide) in the presence of single-stranded DNA. The two proteins are immiscible with dextran and consequently W/W emulsions can be formed when concentrations are above the binodal line. The addition of ssDNA to selected dextran-in-gelatin emulsions resulted in phase reversal to gelatin-in-dextran emulsions, demonstrating that ssDNA promotes the formation of gelatin droplets. In the case of aqueous mixtures of BSA and dextran, ssDNA forms coacervate particles, which can coexist with dextran-in-BSA emulsion droplets (phase diagram shown in Fig. 1). Multiple emulsions can be obtained in both systems, with a morphology similar to cellular membraneless organelles. These systems could be used as synthetic models of MLOs.

Keywords: Water-in-water emulsions, ssDNA, multiple emulsions

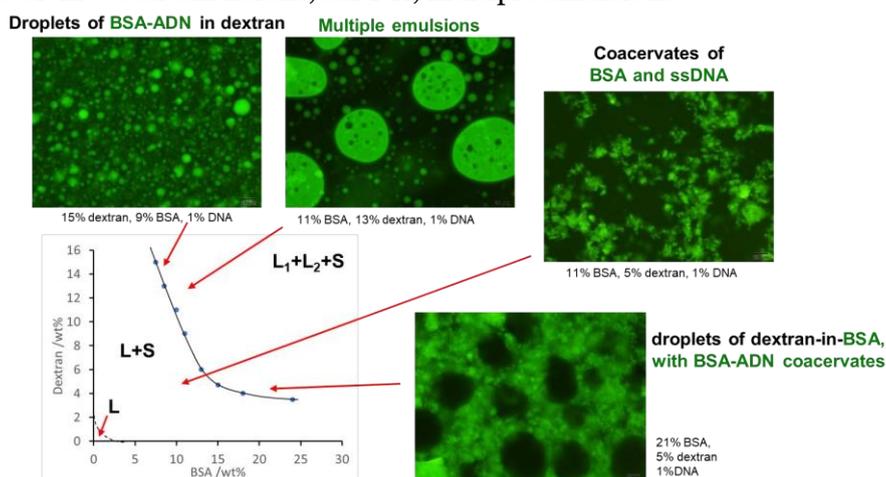


Figure 1. Phase diagram of BSA-dextran aqueous mixtures, in presence of 1 wt% ssDNA

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Extracellular polysaccharides: the origin of their distinctive physicochemical properties.

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Extracellular polysaccharides are widely produced by bacteria, yeasts, and algae. These polymers are involved in several biological functions, such as bacteria adhesion to surface and biofilm formation, ion sequestering, protection from desiccation, and cryoprotection. The chemical characterization of these polymers is the starting point for obtaining relationships between their structures and their various functions. While this fundamental correlation is well reported and studied for proteins, for polysaccharides, this relationship is less intuitive. In this report, the mannan exopolysaccharide from the permafrost isolated bacterium *Psychrobacter arcticus* strain 273-4 and the capsular polysaccharide from both cells and extra extracellular membrane vesicles (EMVs) from *S. vesiculosa* (Gram-negative bacterium) will be considered. In relation to chemical structure, conformation, and self-assembly properties of polysaccharides, some of the distinctive features of the macromolecules are discussed. The mannan exopolysaccharide from the permafrost isolated bacterium *Psychrobacter arcticus* show activity in inhibiting ice recrystallisation that is likely related to a local helical conformation the macromolecule adopts and to its self-aggregation properties. [1] The ability of capsular polysaccharides from cells or EMVs to adhere to synthetic and vesicles formed by a double layer mimicking the bacterial membrane, including lipopolysaccharides, to form a 'corona' that could be involved in the mechanism of biofilm formation are addressed.[2] Finally, the difference and common features of those polysaccharides in relation to their distinctive properties are discussed.

Keywords: Extracellular polysaccharides, extracellular membrane vesicles, inhibiting ice recrystallisation, adhesiveness.

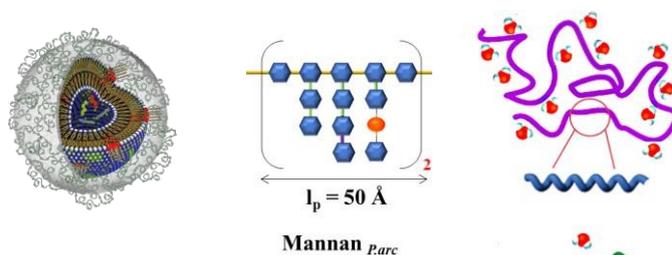


Figure 1. Extracellular polysaccharides: EMVs and mannan exopolysaccharide from the permafrost bacterium *Psychrobacter arcticus*.

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Mussel-Inspired Sticky Surfactants and Polymers for Robust Boundary Layers

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The reduction of greenhouse gas emissions to help slow global warming is one of the most pressing challenges of the 21st century. Transportation consumes 27% of global energy and a staggering 33% of this is consumed to overcome friction.¹ The reduction of friction is therefore a valuable target for reducing global CO₂ emissions, as well as contributing to product longevity.

While the coefficient of friction μ can be reduced by lowering lubricant oil viscosity, this results in more frequent operation in the boundary regime of lubrication, in turn resulting in unwanted asperity contact, wear, and friction. To circumvent this, boundary lubricant additives have been developed which form a robust, lubricating surface coating. These additives take inspiration from nature, mimicking the architecture of mussel foot proteins (mfps) and their extraordinary adhesive capabilities under challenging conditions. This mimicry involves incorporation of the catechol group (1,2-dihydroxybenzene) in the surfactant headgroup, capable of forming hydrogen bonds and complexes with varying surfaces as well as participate in $\pi - \pi$ interactions.²

In this project, five novel catechol-containing polymers and four novel catechol-containing surfactants (**Fig. 1 (right)**) with varying architectures, functional groups and tail lengths are investigated to understand their behaviour at interfaces, in bulk, and under high pressure and temperature conditions. This is to assess their suitability and efficacy as boundary lubricants and inform the design of future industrial additives. X-ray reflectivity (**Fig. 1 (left)**), high-pressure small-angle X-ray scattering (HP-SAXS) and surface force apparatus³ measurements have been carried out to provide complementary information on the self-assembled structure in the bulk solution at the interfaces. The unprecedented results on these molecular surfactants and polymers demonstrate, for the first time, the potential of such biomimetic molecules forming robust boundary layers in nonpolar media.

Keywords: Lubrication, bioinspired, self-assembly, tribology, surfactants, polymers

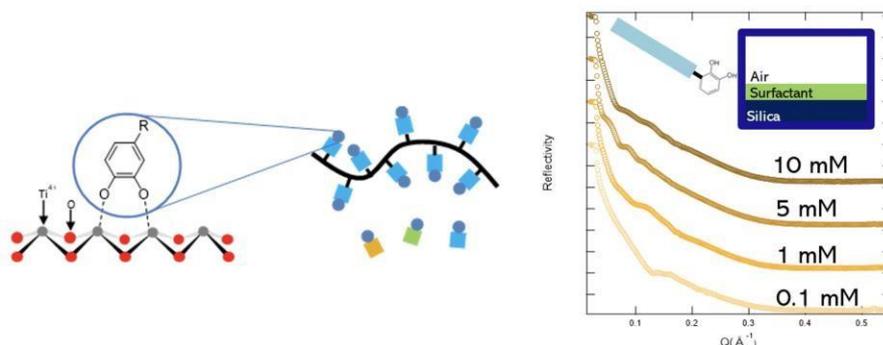


Figure 1. (Left) proposed binding mechanism of catechol to TiO₂ surface (adapted from [2]). (Centre) Representation of catechol containing polymer and surfactants with catechol headgroups. (Right) X-ray reflectivity measurements carried out on catechol-containing surfactant

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A cryo-TEM study of the complexation of DOTAP liposomes with different polyelectrolytes

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Self-assembly is a key process in forming biological materials. Especially the interaction between amphiphiles and polyelectrolytes has been widely investigated in recent years due to their potential application in industry and medicine, with a special focus on gene therapy.

Accordingly, we investigated the formation of lipoplexes by mixing liposomes with selected polyelectrolytes (PE). The cationic lipid DOTAP (1,2-dioleoyl-3-trimethylammonium-propane (chloride salt)) was mixed with different anionic polyelectrolytes, such as NaPA (sodium polyacrylate), CMC (sodium carboxymethyl cellulose) with different degrees of substitution (DS, namely, different charge density) and DNA (deoxyribonucleic acid sodium salt). The goal of this project was to explore the influence of different system parameters, such as the charge ratio $CR = [-]/[+] = [PE]/[DOTAP]$, the charge density of the PE or the type of PE on the morphology of the formed complexes. In additional experiments, the protein BSA (bovine serum albumin, a key blood plasma protein) was added to the lipoplexes to simulate actual transfection processes and gain information about transfection related morphology changes. The investigation of these systems was performed by cryo-transmission electron microscopy (cryo-TEM), and with small-angle X-ray (SAXS) measurements, to support our findings.

In our experiments we obtained a comprehensive picture of the formed lipoplexes, and how their structure depends on the different properties of the employed polyelectrolyte (Figure 1). Although the basic nanostructure of the complexes is usually lamellar (with some hexagonal exceptions), their detailed morphology depends strongly on parameters like the persistence length, charge density, or polymer backbone diameter. Upon addition of BSA, drastic morphology changes occur that may inhibit successful transfection. Understanding these specific interactions will allow the formation of more stable and optimized complexes as they are needed for optimized delivery.

Keywords: lipoplexes, polyelectrolytes, cryo-TEM, transfection

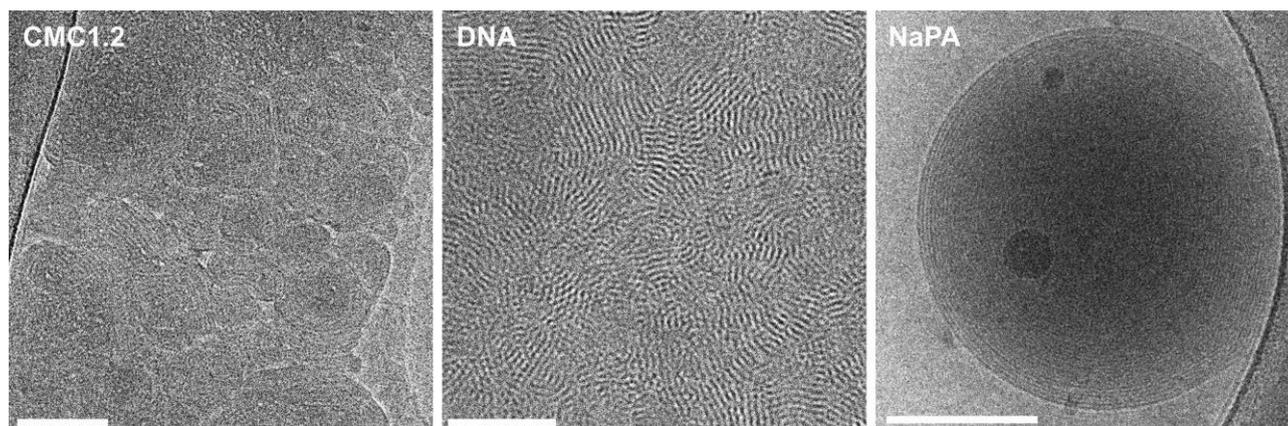


Figure 1. Cryo-TEM images of 1 mM DOTAP mixed with different polyelectrolytes. Left: CMC1.2, middle: DNA, and right: NaPA; all at $CR=2$. All samples form multilayered complexes, but the overall size of the complexes, as well as the order and the spacing of the multilayers depend on the polyelectrolyte. Scale bars are 100 nm.

Mucus-inspired self-regenerating microgel coatings

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Mucus is a viscous, self-regenerating, aqueous secretion of the mucosa membrane, protecting organs from damage by dehydration, abrasion or pathogen invasion. Mucins, which mainly determine mucus structure, are glycosylated proteins, enabling them to form gel-like structures. The polysaccharide chains not only provide the high capacity for water uptake, but also protect the proteins from enzymatic or chemical degradation and serve as recognition sites for selective binding. Inspired by mucus structure, we want to exploit this principle for the fabrication of a self-regenerating coating based on microgels. This coating should increase the durability of artificial biomaterials such as implants as well as their resemblance to natural structures. Microgels are soft, crosslinked, highly swollen polymer networks, which are particularly useful for the uptake of guest molecules and have been previously used for enzyme immobilization. We demonstrate that hyaluronan synthase from *Pasteurella multocida* (*PmHAS*) can be immobilized onto nitrilotriacetic acid (NTA) functionalized microgels by mutual complexation of Ni^{2+} ions. The immobilized enzyme is able to generate hyaluronic acid *in situ*. This way, a protective, self-regenerating polysaccharide layer will be formed covering the microgels. We fabricated a library of Poly(N-vinylcaprolactam) microgels with varying NTA content. *PmHAS* was then bound to these microgels *via* an incorporated polyhistidine-tag, enabling the formation of an enzyme-NTA complex. Interestingly, the activity of *PmHAS*, observed by capillary electrophoresis analysis, showed a decrease with increasing NTA and thus Ni^{2+} content. As *PmHAS* is strongly dependent on the concentration and nature of ions within solution, this leads to the assumption that Ni^{2+} has a disrupting influence on the enzyme activity, so that the influence of other ions onto *PmHAS* will be further investigated. Our final, optimized product will then be used as a coating for artificial biomaterials, increasing their durability and biocompatibility.

Keywords: Self-regeneration, Microgels, Polysaccharides, Biomaterials

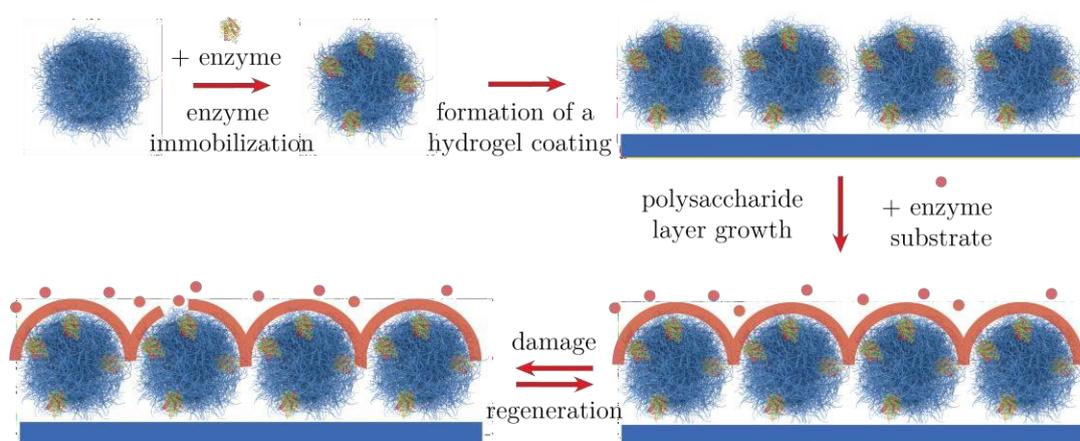


Figure 1. Scientific Goal: A mucus-inspired self-regenerating microgel coating.

Structure and dynamics of bioinspired complex mixtures: a sustainable approach to green formulation chemistry

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The well-established circular model of social growth drives chemical industry to minimize wastage and maximize reuse, recycle and remanufacturing (3R). Formulation chemists have focused on the re-design of current products in an ecological and bioinspired perspectives. However, the simple replacement of polluting chemicals by more biodegradable ones is not enough. The whole formulation process has to be re-drawn on the basis of compatibility and sustainability criteria.

Nature offers a guiding line for a new concept of formulation eco-design [1,2]. Indeed, during evolution all living organisms have set up intra- and/or extra-cellular complex fluids. The physico-chemical analysis of these fluids in terms of the key concept typical of formulation technology as well as in colloid science reveals unexpected analogies between biological and industrial fluids, showing which are the solutions nature has optimized to solve each functional problem.

Bacteria regulate the properties of the extracellular matrix by releasing finely engineered (macro)molecules. From a physico-chemical viewpoint, exopolysaccharides (EPS) are biopolymers acting as rheology modifiers, optimized to work in specific conditions. Diffusion and micro-rheology measurements show that the conformation of the EPS produced by *Zymomonas mobilis*, an ethanologenic Gram negative bacterium, unlike other polymers, is almost unperturbed in the presence of ethanol [3]. For this reason, it is a perfect component of virucidal and bactericidal ethanol-rich formulations.

At the same time, bacterial biosurfactants effectively replace synthetic surfactants. As an example, rhamnolipids produced by *Pseudomonas aeruginosa* can be considered, from a physicochemical viewpoint, as di-chained surfactants able to dramatically lower the medium surface tension and to form large micellar aggregates. Being produced by organisms adapted to live in harsh environments, biosurfactants are less sensitive to changes of the solution conditions. Indeed, we found that they are able to micellize at extremely high content of bio-ethanol and bio-glycerol, naturally occurring co-solvents, playing a variety of roles in complex surfactant mixtures. A deep and large physico-chemical characterization of these bio-inspired formulations, based on surface tension, calorimetry and DLS, as well as on electron spin resonance and spectrofluorescence (using appropriate spin-probes) indicates that biosurfactants and EPS act synergistically allowing to finely tune the mixture structural and rheological properties.

Overall, our results demonstrate that complex fluids naturally occurring in biological systems can be profitably used as models of new-generation bioinspired formulations [4].

Keywords: bioinspired formulations, green chemistry, biosurfactant, rhamnolipid, bioethanol, bioglycerol

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Beyond classic phoresis: new insights into self-phoresis

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The notion of chemophoresis describes the displacement of a particle in a fluid due to an externally imposed gradient in chemical composition, *and in the absence of a net external force and torque*: therefore, the particle's momentum is balanced by the momentum of the flow in the ambient fluid, and the particle is not dragged, but instead it *swims*. The phenomenon of classic phoresis can be understood in the context of linear-response theory: the phoretic velocity \mathbf{V} of the particle in a fluid solution can be obtained as

$$\mathbf{V} = L_{\text{lin}} (\nabla n)_{\text{ext}} ,$$

for a sufficiently small gradient $(\nabla n)_{\text{ext}}$ in solute concentration over the scale of the particle size, in terms of the phoretic coefficient L_{lin} given by a Green–Kubo expression.

A closely related phenomenology is observed for self-phoretic particles, which have attracted much attention in the last years as physical realization of artificial swimmers. In this case, the particle's surface is catalytically active, so that it induces a composition gradient $(\nabla n)_{\text{act}}$. The experimental observations involving self-phoretic particles are then customarily addressed as another instance of classic phoresis but in a self-generated gradient,

$$\mathbf{V} = L_{\text{lin}} (\nabla n)_{\text{act}} .$$

However, an additional role of the particle's chemical activity has been recently identified [1,2], namely, as responsible for a specific *activity-induced response*, so that one has to write

$$\mathbf{V} = (L_{\text{lin}} + L_{\text{act}}) [(\nabla n)_{\text{ext}} + (\nabla n)_{\text{act}}]$$

in the more general scenario, where L_{act} is the activity-induced contribution to the phoretic coefficient. We will describe the theoretical framework behind this result and possible observational consequences. In particular, we argue that the piece L_{act} of the response could actually be as large as L_{lin} in realistic configurations: this would mean a change in paradigm as it disproves the claim that “self-phoresis is phoresis in a self-induced gradient”.

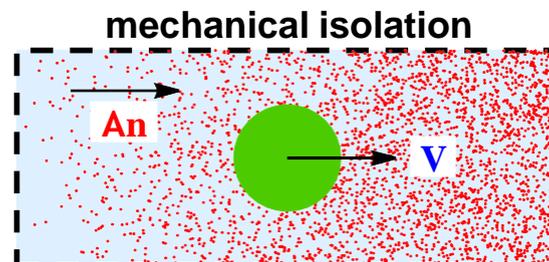


Figure 1: Chemophoresis: a particle is drifted by a concentration gradient while in the absence of an external force.

Keywords: phoresis, swimmers, Stokes flow

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Modular, Multifunctional Microswimmers from Toposelective Nanoparticle Attachment

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Microswimmers are artificial micron and nano-scale objects that can convert energy sources such as light or chemicals into directed motion, much like motile microorganisms. This autonomous motion can transport matter at the microscale and even induce the mixing and pumping of fluids without external agitation. As a result, artificial microswimmers (or active colloids) offer tantalizing opportunities for performing autonomous tasks at small scales in applications ranging from targeted drug delivery to environmental remediation. However, fabricating them in a scalable fashion for specific purposes remains challenging.

Janus microswimmers are arguably the simplest class of active colloids, relying on surface patches with different physiochemical properties to self-propel in the presence of an external gradient. Here, we propose a modular synthesis combining the scalable Pickering-wax emulsion technique [1] with nanoparticle deposition to produce multifunctional Janus microswimmers. Functional nanoparticles are asymmetrically attached to wax embedded SiO₂ microparticles via a post-modified poly(pentafluorophenylacetate) (pPFPA) polymer bridge with appropriate chemical functionalities [2]. From this toposelective thin film attachment, we decorate the exposed portion of the SiO₂ microparticles with various nanoparticles to obtain large (~100 mg) batches of multi-responsive microswimmers. Supporting the nano-catalysts on microparticles also significantly enhances their processability, overcoming a key limitation to the application of nanoparticles.

The use of a post-modified pPFPA backbone presents the opportunity to exploit various coordination chemistries through the introduction of different functional groups. By thus connecting the extensive library of colloidal nanocatalysts with the nascent field of active matter, this versatile material platform lays the groundwork toward designer microswimmers which can swim by catalyzing a broad range of chemical reactions, with potential for future applications.

Keywords: Microswimmers, Active Matter, Nanoparticles, Pickering Emulsion, Multifunctional, Photocatalysis

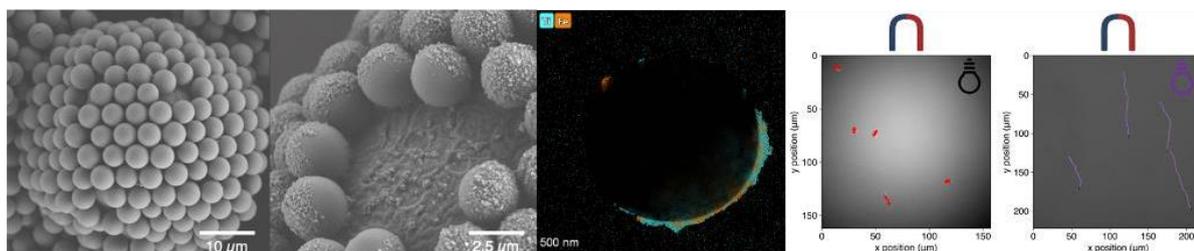


Figure 1. (Left to Right): SiO₂ – Wax colloidosome; Colloidosome after functionalization with TiO₂ P25 and pPFPA; EDX mapping of multifunctional TiO₂-Fe₂O₃ Janus microswimmer; Photo-responsiveness of TiO₂-Fe₂O₃ Janus microswimmer with magnetic control

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Understanding Enhanced Rotational Dynamics of Active Probes in Rod Suspensions

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Synthetic active particles (APs) have received considerable interest for biomedical applications and as model systems for non-equilibrium dynamics. However, because an AP's motion strongly depends on the properties of the surrounding liquid, it can additionally serve as a microrheological probe for the properties of the surrounding medium [1,2]. APs in Newtonian media have been studied in great detail, but much less is known when these particles move in complex fluids. Such a fluid's nonlinear rheological properties can lead to a drastically enhanced rotational diffusion (ERD) coefficient [1-3].

We study the motion of an AP in a polydisperse quasi-two-dimensional suspension of colloidal rods, see Fig. 1 for a simulation snapshot. Compared to previous studies [1,2], wherein we embedded APs in a spherical colloid suspension, the use of rods allows us to unlock a new mode of fast, local structural dynamics. This dynamics enabled a comprehensive understanding of the mechanism underlying ERD. Combining simulations and experiment, we conclude that minute microstructural fluctuations of rods in near contact with the AP, together with the probe's active motion, generate a fluctuating torque on the AP eventually leading to ERD. These fluctuations can be connected to a local stress relaxation, which may be used in the continuum formalism that was proposed [1,3,4] to capture ERD. Our work thus unifies the previously disjoint continuum and particle-based descriptions for this phenomenon. Beyond the rheological characterization abilities of APs, our findings are important to understand the dynamics of microorganisms in their natural (typically viscoelastic) habitat.

Keywords: active, self-propelled, viscoelastic, rheology

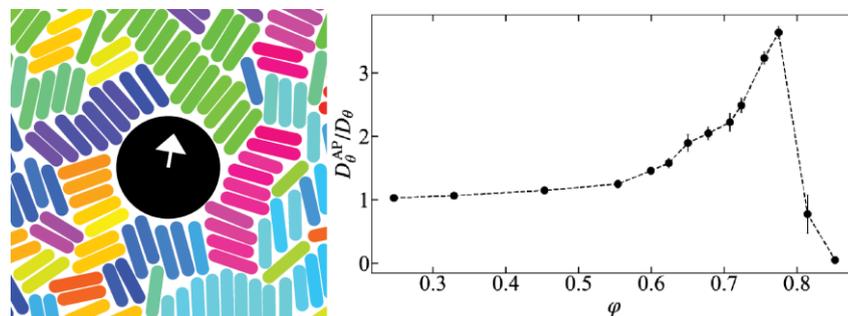


Figure 1. (left) Snapshot of an active probe in our simulation study. The colors indicate rod orientation. (right) The associated ERD as a function of rod area fraction.

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Connecting Microstructural Fluctuations and Enhanced Rotational Dynamics of Active Probes in Rod Suspensions

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Synthetic active particles (APs) typically exhibit motion that strongly depends on the properties of the surrounding liquid. They can therefore serve as a microrheological probes [1,2]. In certain non-complex fluids (colloidal glasses of bidisperse spheres [1,2] and of colloidal rods [3], and polymer suspensions [4,5]), activity causes the probes to show drastically enhanced rotational diffusion (ERD) with respect to their passive state. Previous studies connected this enhancement to a slow relaxation time of the surrounding fluid.

In this poster, we consider the motion of an AP in a polydisperse quasi-two-dimensional suspension of colloidal rods using experiment and simulation, see Fig. 1. The use of rods allowed us to unlock a new mode of fast, local structural dynamics, which helped us understand the microscopic origin of ERD. Rods form 'raft-like' structures that enable minute longitudinal rod displacements; these fluctuations are already present in the passive rod suspension itself. Activity causes the probe's orientational degree of freedom to couple the fluctuations, see sketch Fig. 1. This coupling together with structural heterogeneity leads to an enhancement of the probe's rotational diffusion. Our simulations further hint at a structural origin of maximal ERD and future work will focus on clarifying this relation in the rod suspension and other systems showing ERD of Aps.

Keywords: active, self-propelled, viscoelastic, rheology

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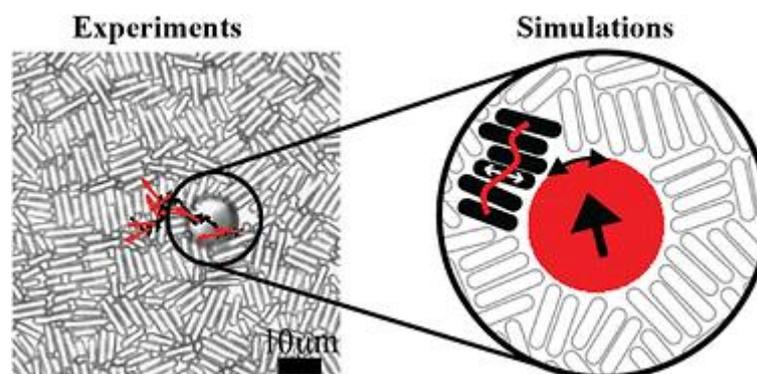


Figure 1. (left) Snapshot of an active probe in our experiments. Red arrows indicate the probe orientation, and the black curve traces out its motion. (right) Part of a simulation snapshot showing the fluctuation-based origin of ERD.

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Preparation of Natural Polyelectrolytes Complex Membranes through Sustainable Aqueous Phase Separation

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Membrane technology plays an important role in lots of fields, such as agriculture, industry, and medicine. Recently, an aqueous phase separation (APS) approach has been successfully developed to prepare synthetic polyelectrolytes complex membranes. This novel approach uses water as both solvent and non-solvent, which effectively eliminates the influence of harmful organic solvent in the traditional nonsolvent induced phase separation (NIPS) method.^[1-2]

In this work, the green APS approach was applied to natural polyelectrolytes to prepare more eco-friendly and sustainable polyelectrolytes complex membranes. Two natural polyelectrolytes, polycationic chitosan (CS) and polyanionic sodium carboxymethyl cellulose (CMC) were used. A homogenous casting solution was obtained at low pH (pH~1) where CMC was uncharged. Integral and stable CS-CMC membranes were obtained in an acetate buffer bath (pH~5). In the bath, CMC became negatively charged, and thus formed complexes with the positively charged CS, leading to the formation of membranes. Meanwhile, branched polyethylenimine (PEI) can be used as a crosslinker to improve the mechanical properties of the membranes. All the membranes showed asymmetric dense structure with low pure water permeability and high BSA retention, which were suitable for water treatment. This work demonstrated that APS is an alternative method to fabricate more sustainable polyelectrolytes complex membranes.

Keywords: natural polyelectrolytes, complex membranes, aqueous phase separation

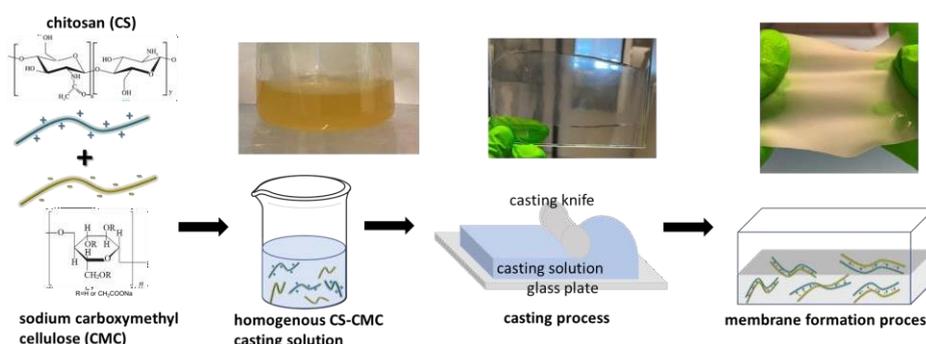


Figure 1. Illustration of the preparation process through aqueous phase separation (APS).

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Interaction of Saponins with Different Lipid Membranes

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Saponins are plant derived bio-surfactants which exhibit an amphiphilic structure built of a hydrophobic steroidal or triterpenic backbone with a varying number of hydrophilic sugar chains. These molecules are part of the plant defense against bacteria and fungi. Some saponins are soap-like and were used for washing. In addition, most saponins have very strong biological effects and are used in pharmacy. Examples are escin which regulates venous tension [1,2] and glycyrrhizin which has strong antiviral activity and is supposed to act e.g. against SARS-COV2. Saponins often strongly interact with lipid membranes and some are even haemolytic. However, the physico-chemical details of the interaction of saponins with biological membranes are still partly unclear and each saponin seems to have different effects at least quantitatively. Therefore, in this contribution the effect of the pure saponins escin [2] and glycyrrhizin on small unilamellar vesicles of DMPC, prepared by extrusion, is investigated mainly by different scattering methods in dependence on the saponin-amount and the temperature [3]. As lipids we use 1,2-dioleoyl-sn-glycero-3-phosphoglycerol (DOPG) and 1,2-Dimyristoyl-sn-glycero-3-phosphocholine (DMPC) and vesicles made of these act as a model membrane in the present work. An incorporation of escin above a critical amount can be deduced from the investigated parameters, namely the thermal phase transition temperature and vesicle size parameters like the radius, membrane thickness and lipid head-to-head distance within one monolayer. At high escin amounts finally lipid nanodiscs (bicelles) are formed. Moreover, saponins can interact with other pharmacologically relevant compounds [4]. Also neutron spin-echo (NSE) results will be presented [5]. NSE reveals the influence of the saponin on the bending elasticity of the DMPC model membranes which depends on the phase state of the lipid.

Keywords: Saponins, SAXS, SANS

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mAb-surfactant stability and rheology at the air-water interface under controlled dilation and shear deformations.

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Monoclonal antibodies (mAbs) are important biotherapeutics to treat numerous human ailments, but the proteins have a natural tendency to aggregate in solution, which reduces drug formulation stability. One concerning source of instability for mAbs occurs at the air-water interface as mAbs are amphiphilic. In this work we study a well-defined NIST reference mAb (RM #8671, pI = 9.3, an IgG1 protein) with and without surfactant poloxamer P188 (Kolliphor®, Sigma-Aldrich) in histidine buffer, and with added electrolyte (NaCl), including competitive adsorption. Surface tension, neutron reflectometry, and interfacial shear rheology are used to characterize the adsorbed mAb interfacial layer with and without P188. Further, we study the effects of a controlled deformation history of the air-water interface using a novel interfacial rheometer (Quadrotrough (Rev. Sci. Inst. 2022, submitted) which enables both pure dilatation/compression and pure shear deformations at air-water interfaces. Using this technique, we first gain insight on isolated interfacial strain-induced behavior of NISTmAb at the air-water interface often attributed to aggregate formation in solution. Primary conclusions are made concerning the individual species and their competitive properties as follows: NISTmAb interface exhibits a strong gel-like network that adsorbs irreversibly as aggregated particles on the air-water interface. Dilatational strains cause interfacial aging as detected by surface pressure measurements, but do not show significant mesoscale differences under compression/expansion by Brewster angle microscopy. This observation suggests that the aging due to structural rearrangement or partial unfolding of mAbs at the interface. NISTmAb exhibits high shear elasticity but is not perturbed by shear straining the interface as detected by surface pressure measurements. Overall, NISTmAb forms a highly stable network at the air-water interface with no signs of unstable desorption under the imposed interfacial dilatational and shear strain conditions. P188 is a non-ionic surfactant used to stabilize protein formulations and forms an inviscid interface with negligible shear viscosity and low dilatational modulus due to its high solubility in aqueous solutions. This surfactant's ability to prevent NISTmAb from reaching the air-water interface depends on the order of addition. P188 is observed to competitively adsorb to the air-water interface and fully prevent NISTmAb adsorption as determined both by rheological and structural measurements. However, P188 only slowly displaces some of the pre-adsorbed NISTmAb at the air-water interface under quiescent state. Instead, it can co-adsorb to the air-water interface and fluidize the NISTmAb network. Dilatational straining is shown to primarily weaken the gel-like NISTmAb network into densified aggregates. Using the unique capabilities of the Quadrotrough, shear and dilation experiments combined with Brewster angle microscopy and neutron reflectivity measurements enable the development of structure-property relationships of protein-surfactant pairings to identify the origin of interfacial formulation instability and provide guidance in designing stabilized formulations through excipient addition.

Keywords: monoclonal antibodies, interfacial rheology, dilation, neutron reflectivity

Buckling and interfacial deformation of fluorescent poly(N-Isopropylacrylamide) microgel capsules

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Hollow microgels are fascinating model systems at the crossover between polymer vesicles, emulsions and colloids as they deform, interpenetrate and eventually shrink at higher volume fraction or when subjected to an external stress. Furthermore, their hollow architecture makes them ideal candidates as nanocarriers. Here, we introduce a new system consisting of micron-sized microgels with a large micron-sized cavity enabling a straightforward characterization *in situ* using fluorescence microscopy techniques. These capsules are found to reversibly buckle above a critical osmotic pressure, conversely to smaller hollow microgels, which were previously reported to deswell at high volume fraction. Simulations performed on monomer-resolved *in silico* microgel capsules confirm the buckling transition and that the presented capsules can be described with a thin shell model theory leading to a direct estimation of their elasticity. When brought to the air-water or oil-water interfaces, these microgel capsules strongly deform and we thus propose to utilize them to locally probe interfacial properties within a soft capsule model adapted from the JKR theory.

Keywords: hollow microgel, buckling, *in silico* synthesis, interface

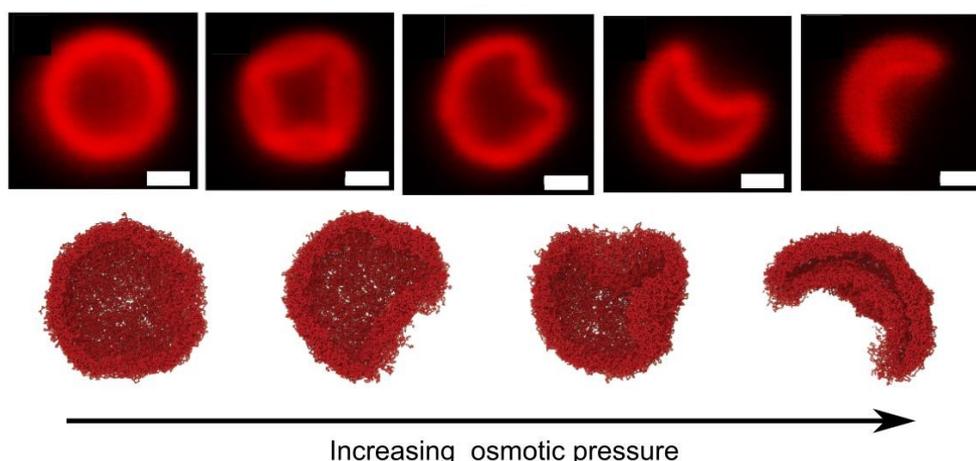


Figure 1. (Top) CLSM micrographs of the microgel capsules obtained from the maximum intensity projection of z-stack highlighting typical configurations observed upon increasing osmotic pressure by addition of PEG 8000. Scale bars: 500 nm. (Bottom) Simulation snapshots of the hollow microgel across the buckling transition.

Emulsion destruction with chemical additives: from characterization with bottle tests to modeling

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A very simple and inexpensive way to investigate coalescence occurring in concentrated emulsions is to perform bottle tests in which the kinetics of bottle samples of emulsions, left at rest under gravity settling are monitored. After a first regime which includes sedimentation (or creaming) of the droplets, a very dense and stable emulsion, known as the DPZ (densily packed emulsion layer) usually forms. By assuming that the destruction process in such systems results from stochastic coalescence events, we establish a simple theoretical model that predicts both the thickness of this DPZ as well as its lifetime as a function of the physical and physico-chemical parameters at play in this problem, namely the mean droplet diameter, the droplet volume fraction, the adsorption properties of the surfactant and the surfactant concentration [1]. Our predictions which are in very good agreement with experimental findings obtained on model W/O emulsion systems, show that the coalescence rate per unit area, W , can be very easily extracted from the value of the DPZ lifetime [2].

Using this methodology, we investigate the role of adding a water-soluble surfactant (Tween 20) that acts as a demulsifier on the stability of water-in-dodecane emulsions stabilized with Span 80. We study the influence of this demulsifier on the coalescence rate and present a simple kinetic model to account for W that we observe with the concentration of the demulsifier. Ultimately, our results prove that the efficiency of a demulsifier agent to break a W/O emulsion strongly correlates to its adsorption strength at the W/O interface, providing a novel contribution to the selection guidelines of chemical demulsifiers [3].

Keywords: emulsion-stability-coalescence

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Mimetic bacterial membranes challenged by multivalent cations and antimicrobial peptides: Nanostructural insights

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Lipopolysaccharides (LPS) is the main component of the Gram-negative bacteria outer membrane which can trigger lethal septic shocks when released into a host's bloodstream. Its anionic phosphorylated and carboxylated headgroup can be targeted by cations which affect the elastic properties and structural integrity of bacterial membranes, as well as altering the LPS virulence. In this project, the effects of multivalent cations and quadruply-charged peptide were studied to improve our fundamental understanding of their interactions with LPS membranes using several techniques, including Brewster angle microscopy, synchrotron X-ray and neutron scattering.

Brewster angle microscopy revealed closed tubular structure self-assembled from LPS-Ra (a variant) at the air-water interface. The addition of Ca^{2+} prompted the formation of densely packed monolayer at interface due to the cross-linking effects [1]. La^{3+} addition induced significant increase in the membrane elastic modulus and the rigidified LPS membrane broke into randomly shaped fragments with multilayer structure due to strong electrostatic interactions.

X-ray reflectivity (XRR) results of the LPS-Ra monolayer at the air-water interface gives further insights on molecular reorganization giving rise to the membrane thickness observed. The data fitting showed an increase in the scattering length density (SLD) profile of the LPS monolayer at the inner core region, attributed to cation binding. It also indicated the formation of a staggered layer in the presence of La^{3+} with the interpenetration between the LPS tails and the inner core. Small angle neutron scattering showed that highly charged peptides (+4 charges per peptide) increased the membrane hydration level and altered the aggregate structure by adsorbing at LPS-Ra liposome surface and subsequent penetration into the liposome membrane.

Such unprecedented results offer nanoscopic insights on the effects of highly charged molecular species on bacterial lipids and their self-assembled structure, with fundamental implications to rational design of novel physical approaches to disrupt bacterial membranes.

Keywords: Bacteria membrane, Structure integrity, Elastic property, Self-assembly

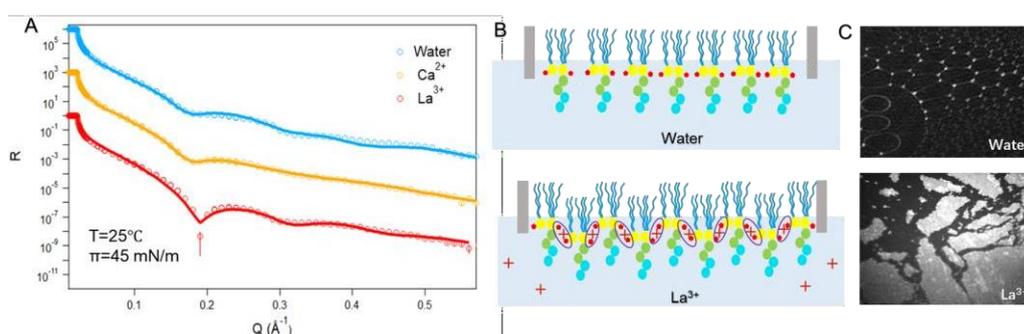


Figure 1. (A) XRR results of LPS monolayer at air water interface in the absence (blue) and presence of Ca^{2+} (yellow) and La^{3+} (red). (B) A schematic representation of LPS monolayers and (C) corresponding BAM results.

Acknowledgements: We acknowledge the Diamond light source and ISIS for the awarded beamtime and China scholarship Council for the funding.

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Microgravity Study of Emulsions Destabilisation by Diffusing Wave Spectroscopy within the EDDI Project

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Microgravity (weightlessness) conditions offers unique opportunities for the investigation of the mechanisms responsible for emulsion destabilisation, such as droplet coalescence and Ostwald ripening, decoupled from droplet creaming.

The international experiment EDDI (Emulsion Dynamics and Droplet Interface) aims at the investigation between the above mechanisms and the chemico-physical properties of the droplet interface within the emulsion. In addition to investigations under laboratory conditions, microgravity experiments are planned to characterise the overall emulsion destabilisation and the features and effects of the destabilisation mechanisms. These experiments are under way on board the International Space Station, using the ESA facility Soft Matter Dynamics (SMD) [1], to investigate a set of emulsion samples with volume concentrations ranging from 20 to 30% and stabilised by non-ionic (polyoxyethylenated alcohols) surfactants. SMD is an experimental apparatus conceived to investigate structural and dynamic properties in emulsions, foams and granular materials, using Diffusing Wave Spectroscopy (DWS): a powerful optical diagnostics based on the analysis of the intensity of laser light diffusing in a multiphase disperse system [2,3].

The concepts underlying the EDDI project are given here together with principles of the DWS diagnostics within the SMD facility. Result examples taken from the early analysis of the ongoing microgravity experiments are also presented.

Keywords: emulsions, coalescence, liquid-liquid interface, microgravity, DWS

Acknowledgements: European Space Agency (ESA) MAP project “Emulsion Dynamics and Droplet Interface - EDDI” (Contract n. 4000128643/19); National Aeronautics and Space Administration (NASA) project “Particle Stabilized Emulsions and Foams – PASTA (Grant 80NSSC21K2080).

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Antioxidant nanocarriers for stabilization of algae oil emulsions rich in omega-3 fatty acids

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In this study, whey protein isolate (WPI) and low methoxyl pectin (LMP) bioparticles carrying thymol, as potential natural antioxidant, were assembled through electrostatic interaction. These complexed particles were ultimately used for the stabilization of Pickering emulsions containing an oil from algal organisms (*Schizochytrium sp.*) rich in docosahexaenoic acid (DHA) which is highly susceptible to oxidation. Different ratios of WPI-LMP were used to form the nano-scale cargos for thymol. Our experiments showed that a ratio of 4:1 (WPI to LMP) at pH 5.0 was the lowest possible ratio to form a stable dispersion of thymol nanocarriers with a z-average particle diameter of around 250 nm. Fluorescence spectroscopy was performed to monitor the possible quenching of the tryptophan and tyrosine residues in WPI. The stabilized colloidal carriers by the complexes at different WPI-LMP ratios at pH 5.0 showed a homogeneous and opaque visual appearance with a droplet size ranging from 9 to 13 μm . On the other hand, the emulsions stabilized by WPI only carrying thymol showed a larger droplet size (33 μm) and a thick cream layer with severe phase separation. The morphology of the emulsions was characterized using CLSM and SEM, which exhibited that emulsion oil droplets were successfully formed in which the particles responsible for the stabilization were accumulated at the interface.

The outcomes revealed that these engineered nanocargos were able to successfully stabilize DHA based oil emulsions. The results of this study could be applied for the design of partially or fully plant-based emulsions carrying an algae oil.

Keywords: Algae oil, Emulsion, Natural antioxidant

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Theory for Heterogeneous Water/Oil Separation

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Oil-polluted water is produced in large quantities in both domestic and industry utilities, which necessitate the development of new functional materials for fast and cheap phase separation. It was shown in laboratory that membranes designed as hydrophilic or hydrophobic may separate oil/water mixtures. The membrane pores possess specific affinity to water or oil, so that to favor the passage of the same phase through the pores and repeal the opposite phase away from the membrane.

We employ classical density functional theory (DFT) to elucidate the physical mechanisms governing the phase separation of water/oil emulsion near a membrane surface which possesses specific affinity to oil, at near-equilibrium. We capture emulsion concentration variations near the membrane surface while accounting for the finite volume of oil droplets in the emulsion's bulk and surface forces of molecular origin, i.e., hydrophobic, Van Der Waals (VDW), and electrical double layer (EDL) interactions, between the emulsion droplets.

We establish a clear connection between the size of drops, the surface forces between drops in the suspension and the variation in the concentration of droplets next to the membrane. We observe an increase in the concentration of oil droplets next to the lipophilic membrane surface at approximately 10 drop radii. Hence, pores in the membrane will support phase separation if their diameter corresponds to the length scale where the concentration of oil droplets near the solid is appreciably greater than the one in the liquid bulk. Moreover, we observe that the contribution of surface forces to the oil film (wetting the surface) thickness becomes appreciable for droplets smaller than 1 micron. Energy barriers to droplet attachment, which originate in surface forces, appear to increase the dense oil region volume next to the membrane.

Keywords: colloids, emulsions, surface forces, statistical thermodynamics, DFT, membranes

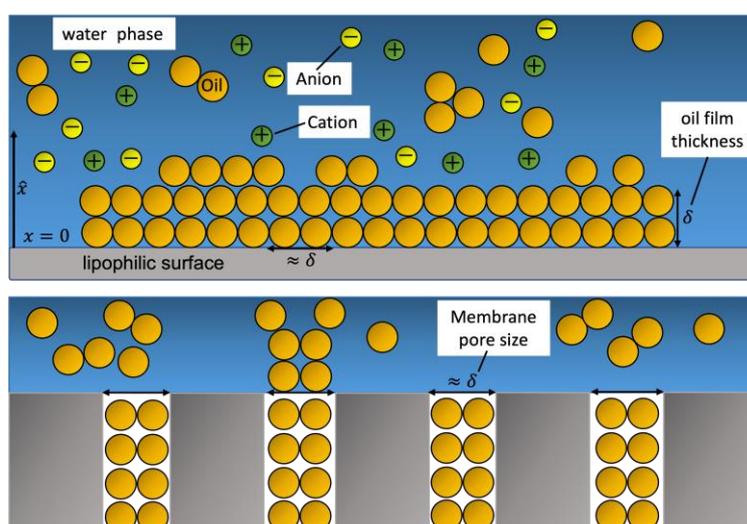


Figure 1. A semi-finite system with oil droplets (brown spheres) in water near a lipophilic solid surface (in gray). The oil droplets wet the membrane due to their chemical affinity to the lipophilic surface to form an oil film of thickness δ , which should be roughly equal to the pore size of a corresponding membrane to separate the mixture.

Non-close packed Bravais lattices via self-assembly of core-shell microgels

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Functional materials which exhibit distinct optical properties gained huge interest over the last decade because of their possible application in photonics and/or sensing.[1] When using core-shell microgels, the inorganic core can introduce optical activities like localized surface plasmon resonance (LSPR) and the shell can act as stabilizer and interparticle spacer. At the air/water-interface, the microgels self-assemble in highly periodic, hexagonally ordered monolayers. The assembled microgels can be transferred onto a solid substrate from the interface. However, non-hexagonal arrangements could offer new possibilities to tailor optical properties.

In this work, we present a simple route to prepare any of the five possible Bravais lattices of non-close packed gold nanoparticles. Gold-poly(*N*-isopropylacrylamide) (Au-PNIPAM) core-shell microgels are self-assembled into a hexagonal monolayer at the air/water-interface. A hydrophobic substrate is immersed through the monolayer and is thermally annealed prior to removal from the water.[2] During the immersion, the hexagonally ordered arrays are stretched into the different Bravais lattices (see Figure 1) in dependence of the contact angle. As the shell only functions as interparticle spacer during the self-assembly, it can be later removed by plasma treatment of the substrate supported monolayer. Thus, Bravais lattices of non-close packed gold nanoparticles are prepared. The structures are exhibiting plasmonic properties and coupled surface phenomenon due to the gold nanoparticles. Thanks to the macroscopic size of the monolayers, they can be studied using standard UV/Vis absorbance spectroscopy.

Keywords: core-shell microgels, self-assembly, non-close packed Bravais lattices, contact angle

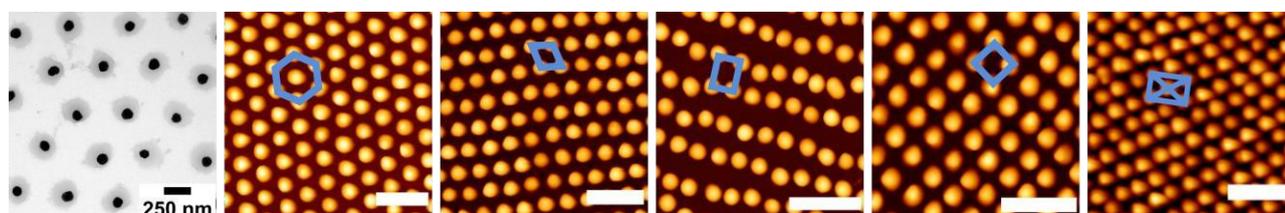


Figure 1. Transmission electron microscope image and atomic force microscope images of the five Bravais lattices: hexagonal, oblique, rectangular, square and centered rectangular of Au-PNIPAM microgels (from left to right). Scale bars of the AFM images are 1 μm .

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Sequential adsorption of polyglycerol polyricinoleate and protein at the oil-water interface: An interfacial rheology study

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Polyglycerol polyricinoleate (PGPR) is widely used as low-hydrophilic-lipophilic balance emulsifier in the preparation of water in oil (W/O) emulsions or double (W/O/W) emulsions due to its excellent surface activity. Several authors have reported that the presence of water-soluble surface-active compounds (e.g. proteins) strongly influences the absorption behaviour of PGPR at oil-water interfaces, where the simultaneous adsorption of PGPR and proteins has been studied by dynamic surface tension and interfacial dilatational rheology [1]. In order to further understand the interaction between proteins and PGPR in the emulsion stabilization mechanism, this study investigated the sequential adsorption of PGPR and proteins (i.e. whey protein isolate (WPI), sodium caseinate (NaCas) and bovine serum albumin (BSA)) at the oil-water interface by using a modified drop tensiometer allowing external phase exchange. During the experiments, Milli-Q water was replaced by a protein solution after 0.2 % PGPR 4175 (Palsgaard) was equilibrated at a glyceryl triheptanoate/water interface for about 3 hours.

The obtained results showed that the interfacial tension of the pre-adsorbed PGPR 4175 films was stabilized at around 6 mN/m and decreased with the addition of WPI and NaCas, whereas the addition of BSA had no effect. Moreover, the addition of the three types of protein increased the dilatational elasticity modulus of the PGPR 4175 films. In addition, no change in the modulus of the PGPR 4175 films was detected at the initial stage of protein addition. These results indicated that the proteins may interact with previously adsorbed PGPR at the oil-water interface through hydrophobic interactions rather than replacing PGPR at the interface, thereby increasing the thickness of the interfacial film.

Keywords: PGPR, protein, sequential adsorption, interfacial rheology

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Stabilization of oil-in-water emulsions by amphiphilic xanthan synthesized under green conditions

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Among others, amphiphilic modified polysaccharides represent one of the green solutions to replace conventional surfactants [1], these latter being controversial because of their harmful toxicological and environmental impacts [2]. The enthusiasm of the exploitation of polysaccharides is explained by several advantages [3]: availability, biodegradability, non-toxicity, low cost; another advantage is their potential for chemical modification which allows them to acquire outstanding physicochemical properties. In the present project, xanthan polysaccharide was hydrophobically modified following the principles of green chemistry in order to enhance its interfacial properties next to its remarkable inherent thickening and viscosifying capacities.

We have developed and optimized a protocol allowing grafting of alkenyl chains on the hydroxyl functions of xanthan following the principles of green and sustainable chemistry: no toxic solvent or chemical agents, low temperature, etc. The grafting density (GD) of the corresponding Hydrophobically Modified Xanthan (HMX) can be tuned according to different experimental parameters, namely pH, duration, molar ratio and alkyl chain length. The resulting GD as determined by proton NMR is comprised between 1 and 16 %.

The physicochemical characterization shows that hydrophobic alkenyl grafted moieties induce surface activity for HMX when native xanthan is described as hydrophilic non-adsorbing polysaccharide owning poor or no surface activity in water [4]. Finally, unprecedented emulsion stabilization ability was evidenced for these original xanthan derivatives as illustrated on Figure 1.

Keywords: Xanthan polymer, Chemical modification, Green grafting, Emulsifying properties

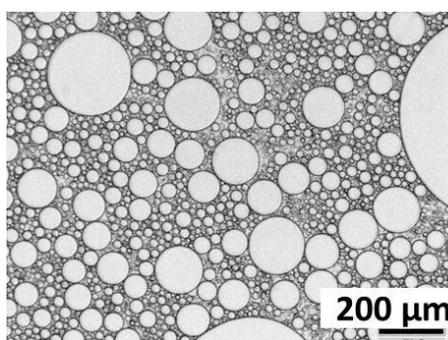


Figure 1. Optical microscopy image of oil-in-water emulsion stabilized by hydrophobically modified xanthan after 30 days at rest

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Miscible antifoams: Leveraging evaporative solutocapillary flows for a novel antifoam mechanism

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Foaming is often problematic in non-aqueous fuels and lubricating oils, leading to the use of additives called antifoams. Existing antifoams are solid particles or immiscible liquid droplets requiring specialized high shear machinery for incorporation. These antifoams are prone to gravitational separation, or removal under dynamic operation conditions – rendering them ineffective. A miscible liquid that is effective as an antifoam would overcome these obstacles.

Evaporation greatly influences thin film stability, stabilizing or destabilizing depending on the volatility and surface tension of liquid components. A fluid with higher surface tension and higher volatility destabilizes a thin film as it evaporates. We hypothesize that such a fluid would act as a miscible antifoam, leveraging evaporation driven solutocapillary flows. We test this utilizing a custom experimental platform that probes thin film dynamics and foam stability at the single bubble level. We investigate several potential miscible antifoam systems with a range of surface tension deficits and viscosity ratios. With performance equivalent to or better than conventional and the added benefit of ease of use, miscible antifoams have the potential to be groundbreaking.

Keywords: Foaming, Defoaming/Antifoaming, Air entrainment/release, Non-aqueous foams, Aqueous foams, Lubricants,

pH-dependent charge and structural properties of transfection lipid layers for RNA delivery

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Some of the most effective COVID-19 vaccines are based on cationic lipid-based delivery systems for messenger RNA (mRNA). This is a promising technology for a broader use in biomedical applications, whose efficiency depends on the physicochemical properties of the involved molecules, specifically on their charge and its dependence on pH.

We combine synchrotron-based x-ray scattering [1, 2] and x-ray fluorescence [3] on monolayers of positively chargeable transfection lipid mixtures with atomistic molecular dynamics (MD) simulations [1] in order to determine their pH-dependent structural properties and the protonation degree. Both are important aspects for the interaction with RNA. While the experiments yield electron density profiles and surface charge densities, the MD simulations yield the area per molecule, the conformation of different lipid species, and the counter-ion distributions. The self-consistent analysis of experimental and simulation data provides unambiguous and detailed information on the transfection lipid layer characteristics.

Keywords: lipid layers, RNA delivery, x-ray scattering, x-ray fluorescence, MD simulations

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Confinement Effects on the Structure of Bicontinuous Microemulsions inside Porous Materials

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In bulk, the diverse phase behavior and manifold structures of complex fluids, such as polymer solutions and microemulsions, have been intensively studied and are well understood. However, these studies neglect the influence of geometrical restrictions exerted, for example, by a porous network. Earlier studies with binary mixtures showed the effect of confinements on the phase behavior of such simple mixtures [1]. In the case of thermodynamically stable microemulsions, an exciting question is whether the confinement leads to inner structural changes, the occurrence of microphase separation, and thus shifts of the phase boundaries.

In this work, we explore bicontinuous microemulsions of a well-studied ternary phase system (water/octane/ $C_{10}E_4$) inside various controlled-pore glasses (CPG, pore diameter between 75 – 1000 Å) serving as confinement. The naturally hydrophilic surfaces of the CPGs were hydrophobically modified to analyze the influence of the surface polarity on the behavior of the microemulsions inside the pore network. So far, the effect of the chemical nature has been only studied on planar solid surfaces with sugar surfactant-based microemulsion [2]. We combined cryo-SEM imaging and SAXS measurements to characterize the structures in bulk and inside the pores. Additionally, we employ the Washburn method which gravimetrically determines the advancing contact inside the hydrophilic and hydrophobically modified pores. The experiments suggest the enrichment of oil at the walls of the porous network and a concomitant alteration of the phase behavior. These experiments are accompanied by numerical studies using COMSOL to further characterize the wetting and imbibition in the porous network.

Understanding the phase behavior of bicontinuous microemulsions in pores yields fundamental insights into the behavior of complex nanostructured fluids in such materials and it is essential for their application in cosmetics, pharmaceuticals, enhanced oil recovery, and decontamination.

Keywords: structure, Washburn method, confinement, controlled-pore glasses

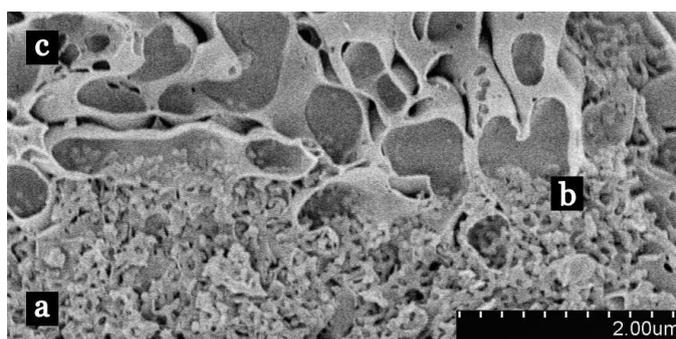


Figure 1. Cryo-SEM micrograph of a bicontinuous microemulsion (a) imbibed (b) in a porous network with a mean pore diameter of 1000 Å (c).

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Membrane fusion mediated by hydrophobic nanoparticles

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As nanoparticles (NPs) find wider applications in medical and other industries the gap in knowledge surrounding their toxicity becomes more of a concern. When a cell is exposed to NPs they may cross the cell membrane and enter the cytoplasm or may remain outside the cell. A directly relevant fundamental area on the mechanisms of NP cellular entrance but remains largely unexplored is how NPs would affect the mechanism of membrane fusion. Quantum dots (QDs) are among the most promising functional NPs due to their unique optical and electronic properties.

The main goal of study will be to investigate the interactions and fusion between mixed 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) / 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phospho-ethanolamine (POPE) supported lipid bilayers containing hydrophobic cadmium sulphide (CdS) QDs of size ranging from 2.7 nm to 5.4 nm, using the surface force apparatus (SFA) *in situ* and *in real* time. The supported bilayers will be obtained by incubating the positively charged polyethylenimine (PEI) – coated mica substrate in QD-intercalated POPC/POPE liposomes in PBS buffer. The effect of temperature on the membrane fusion will be also studied.

The obtained results will provide unprecedented data and information on the fundamentals of NP-mediated membrane fusion, relevant to our understanding of how NP gain cellular entry.

Keywords: membrane fusion, nanoparticles, supported lipid bilayers

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Effect of salt on the formation and stability of water-in-oil Pickering nanoemulsions stabilized by diblock copolymer nanoparticles

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Sterically-stabilized diblock copolymer nanoparticles are prepared in n-dodecane using polymerization-induced self-assembly. Precursor Pickering macroemulsions are then prepared by the addition of water followed by high-shear homogenization. In the absence of any salt dissolved in the aqueous phase, high-pressure microfluidization of such precursor emulsions leads to the formation of relatively large water droplets with DLS measurements indicating a mean diameter of more than 600 nm. However, systematically increasing the aqueous salt concentration produces significantly finer droplets after microfluidization, until a limiting diameter of around 250 nm is obtained at 0.11 M NaCl. The mean size of these aqueous droplets can also be tuned by systematically varying the nanoparticle concentration, applied pressure, and the number of passes through the microfluidizer. The mean number of nanoparticles adsorbed onto each aqueous droplet and their packing efficiency is calculated. SAXS studies conducted on a Pickering nanoemulsion confirms that the aqueous droplets are coated with a close-packed monolayer of nanoparticles. The effect of varying the amount of NaCl dissolved in the aqueous droplets on their initial rate of Ostwald ripening is investigated using DLS. Finally, the long-term stability of these water-in-oil Pickering nanoemulsions is examined using analytical centrifugation. The rate of droplet ripening can be substantially reduced by using 0.11 M NaCl instead of pure water. However, increasing the salt concentration up to 0.43 M provides no further improvement in the long-term stability of such nanoemulsions.

Keywords: Emulsions, Pickering Emulsions, Block Copolymers

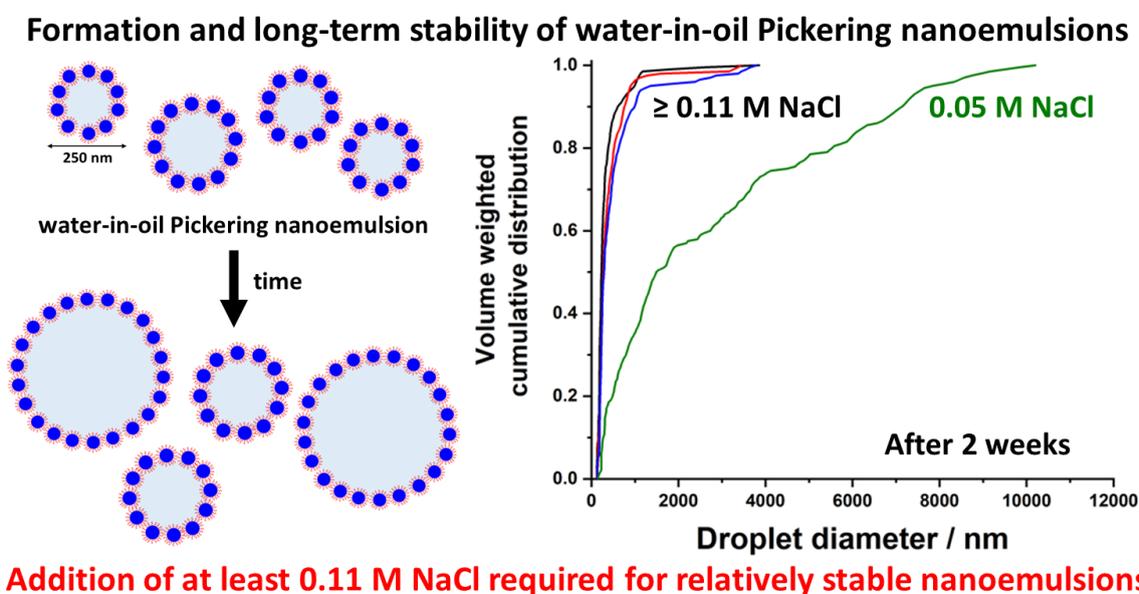


Figure 1. Pickering nanoemulsions prepared using various amounts of NaCl dissolved in the aqueous phase after aging for two weeks at 20 °C.

Building stable structures of ethanol-water droplets at the oil-water interface

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Droplets are constantly interacting with their environment: a prototypical example is the case of a sessile droplet evaporating on a solid substrate [1]. As a result, they are often in a non-equilibrium state and exhibit complex flows and behavior that drive motion and self-assembly processes [2]. Droplet behavior has been widely studied on solid (rigid) surfaces, lubricated surfaces, in a liquid bath, and on soft substrates made from polymers or gels [2]. Here, we explore their behavior in a novel setting: deeply metastable droplets sit at an oil-water interface, whose stability can be easily tuned from seconds to days. While pure water and pure ethanol droplets coalesce within seconds with the aqueous phase below, the addition of EtOH in a broad range of compositions, remarkably, produces droplets that sit at the oil-water interface and are metastable against coalescence up to several days. We discuss the effect of assembling a solid-like monolayer of cellulose nanocrystal surfactants (CNCS) at the oil-water interface, which acts as a platform for droplets to interact with each other. Similar to droplets on soft substrates, our droplets deform the CNCS membrane, leading to elastocapillary interactions [3]. This leads to the self-assembly of monodisperse droplets into hexagonal structures with tunable stability (Fig. 1). Such extended stability against merging allows us to build different ensembles of droplets at the oil-water interface in a controllable way. Finally, we describe a number of new phenomena in our system, including wetting transitions of droplets at the water-oil interface, and active behavior of droplets driven by functionalization of the NCS assembly. Our work outlines a new system for the study of metastable phenomena, active matter, and the manufacturing of synthetic soft materials.

Keywords: oil-water interface, droplets, self-assembly, Nanocrystal surfactants

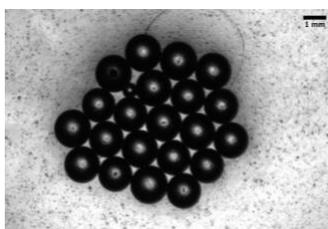


Figure 1. A hexagonal self-assembly of 25 v/v % ethanol droplets at the dodecane-water interface.

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Thermal and structural analysis of zwitterionic SOPC lipid membranes entrapped with gold nanoparticles

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Gold nanoparticles (AuNPs) are promising candidates in various biomedical applications such as sensors, imaging, drug delivery, and cancer therapy [1-3]. Formulation of liposome-AuNP hybrids provides a biologically inspired route to design multifunctional therapeutic agents. Therefore, studies pertaining to the effects of nanoparticles various biophysical properties of lipid membranes are important to gain a fundamental understanding and assure safety. In this regard, the present study aims to analyze the influence of AuNPs on the structural and thermal properties of zwitterionic SOPC lipid membranes as a function of temperature and different nanoparticles concentrations (0.5, 1, and 2 w %) by using two noninvasive techniques, namely Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The transmission electron microscopy (TEM) images have indicated the size of the dodecanethiol functionalized hydrophobic AuNPs to be 2.2 ± 1.1 nm. Due to the smaller size and hydrophobic coating, we expect that the AuNPs will be efficiently entrapped between the hydrophobic tail region of the lipid membrane as shown in Figure 1. The DSC results have shown that the AuNPs strongly influence the phase behavior of the membrane lipids and alter their phase transition temperature by a few degrees. FTIR results have indicated that the entrapped AuNPs induces a gradual increase in the relative intensity of P=O and C=O stretching and CH₂ scissoring bands, while the band positions were unaffected. The results of this study provide insight into nanoparticle-membrane interactions and contribute to the design of novel liposome-AuNP formulations with improved therapeutic efficacy.

Keywords: gold nanoparticles, lipid membranes, phase transition, fluidity, bending elasticity

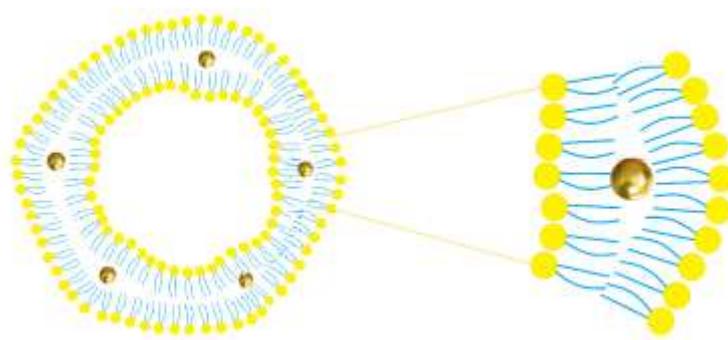


Figure 1. Schematic presentation of a lipid bilayer membrane entrapped with hydrophobic gold nanoparticles.

Acknowledgments: We gratefully acknowledge the financial support from the project AuLip KP-06-DB-8/01.12.2020 with the Bulgarian National Science Fund under the National Scientific Program P. Beron 2020.

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Effect of oscillating piston characteristics on small volume emulsion generation

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A miniature pulsating device has been designed and constructed for emulsification experiments. The core of the device is an experimental cell while the necessary shearing for the proper mixing of the two liquids is generated by the linear periodic movement of a piston up and down inside the cell. For the present study, five different pistons are constructed which differ in the length or in the height of their plate sides. These features dictate different width and height of the gap between the plate and the cell walls. Their performance is assessed by performing emulsification experiments over a wide variety of piston stroke frequency and emulsification duration for a specific non-coalescing system (fixed oil fraction and surfactant concentration). The resulting droplet size distributions are estimated by monitoring the evolution of phase separation versus time and determining the initial oil droplet size distribution by means of optical measurements. The combined information from these techniques is necessary in order to register the broad size range of droplets.

A semiquantitative analysis of the flow field in the gap reveals that droplet breakage process starts at the laminar boundary layers developed between the piston and the cell walls and allows characterization of this field. A discussion on the mechanism of droplet breakup is presented. The analysis of experimental results demonstrates that four of the five tested piston plates are appropriate for emulsification regarding the generated droplet size distribution and the choice among them requires additional criteria, e.g. energy requirements.

Keywords: emulsification; oscillating piston; droplet size distribution; droplets breakage

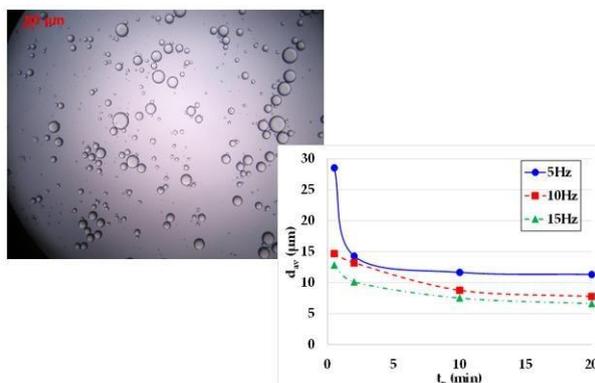


Figure 1. Number based droplet average diameter d_{av} versus emulsification time for different stroke frequencies

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Destabilization of a microfluidic air thread through Marangoni effects

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It is well known that a fluid stream injected into a co-flowing fluid in rectangular conducts can only break into drops or bubbles when its width, w , becomes smaller than the channel height, H [1-2]. We herein demonstrate experimentally that this picture is not valid when Marangoni effects are considered. We show that the Marangoni effects generated by the fast adsorption of small length alcohol molecules onto the gas-liquid interface may destabilize a confined gas-water stream ($w > H$). This destabilization either leads to the propagation of solitons or to the production of monodisperse bubbles. We characterize these solitons and then develop a simplified hydrodynamical model that will describe our observations.

Keywords: Interfacial flows, Flow instability, Microfluidics, Marangoni effect

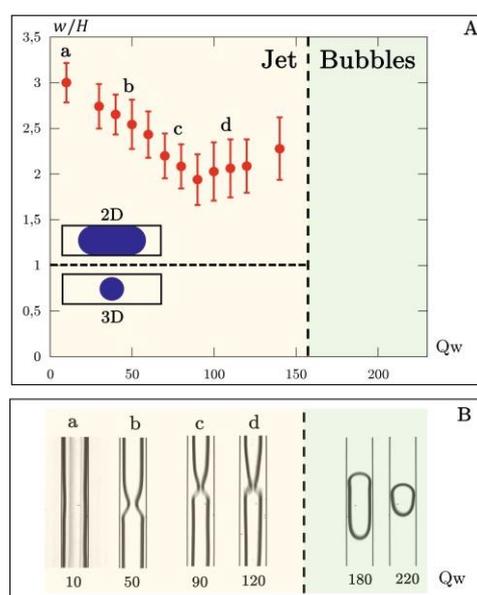


Figure 1. A) Jet mean width as a function of the liquid flow-rate Q_w . B) Images of the two-phase flow for different values of Q_w (system with butanol). Insets of A) represent the cross-section of 2D and 3D jets.

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Study of the stability of gas/liquid interfaces in liquid bridges using an electrical conductance method

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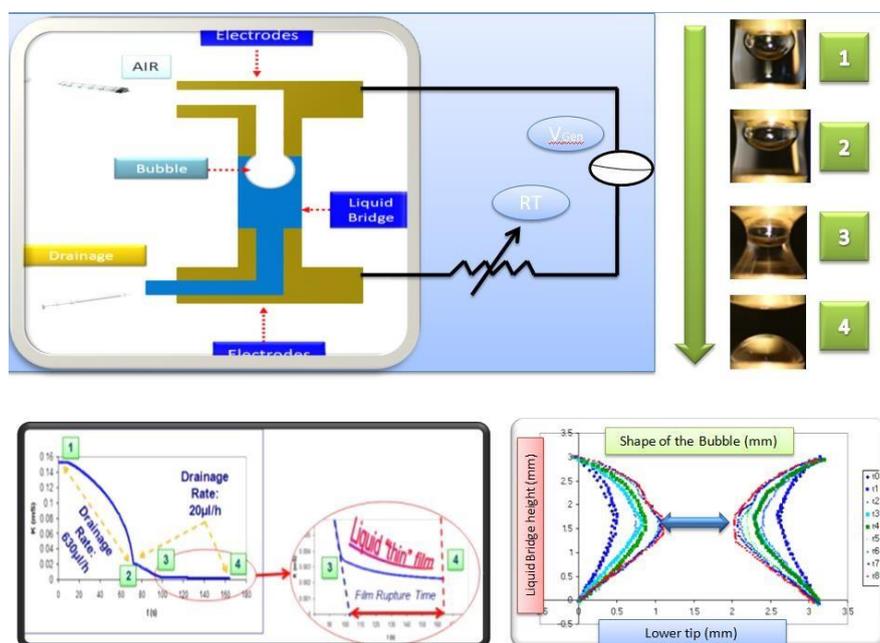
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Air-liquid interfaces and the liquid film between them are structural characteristics of foams so their study is of particular importance to determine foam stability. Specifically, the more stable the interfaces are, the more stable the foam will be. A new electrical technique for the study of these interfaces' stability, is proposed in the present work. In particular, a bubble is created inside the liquid bridge. The latter is surrounded by air, creating interfaces and liquid films similar to those found in a foam. During control drainage of the liquid bridge, electrical measurements take place. Through these measurements, it is possible to determine the stability of the film created between the bubble and the liquid bridge and consequently to estimate the stability of the foam generated by the type and amount of employed surfactant.

Experiments took place with liquid bridges of various solutions of surfactants (e.g. SDS, BaC 50, Ethylan 1008) at different concentrations, for various mixtures of the above surfactants, in the presence and in the absence of NaCl, under stable ambient conditions (i.e. temperature and moisture), and for various liquid drainage rates (e.g 10 and 20 μ l/h). These experiments showed that the highest the concentration of the surfactant, the highest the strength against thinning of the liquid film and so the longest the time until its rupture, thus the stability of the foam created for the particular concentration of surfactant is also the highest.

Keywords: foam stability; liquid bridge; surfactant.



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Adsorption mechanism and stability of polyelectrolyte multilayers containing GTMAC modified chitosan

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The main purpose of this research was to determine the adsorption mechanism and stability of four bilayer system in two configurations: (glycidyltrimethylammonium chloride modified chitosan: chitosan-GTMAC/ heparin)₄ and (chitosan-GTMAC/ carrageenan)₄.

Heparin is a highly negatively charged polysaccharide of high polydispersity and proven biological activity. Carrageenans are non-toxic, biocompatible polysaccharides of large viscosity and good solubility in water [1]. Chitosan- GTMAC is a biocompatible cationic chitosan derivative with a more stable charge in physiological conditions [2].

The following techniques were employed to analyze these multilayer systems: streaming potential measurements (SPM), optical waveguide spectroscopy (OWLS), and quartz crystal microbalance with dissipation (QCM-D). These selected research methods enable to determine the adsorption mechanism during the polyelectrolyte assembly, mainly controlled by electrostatic interactions. The stabilities of adsorbed multilayers in pure electrolyte were also established. The collected data confirms that positively charged chitosan- GTMAC as well as negatively charged heparin and carrageenan adsorbs irreversibly via layer by layer method on silica covered surface. Furthermore, the bilayer system undergoes structural viscoelastic deformations along deposition of each biopolymer.

The obtained results, apart from their significance for basic sciences, can be used to develop procedures allowing to obtain biocompatible and stable macroion multilayers with well-defined electrokinetic properties for the use as biosensors.

Keywords: polyelectrolytes, adsorption mechanism, electrostatic interactions

Acknowledgements: This work was funded by the National Science Centre, Poland, Opus Project, UMO-2018/31/B/ST8/03277

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Solid foams from photocatalytic nanoparticles for luminous air purification

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Photocatalytic Oxidation (PCO) recently emerged as an attractive answer, to widespread needs of efficient air purification, thanks to its potentials to treat simultaneously Volatile-Organic-Compounds (VOC) and microorganisms. Nevertheless, efficacy of current PCO systems is unsatisfactory. Two bottlenecks are identified: 1) limited photocatalytic activity of the structures employed; 2) limited extension of the activated surface. To overcome both bottlenecks, we suggest an approach based on concepts of material and surface sciences: the formation of a high surface density hierarchic structure based on a solid foam spanning multiple length-scales and exposing photocatalytic titania (TiO₂) nanoparticles [1].

In view of this goal, we will demonstrate here very recent results on the production of metal-doped titania nanoparticles (NP) which combine good PCO activity, thermal stability of the PCO-active phase (desirable for the process of formation of solid foam) and reduced band gap, thus allowing photoactivation by visible light. Their morphology, crystalline structure and optical properties are investigated by Dynamic Light Scattering, SEM electron microscopy, X-ray diffraction, Raman and UV-Vis spectroscopies. Next, we optimize the self-assembly of amphiphilic complexes between NPs and CTAB surfactant. These complexes are used to stabilize liquid foams, which are then jellified to form solid foams whose structure contains the photocatalytic NPs. These results substantiate the possibility to use photocatalytic NPs to fabricate objects of hierarchical porosity to be employed as energy efficient PCO filters, with applications to air purification in demanding sectors, like aerospace.

Keywords: Photocatalytic Oxidation (PCO), Titania nanoparticles, Foams, Solid Foams

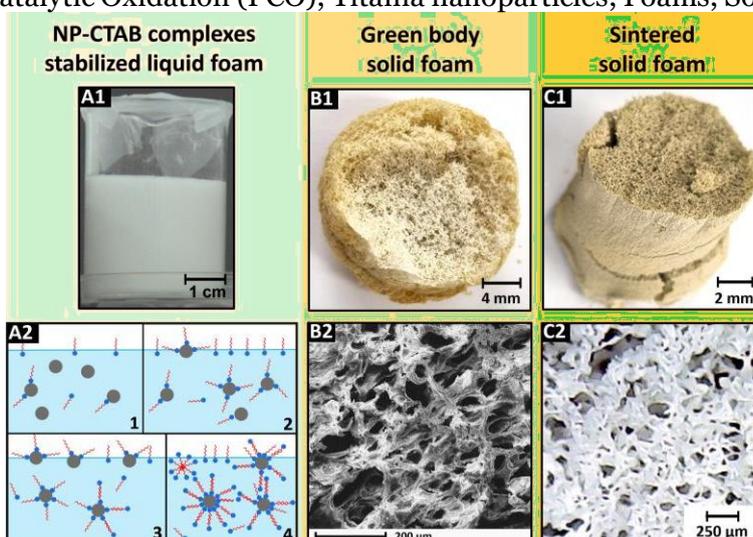


Figure 1. Steps for the formation of solid foams based on photocatalytic titania. Top panels, left to right: the liquid foam, the green body solid foam and the sintered solid foam. Bottom panels: sketches and micrographs of the corresponding structures.

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Biomimetic membranes interacting with pro-apoptotic peptides

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Synthetic antimicrobial peptides with bacteriostatic and cytotoxic activity are designed to exhibit modified selectivity and propensity to α -helical conformation in amphipathic environment. Our previous studies on a series of shortened analogues of (KLAKLAK)₂ revealed that KL β AKL β AK-NH₂ has very good antiproliferative effect against MCF-7 tumor cell lines with SI = 8.35. Moreover, its activity against MCF-7 tumor cell lines is more than 11 times higher than those of parent molecule KLAKLAK-NH₂ [1]. On the other hand, doubled sequenced parent compound (KLAKLAK)₂-NH₂ shows around 10 times higher antiproliferative effect in comparison with doubled analogue containing β -Ala (KL β AKL β AK)₂-NH₂ in the primary structure [2]. Here we probe the ability of these compounds containing natural or unnatural amino acid β -Ala to penetrate cell membrane thus initializing apoptosis. The bending rigidity of model lipid bilayers is measured by thermal shape fluctuation analysis of quasispherical unilamellar vesicles monitored in phase contrast light microscopy. The electrical properties of planar lipid bilayers are assessed by fast Fourier transform electrochemical impedance spectroscopy. At peptide concentrations of $\sim 20 \div 30$ $\mu\text{mol/L}$ and peptide-to-lipid total molar ratios $\sim 0.55 \div 0.80$ the membrane bending elasticity is unaltered, which indicates transbilayer insertion of the shortened non-modified analogue. The acquired results provide useful knowledge in tailoring the structure of antimicrobial peptides to achieve strengthened stability towards enzymatic degradation.

Keywords: lipid bilayers, bending elasticity, electrical capacitance, antimicrobial peptides

Acknowledgements: Financial support of Bulgarian National Science Fund (KP-06-N58/6/2021) is acknowledged.

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Interfacial shear viscosity and surface tension measurements of anionic–nonionic surfactant binary mixtures, used as minerals flotation reagents

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Binary mixtures of ionic - nonionic surfactants feature enhanced interfacial properties compared to the individual ionic and nonionic surfactant components [1]. In terms of minerals flotation technology, these binary mixtures can be used as collector reagents and they are expected to improve bubble-particle attachment efficiency and thus facilitate the recovery of mineral particles.

Up to date, the synergistic action of ionic and nonionic surfactant molecules, has been studied by performing static surface tension measurements [1]. For the first time, the present work tests interaction between sodium oleate (NaOl, anionic surfactant) and five different ethoxylated/alkoxylated alcohols (nonionic surfactants) by measuring the interfacial shear viscosity of their aqueous solutions at a wide range of shear rates. Measurements are conducted using a Physica MCR 301 Anton Paar rheometer equipped with an interfacial rheology system (IRS) employing a bicone bob geometry [2]. Different anionic-nonionic mass ratios are tested, keeping the concentration of NaOl at 1CMC.

Results show that nonionic molecules tend to displace NaOl molecules from the air/liquid interface. Upon some critical nonionic concentration, interfacial shear viscosity of the binary mixture is governed by the nonionic molecules, indicating that these molecules occupy the interface. However, supporting surface tension measurements show that at this critical concentration there are still NaOl molecules attached on the interface. Critical concentration level depends on the chemical structure of nonionic molecules, i.e. length of the hydrophilic head, branch at the hydrophobic chain. Furthermore, oscillatory rheological runs reveal the dominant viscous character of all tested binary mixed monolayers with only a marginal elastic component.

Keywords: interfacial shear viscosity, viscoelasticity, surfactants, flotation

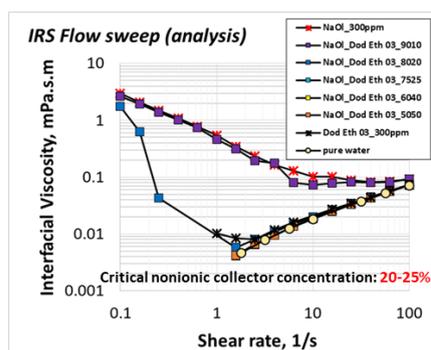


Figure 1. Interfacial viscosity of aqueous solutions of NaOl – Dodecyl Ethoxylate 3 binary mixtures, at different mass ratios, under a wide range of constant shear rates.

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Multifunctional TiO₂ Nanoparticles as Stabilizing Agents for and Catalytically Active Phases in Bijels

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Bicontinuous interfacially jammed emulsion gels (bijels) are soft materials with a variety of potential applications in catalysis and separation processes. Bijels consist of two interwoven immiscible liquid channel networks, stabilized by a jammed layer of colloids at the interface. [1-2] For a stable bijel, the colloids need to be wetted by both fluids equally. However, most colloids are hydrophilic due to polar groups on their surfaces. Thus, surface functionalization for the colloids need to be developed to obtain stable bijels.

Here, we investigate the stabilization of bijels with titania (TiO₂) nanoparticles as stabilizing agents, considering their photocatalytic activity. The suitability of different surface functionalizations, including the physisorption of surfactants, the covalent bonding of hydrophobic groups, or the adsorption of polyelectrolytes are compared. The functionalized titania particles are characterized by zeta potential, dynamic light scattering, three phase contact angle, titration and scanning electron microscopy analysis. The 3-dimensional fluid channel networks of bijels formed with the functionalized particles is investigated via confocal microscopy analysis. Our work represents the first step to establish the bijel for heterogeneous catalysis with titania particles (Figure 1). Future work will make use of the unique transport properties of bijels for realizing reactive separations within the fluid bicontinuous network, important for a sustainable chemical industry. [3-4]

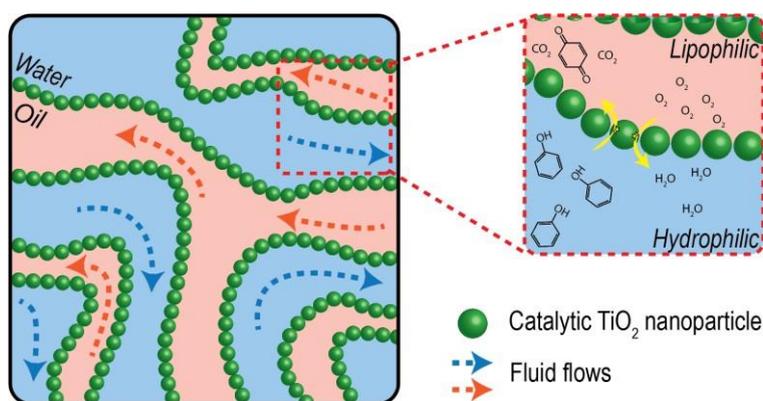


Figure 1. Schematic depiction of a TiO₂-based bijel structure for catalytic purposes.

Keywords: bijels, titania nanoparticles, self-assembly, surface modification, phase separation

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Droplet size distribution in emulsions

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The mixing of one fluid into another immiscible fluid results in the dispersion of droplets in a continuous phase, namely an emulsion. This process has been widely studied, mainly because of its ubiquity in various industrial applications [1]. In particular, the rheological properties of emulsions are of great interest for food and cosmetic products [2]. However, the impact of the fluid properties and the mixing process on the rheology of the emulsion is not fully understood [3]. In this work, we study how the droplet size distribution is influenced by the properties of the continuous phase, the mixing speed, and the mixer geometry in order to predict the rheological behavior of the emulsion.

Keywords: Emulsion, droplet size distribution, rheology

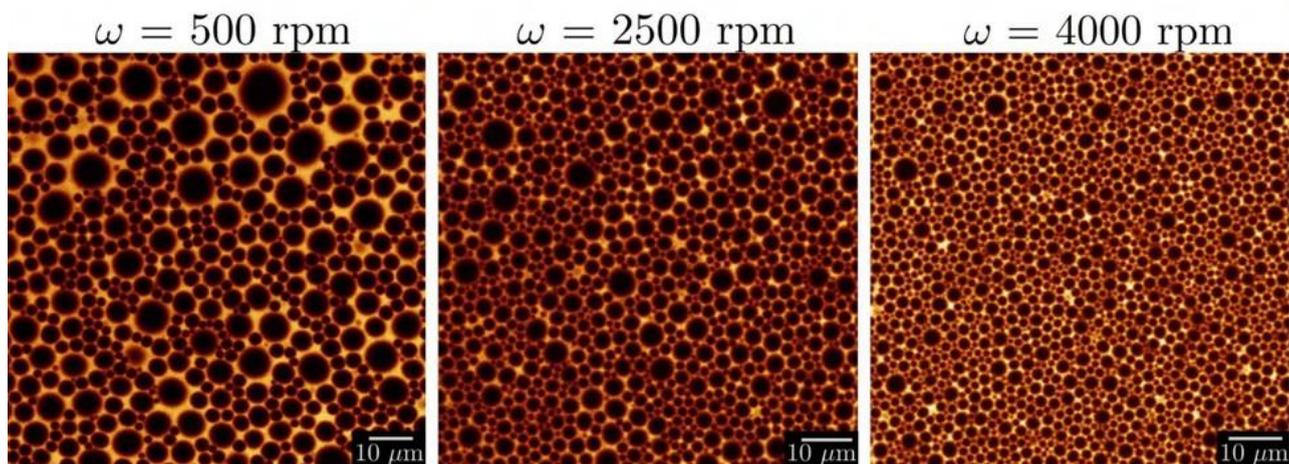


Figure 1. Confocal images of same emulsion at successive rotation speeds ω . The oil droplets (in black) are dispersed in water and their size decreases as the speed increases.

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Molecular dynamics simulations of droplet coalescence

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Coalescence is a particularly important event in the field of colloids and interfaces as it governs many processes and phenomena such as the stabilisation of foams and emulsions. An important difficulty is that it cannot be directly described by hydrodynamic laws; while these can describe the preliminary drainage to coalescence, the break-up of the film is a stochastic event that requires its own description. In this context, we set out to model these issues from a molecular description for a system composed of water and oil (heptane). The aim here is not only to simulate the phenomenon but above all to validate or generalise the macroscopic laws of a hydrodynamic nature governing coalescence.

We were thus able to show that drainage was accelerated for small distances between drops by a more important slip phenomenon than the one taking place for liquid/solid interfaces. The relative diffusion of the two species leads to a rapid relaxation of the friction between the two fluids and thus to a greater slip. Direct simulation shows that the process is a random phenomenon that can be described practically by a Poisson distribution. The results can be understood by a thermodynamic interface model. Coalescence is thus an activated process that becomes possible when the transverse fluctuations are of the order of magnitude of the distance between the two drops. We believe that these multi-scale approaches allow us to provide a new description of this phenomenon, in particular by interpreting its stochastic nature and by making the link between hydrodynamics and thermodynamic fluctuations.

Keywords: Coalescence; molecular dynamics; droplets; drainage; film; thermodynamic noise; slip; boundary conditions;

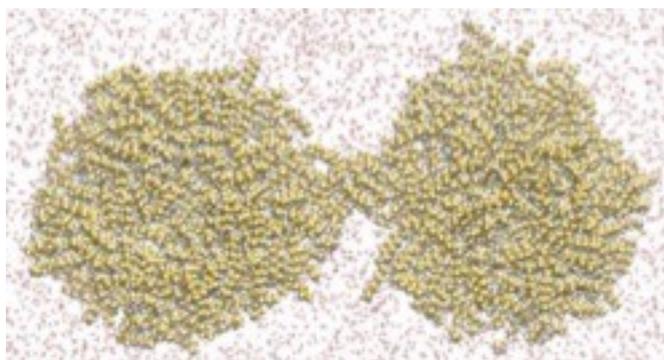


Figure 1. Coalescence of two heptane droplets in water modelled by molecular dynamics

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Following the lipolysis of a thin triolein film

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The triglyceride aqueous interface has an important role in many processes, none more so than lipase activity. Lipases, such as *Thermomyces lanuginosus* lipase (TLL), are responsible for the degradation of triglycerides to smaller components, such as diolein, monoolein, glycerol and fatty acids. TLL attracts considerable interest in the food and pharmaceutical industries due to the catalytic behavior it possesses [1]. While the TLL lipolysis of triglyceride films has previously been investigated, [2,3] the influence of the reaction products on this process is poorly understood.

This aim of this study was to identify the chemical species present in a triolein film before and after TLL digestion and to monitor the physical properties of the film with high time resolution throughout the lipolysis after the addition of TLL. The thickness, mass, and elasticity of the film was continuously monitored over several hours enabling a detailed in-sight into the changes to the physical properties of the triolein film throughout these processes. These findings were used to optimize the experimental design and sample preparation for the subsequent neutron reflectometry experiments performed at ILL and ISIS. Here, it was possible to measure the reflectivity profile of the equilibrated triolein film before and after exposure to lipase (Fig. 1) as well as monitor the kinetics of the lipolysis throughout the digestion.

Keywords: triolein, lipolysis, neutron reflectivity, kinetics

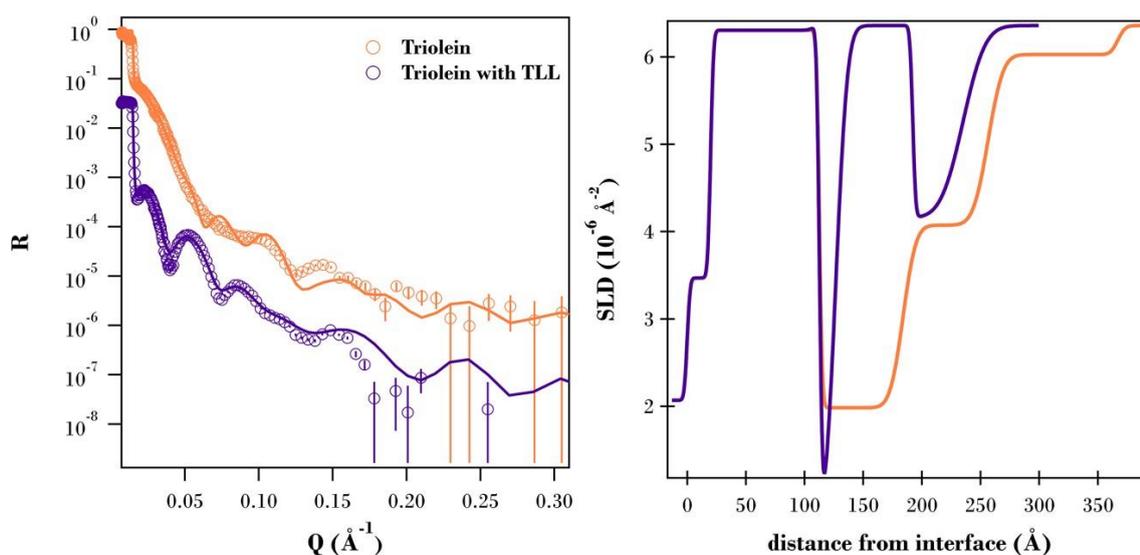


Figure 1. Reflectivity measurements for the hydrated triolein film (orange) and TLL digested triolein film (purple) with the corresponding SLD profiles

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Microgravity Study of Emulsions Destabilisation by Diffusing Wave Spectroscopy within the EDDI Project

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Microgravity (weightlessness) conditions offers unique opportunities for the investigation of the mechanisms responsible for emulsion destabilisation, such as droplet coalescence and Ostwald ripening, decoupled from droplet creaming.

The international experiment EDDI (Emulsion Dynamics and Droplet Interface) aims at the investigation between the above mechanisms and the chemico-physical properties of the droplet interface within the emulsion. In addition to investigations under laboratory conditions, microgravity experiments are planned to characterise the overall emulsion destabilisation and the features and effects of the destabilisation mechanisms. These experiments are under way on board the International Space Station, using the ESA facility Soft Matter Dynamics (SMD) [1], to investigate a set of emulsion samples with volume concentrations ranging from 20 to 30% and stabilised by non-ionic (polyoxyethylenated alcohols) surfactants. SMD is an experimental apparatus conceived to investigate structural and dynamic properties in emulsions, foams and granular materials, using Diffusing Wave Spectroscopy (DWS): a powerful optical diagnostics based on the analysis of the intensity of laser light diffusing in a multiphase disperse system [2,3].

The concepts underlying the EDDI project are given here together with principles of the DWS diagnostics within the SMD facility. Result examples taken from the early analysis of the ongoing microgravity experiments are also presented.

Keywords: emulsions, coalescence, liquid-liquid interface, microgravity, DWS

Acknowledgements: European Space Agency (ESA) MAP project “Emulsion Dynamics and Droplet Interface - EDDI” (Contract n. 4000128643/19); National Aeronautics and Space Administration (NASA) project “Particle Stabilized Emulsions and Foams – PASTA (Grant 80NSSC21K2080).

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At interfaces absorbed microgel particles stabilize emulsions as a function of pH and microgel particle concentration

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Emulsion-based food products, such as drinks, salad dressings, desserts, and sauces, are part of our daily lives. These products are composed of two immiscible liquids (oil and water), and are thermodynamically unstable, thus, they require the use of emulsifying and often thickening agents in order to guarantee stability, and avoid phase separation (1). There is a wide range of emulsifying agents useful for this purpose, such as proteins and hydrocolloids, but also particles and low molecular weight surfactants. This contribution draws focus to a relatively new kind of emulsifying agents: Microgel particles (MGPs) based on biopolymers for food applications. Microgel particles are lyophilic, particulate polymer networks, whose properties are more complex than those of single polymer chains and particles.

Based on polyelectrolytes, pectin-based MGPs are assumed to be pH and ionic strength sensitive, in a similar manner to MGPs of synthetic polymers (2). Besides building a barrier around the oil droplets, charged MGPs repulse each other. Thus, the stabilisation mechanisms of pectin-based MGP should be both steric and electrostatic.

To investigate this, emulsions were homogenised with MGP concentrations ranging from 0.5 to 2 wt% MGP. After emulsification, the pH of the emulsions was adjusted to 4, 3, or 2; and the resulting droplet sizes were measured. We found out that the droplet size and the appearance of agglomerates increased with decreasing pH values. It was found that both a change in pH and an increase in ionic strength led to destabilization of the emulsions, with very rapid phase separation in the case of high ionic strengths and at $\text{pH} < \text{pKa}$. These results help understand the emulsion stabilisation mechanisms of pectin-based MGP and the effects of formulation parameters on the long-term stability of MGP-stabilised emulsions (3).

Keywords: microgel particle, emulsion, pectin

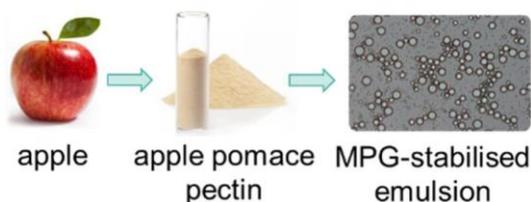


Figure 1. Apple pectin produced from apples is used for the production of pectin-based microgel particles

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Design of an experimental device, qualified for parabolic flights, for the dynamic behaviour and stability study of emulsions

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Emulsions are systems consisting of two immiscible liquids and are commonly found in oil, food and cosmetics industry. On earth, gravity triggers the rapid separation of the two phases after the end of the emulsification process. Thus, motion of droplets as well as droplets interactions due to interface driven processes are evolving too fast to enable their investigation and in-depth understanding of underlying phenomena. Microgravity, on the other hand, provides a simplified environment where gravity driven processes are eliminated and, thus, the motion of droplets and droplet-droplet interactions which strongly affect emulsion destabilization get slower. As a result, they can be studied thoroughly employing conventional diagnostics (e.g. optical and electrical methods).

This study aims to exploit the low gravity conditions evolving during parabolic flights to study the dynamic behavior and stability of the produced emulsions. An experimental setup is under development, the core of which is the emulsification unit incorporating an innovated miniature pulsating emulsification device designed and constructed by Chondrou et al. [1]. Different advanced diagnostics will be used for monitoring emulsions' dynamic behaviour and stability in low gravity conditions. Four different parameters are about to be examined: a) Surfactant concentration, b) Piston stroke frequency, c) Oil to water ratio and d) Duration of emulsification. A high speed camera (750.000 f/s) will monitor droplets breakup and motion, while a high resolution camera (20 MP) will capture images to determine oil droplet size distribution. In parallel, a novel ultra-sensitive electrical impedance spectroscopy technique (EP 3005942 A1, 2016) will be used to record the evolution of oil volume fraction and validate droplet size distribution.

Keywords: emulsions; droplet interactions; microgravity; droplet size distribution

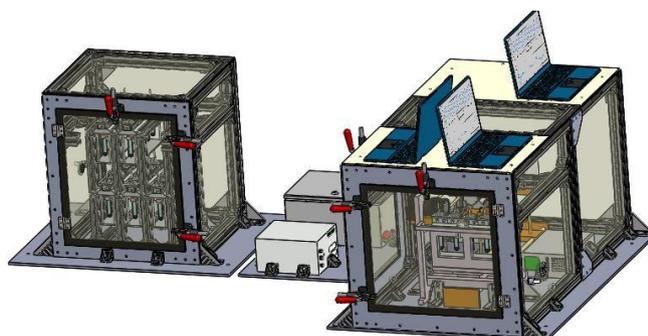


Figure 1. Experimental setup overview

Acknowledgements: This research was supported by the European Space Agency (ESA) PRODEX PROJECT “Dynamics of Emulsion Droplet Interactions in Low Gravity Conditions (Low-G-Emulsion)” – Contract No.: 4000132920.

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Photoisomerization of Arylazopyrazole Surfactants Drives Property Changes of Polyelectrolyte/Surfactant Mixtures

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Polyelectrolyte/surfactant (P/S) mixtures already find many applications but in most cases the systems are static, which renders them invariable for property changes by an external stimulus. Recently we reported that mixtures of a photoresponsive arylazopyrazole (AAP) surfactant with poly(sodium polystyrene sulfonate) (PSS) demonstrates reversible property changes like aggregate sizes and charging states [1].

Here, we present new information on poly(diallyl dimethylammonium chloride) (PDADMAC) mixtures with three alkyl-arylazopyrazole butyl sulfonates (C_n AAPC₄S) that exhibit different alkyl tails (H, butyl[2] and octyl). The *E* and *Z* configurations of the photoswitches show substantially different hydrophobic interactions which influences their interfacial and bulk behavior and is related to their binding affinity of the *E/Z* form to PDADMAC. For P/S mixtures, we have fixed the surfactant concentration to a value where the surfactants exhibit the largest surface tension changes when they are switched using 365 nm UV light (*Z*) and 520 nm green (*E*) light. Measurements of the electrophoretic mobility show that photoisomerization of C_n AAPC₄S surfactants causes a charge reversal of the P/S aggregates from negative to positive values. In addition, the low colloidal stability leads also to larger aggregates that are formed in the bulk and which can be redissolved by irradiation with UV light when the surfactants alkyl chain is short enough. Vibrational sum-frequency generation (SFG) spectroscopy reveals that similar to the changes in the bulk, the charging state at the air-water interface can be modified when the light irradiation changes. For SFG spectroscopy we have interrogated the O-H modes of interfacial water which are heterodyned by the strong non-resonant contribution of the C_n AAPC₄S surfactants and provide information on surface charging. These results from SFG are complemented by neutron reflectometry experiments where we have resolved the polyelectrolyte and surfactant composition at the air-water interface as a function of mixing ratio and light irradiation.

Keywords: polyelectrolytes, surfactants, photoresponsive, SFG-spectroscopy, neutron reflectometry

Acknowledgements: We gratefully acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project-ID 433682494-SFB 1459. We also thank the ILL for allocations of neutron beam time on FIGARO (DOI: 10.5291/ILL-DATA.9-11-1984 and 10.5291/ILL-DATA.9-12-652).

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Anisotropic emulsions as a template for non-spherical microcapsules

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Microencapsulation is an area of growing interest for targeted delivery of a multitude of actives of interest (AIs) including fragrances, pharmaceuticals and flavourings. One aspect of encapsulation which garners substantial interest is efficacy of AI retention. Previous work[1-2] has demonstrated that an impermeable metal shell may be grown on a Pt-PVP stabilised Pickering emulsion allowing for long-term retention and triggered release of encapsulated actives. However, an additional obstacle to efficient capsule delivery is adhesion of microcapsules to a target substrate. One approach to overcome this obstacle is the use of non-spherical microcapsules. By increasing the surface area to volume ratio of the capsule and by extension the contact area to encapsulated AI, the efficiency of active delivery may be improved.

In this work we present the preparation of non-spherical oil-in-water emulsion droplets stabilised by a combination of surfactant, particles and polymer as a template for microcapsule preparation. These droplets appear to be a result of an arrested coalescence process driven by the concentration and interaction of these stabilising components, and have demonstrated long term stability. In addition to this, attempts have been made to form impermeable metal shells on the surface of these emulsions.

Keywords: Microcapsules, Emulsions, Pickering, Composite, Anisotropy



Figure 1. Hexadecane in water emulsion stabilized by SDS, PtNPs and polypyrrole.

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Role of Alkyl Tails on the Structure and Photoswitching Ability of Arylazopyrazole Sulfonate Surfactants at Air-Water Interfaces

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Interfaces that can change properties and are responsive to triggers such as light are of great interest for the development of responsive materials. One example is the use of photoswitches such as alkyl-arylazopyrazole sulfonates (C_n AAPC₄S) that undergo E/Z photoisomerization when irradiated with green and UV light. Using butyl-AAPC₄S surfactants we have previously demonstrated large changes in surface tension at air-water interfaces with light irradiation, which were attributed to a monolayer to bilayer phase transition of the butyl-AAPC₄S moieties at the interface [1].

In order to address these remarkable changes of butyl-AAPC₄S surfactants at the air-water interface and to associate the changes to molecular structure motives of the surfactant, we have synthesized two new C_n AAPC₄S surfactants where the butyl chain is exchanged by an octyl chain or simply by hydrogen. Surface tensiometry reveals that the alkyl chain length influences the surface activity drastically, as expected, but also the ability of the surfactants to change the surface tension γ when switched from the E to the Z state strongly depends on the alkyl tail. The highest changes in γ are observed for the C₄AAPC₄S ($\Delta\gamma \sim 27$ mN/m), while the ability to change γ upon light irradiation is reduced to ~ 20 and even to < 10 mN/m for octyl and H residues. Using vibrational sum-frequency generation (SFG) we provide molecular-level information of the surfactants at the air-water where we have addressed the interfacial composition as well as the molecular order of the surfactants. From a comparison of the SFG amplitudes of S-O (head) and C-H bands (tail) with the surface excess from neutron reflectometry, we provide qualitative information on orientational changes of the surfactants at the interface. Experimental results are then complemented by a comparison with ultra-coarse-grained simulations where properties of the individual surfactants like its surface activity or intermolecular interactions can be adjusted to closely reflect the experimental situations.

Keywords: air-water interface, photo-responsive, SFG spectroscopy, neutron reflectometry, ultra-coarse-grained simulations

Acknowledgements: We gratefully acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project-ID 433682494-SFB 1459. We also thank the ILL for allocations of neutron beam time on FIGARO (DOI: 10.5291/ILL-DATA.9-12-652 and 10.5291/ILL-DATA.9-10-1573).

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The structure and dynamic composition of lipid reservoirs mediated by lung surfactant protein-B at low surface tension

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Infant respiratory distress syndrome (IRDS) is an acute condition suffered by premature babies who have suppressed amounts of lung surfactant protein SP-B. The protein functions by nucleating lipid reservoirs at the air/water interface as the surface of the lungs is compressed during expiration, allowing lipid confined close to the surface monolayer to spread rapidly and maintain very low surface tension during inhalation, avoiding lung collapse. Important aspects of the structure, morphology and mechanism of lung surfactant reservoirs remain unknown due to the extreme experimental challenge of resolving structures at fluid interfaces under dynamic physical conditions near-zero surface tension that mimic respiration. Our recent work builds on data where an SP-B analogue called Mini-B modulates lipid squeeze out from the surface monolayer at near-zero surface tension during surface area compression in lung surfactant models comprising the saturated lipid DPPC with different unsaturated lipids. Using neutron reflectometry, we have exploited a novel structural dynamic analysis to elucidate the lipid component squeezed out near-zero surface tension thanks to selective deuteration of components in different lung surfactant models in the absence and presence of Mini-B. Furthermore, off-specular neutron scattering shows that the interface exhibits macroscopic buckling only when phosphatidylglycerol is present in the membrane model, which is supported by fluorescence microscopy. Complementary reflectometry studies have been performed using ellipsometry and Brewster angle microscopy to probe different medial and lateral length scales of the 3D structures and morphologies formed upon monolayer collapse. Excitingly, this research leads onto work on more advanced lung surfactant models incorporating cholesterol and SP-C into the interfacial matrix to elaborate the key characteristics that stimulate dynamic reservoir formation at near-zero surface tension. Our new approach has the potential to form a diagnostic suite of techniques to screen new synthetic additives and therapies in formulations to treat babies born with IRDS.

Keywords: lung surfactant, infant respiratory distress syndrome, neutron and optical reflectometry, diagnostic techniques suite

Durotaxis of Passive Nanoparticles on Elastic Membranes

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Transporting macromolecules and nanoscopic particles to a target cellular site is a crucial aspect in many physiological processes, such as cellular signalling and trafficking. This directional motion must be ensured even across membranes and is generally controlled via active mechanical and chemical processes. In this contribution [1], we show by means of molecular dynamics simulations and an analytical theory that completely passive nanoparticles can exhibit directional motion when embedded in non-uniform mechanical environments.

Specifically, we study the motion of a passive nanoparticle adhering to an elastic membrane with a gradient in bending rigidity. As a function of rigidity, we observe a non-trivial adhesion affinity of the particle to the membrane, which is non-monotonic and is correlated with preferential localisation in regions of precise stiffness. We measure and account analytically for the combination of adhesion, bending and entropy: the consequent free energy imbalance results in transport of the particle, that, depending on the values of the involved rigidities, can be both up or down the rigidity gradient (corresponding, respectively, to positive and negative durotaxis). This behaviour is retained when the membrane is crowded with several nanoparticles (Fig. 1), suggesting that rigidity gradients can guide the accumulation of passive macromolecules in areas of preferred mechanical properties, and possibly sort them according to their size and adhesion properties.

We propose that this novel physical mechanism can contribute to transport across membranes with heterogeneous elasticity, be the heterogeneity due to their chemical composition or to underlying cytoskeletal processes. Such membranes have been widely observed in living beings and are thought to fulfil key, yet ill-understood, biological functions.

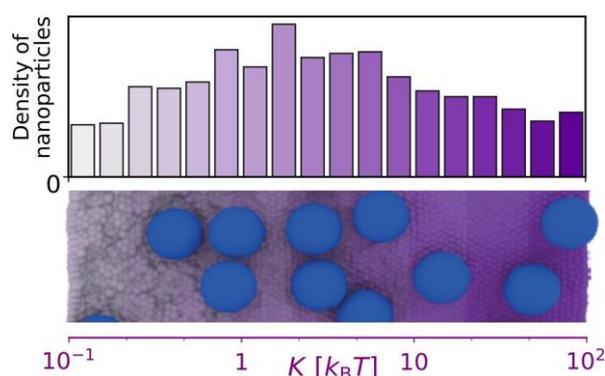


Figure 1. A membrane with a gradient in bending rigidity K is crowded with identical adhesive nanoparticles. These accumulate in regions of preferred rigidity $K \sim 2 k_B T$.

Keywords: membranes, rigidity gradients, transport, molecular dynamics

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Interaction of Surfactants With Phospholipid Vesicles: Mechanism of Membrane Disruption

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The recent pandemic caused by COVID-19 has put to the test the current disinfection technologies. The challenge is the development of new virucidal formulations that are less expensive and more environmentally friendly. Surfactants are frequently components of disinfectant formulations. As such, they could be used in aqueous solution to inactivate viruses (especially enveloped viruses).

We investigated the interactions between archetypal surfactants and lipid membranes, in order to understand the mechanisms underlying the possible inactivation of the virus. We have used negatively charged Small Unilamellar Vesicles (SUVs) to simulate the negatively charged viral envelope and surfactants (commonly found in commercial formulations) with different electric charges: anionic (Sodium Dodecyl Sulphate), cationic (Cetylpyridinium Chloride) and non-ionic (C10EO8).

We used both Dynamic and Electrophoretic Light Scattering to study variations in size and surface charge of the vesicles. These measurements allow the detection of the minimum surfactant concentration that has effect on the vesicles. By means of both Fluorescence Spectroscopy and Fluorescence-Lifetime Imaging Microscopy, we have also examined the effect of surfactants on the integrity of the membranes, using a fluorescence approach based on the self-quenching of highly concentrated calcein entrapped inside phospholipid vesicles. Surfactant induced changes in permeability or breakdown of vesicles allows calcein “leakage” causing an increase in fluorescence intensity.

Irrespective from the chemical nature of the surfactant, SUV membranes start to be challenged by surfactants at concentrations around their CMC. Our results show that the rate-determining step for the permeabilization of the lipid bilayers is not the electrostatic interaction between surfactants and SUVs but the energetic cost of surfactant molecules flip-flop through the lipid bilayer.

Keywords: surfactant, lipid vesicles, calcein, DLS, Fluorescence

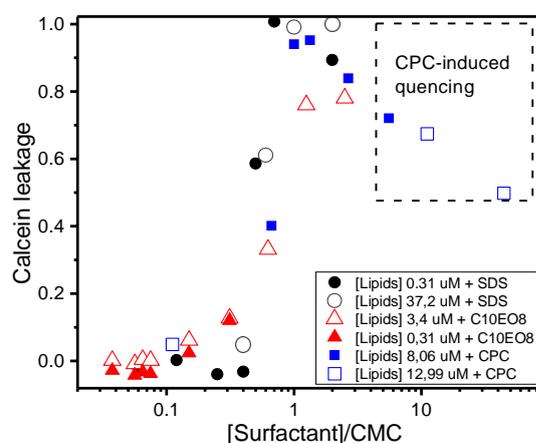


Figure 1. Calcein leakage vs [surfactant]/CMC ratio.

Foam coarsening in a viscoelastic medium

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Foams are dispersions of gas bubbles in a continuous phase, that can be solid or liquid. As a form of matter, they exhibit unusual mechanical properties based on their typical cellular structure and the rearrangement dynamics of the bubbles. Combined with their lightness and high interfacial area, this makes them interesting for many industrial applications.

However, a primary concern regarding liquid foams is their stability, as drainage, coalescence and coarsening may alter their internal structure, causing foams to destabilise over time. This destabilisation, leading to inevitable foam damage, raises industrial issues regarding their longevity and requires a better understanding of foam stability. We are interested in foams with viscoelastic continuous phases, where the continuous matrix significantly modifies the coarsening process.

We study the impact of the mechanical properties of the continuous medium on the bubble pattern evolution during the coarsening process. The continuous phase of the foamed emulsions is concentrated oil-in-water emulsions which, at high oil droplets concentrations, are elastic. We thus vary the elasticity of the foamed emulsion continuous phase by adjusting the emulsion oil fraction. In order to neglect both drainage and coalescence, we study foamed emulsion coarsening in quasi-2D foam systems, where we follow the foam structure over time. The balance between Laplace pressure, that drives the coarsening process, and elasticity of the emulsion, which hinders it, is influenced by the foam structural parameters, which we modify through the liquid fraction.

We show that the viscoelasticity of the continuous phase strongly influences the evolution of foamed emulsions, causing the bubble growth rates to slow down. We also show that increasing the viscoelasticity of the continuous phase results in a spatially heterogeneous coarsening. This deeply affects the foam structure, as peculiar bubble patterns, quite distinct from what we usually observe, appear.

Keywords: foams, emulsions, coarsening, elastocapillarity

Small-Angle and Inelastic Neutron Scattering from Polydisperse Oligolamellar Vesicles Containing Glycolipids

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Glycolipids are known to stabilize biomembrane multilayers through preferential sugar-sugar interactions that act as weak transient membrane crosslinkers [1, 2]. We use small-angle and inelastic neutron scattering on oligolamellar phospholipid vesicles (see Fig. 1) containing defined glycolipid fractions in order to elucidate the influence of glycolipids on membrane mechanics and dynamics.

Small-angle neutron scattering (SANS) reveals that the oligolamellar vesicles (OLVs) obtained by extrusion are polydisperse with regard to the number of lamellae, n , which renders the interpretation of the inelastic neutron spin echo (NSE) data [3] non-trivial. To overcome this problem, we propose a method to model the NSE data in a rigorous fashion based on the obtained histograms of n and on their q -dependent intensity-weighted contribution. This procedure yields meaningful values for the bending rigidity of individual lipid membranes and insights into the mechanical coupling between adjacent membrane lamellae, including the effect of the glycolipids.

Keywords: biomembranes, neutron scattering, membrane dynamics, membrane mechanics

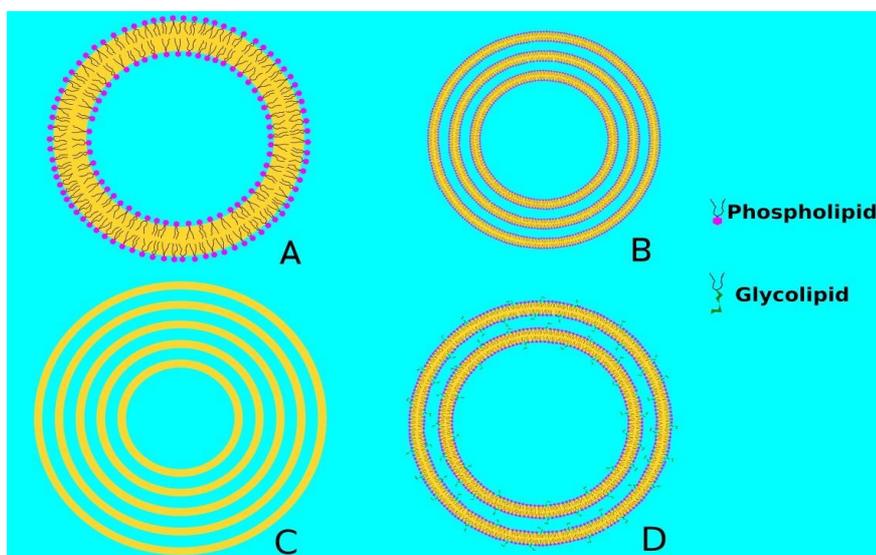


Figure 1. Schematic illustration of polydisperse oligolamellar vesicles. (A) With number of lamellae $n=1$. (B) Larger vesicle with number of lamellae $n=3$. (C) Large vesicle with $n=5$. (D) Vesicle with glycolipids

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“Double Pickering stabilization” of water-in-oil (W/O) emulsions using biocompatible particles

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In recent years, there has been a resurgence of interest in Pickering emulsions because of the recognition of the unique high steric stabilization provided by particles at interfaces. This interest is particularly keen for water-in-oil (W/O) emulsions because of the limited range of suitable Pickering stabilizers [1-3]. We demonstrated for the first time that W/O emulsions can be stabilized by using crystals from naturally occurring polyphenols (curcumin and quercetin particles) [4]. We also demonstrated that Pickering stabilization of water droplets using polyphenol crystals (quercetin or curcumin) when complexed with a biopolymer such as whey protein isolate (WPI) allowed incorporation of up to 10 wt% water into the oil continuous phase [5-6]. Here, we report a novel “double Pickering stabilization” of water-in-oil (W/O) emulsions, where complex formation at the interface between Pickering polyphenol particles adsorbing from the oil side and whey protein microgel (WPM) particles co-adsorbing from the aqueous side of the interface is investigated. The interfacial complex formation was strongly dependent on the concentration of WPM particles. At low WPM concentrations, both polyphenol crystals and WPM particles are present at the interface and the water droplets were stabilized through their synergistic action, while at higher concentrations, the WPM particles acted as “colloidal glue” between the water droplets and polyphenol crystals, enhancing the water droplet stability for more than 90 days and prevented coalescence. Via this mechanism, the addition of WPM up to 1.0 wt % gave a significant improvement in the stability of the W/O emulsions, allowing an increase to a 20 wt % water droplet fraction. The evidence suggests that the complex was probably formed due to electrostatic attraction between oppositely charged polyphenol Pickering particles on the oil side of the interface and WPM Pickering particles mainly on the aqueous side of the interface. Interfacial shear viscosity measurements and monolayer (Langmuir trough) experiments at the air–water interface provided further evidence of this strengthening of the film due to the synergistic particle–particle complex formation at the interface.

Keywords: colloids; organic crystals; Langmuir trough; microgel; particle-stabilization; polyphenols

Acknowledgements: The Engineering and Physical Sciences Research Council (EPSRC) funded Centre for Doctoral Training in Soft Matter and Functional Interfaces (SOFI), Grant ref no. EP/L015536/1, as well as Nestlé PTC Confectionery (York, U.K.) are acknowledged for financial support for this work.

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Towards Rapid Prototyping Of Graded Macroporous Polymer Foams

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Graded polymer foams (GPFs) are found in various natural and technical materials because they combine unique thermal, acoustic and substantial mechanical properties while being lightweight. Their versatile properties are particularly sought-after in applications like interfacial tissue engineering (ITE). For example, an ITE scaffold connecting cartilage and a bone requires a gradient in the Young modulus from 100 kPa -1500 MPa [1]. Such a gradient could be implemented by GPFs if local structural finetuning is enabled by the manufacturing technique.

Conventionally, GPFs are produced by reaction injection moulding, for example, although this technique does not provide control over the actual pore size and the direction of the gradient. In contrast, foam templating using microfluidics allows adjusting GPF parameters like the pore size or the degree of polydispersity with ease. Moreover, it can be scaled to liter per hour production rates [2-4]. However, only spherical structures with sizes limited to roughly 100 – 1000 µm are attainable. Costantini et al. [5] introduced a PDMS chip to formulate gradient foams with controlled bubble sizes spanning one order of magnitude in real time. Conversely, additive manufacturing of GPFs using two-photon-polymerization or stereolithography (SLA) offers tantalizing avenues due to extensive design space freedom. Nevertheless, sequential fabrication puts stringent limits on suitable fabrication volumes.

This work seeks to establish a combined microfluidic SLA 3D-printing approach for the synthesis of GPFs to combine the advantages of both techniques. For this purpose, ultracompact 3D microfluidic engineering [6] will be tailored for rapid foam production rates, increased bubble size ranges, as well as precise local foam property control. The morphology and the mechanical properties of the resulting GPFs are studied and compared. Our approach will expand the scope of designing innovative functionally graded materials for tissue engineering, energy absorption, or insulation applications.

Keywords: Functional graded polymer foams, Microfluidics, 3D-Printing

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pH-responsive emulsions from self-assembled amphiphilic bottlebrush copolymers

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Amphiphilic bottlebrush block-random copolymers are composed of acrylic acid and n-butyl acrylate polymer units to achieve dynamic self-assembly properties [1,2]. As a result, these polymers exhibit a behavior that can be tuned with an external stimulus, in this case a change in pH. In this work, we highlight the possibility to use these polymers to prepare pH-sensitive emulsions with controlled polydispersity and size.

Depending on their ionization degree, the polymer chains self-assemble into micelles which can be seen as polymer nanoparticles. This molecular-to-“nanoparticles” transition results in a different ability to stabilize oil/water interfaces. Indeed, at high ionization degree, amphiphilic polymer chains behave as polymeric surfactants and are efficient to stabilize emulsions, but with a poor stability. On the other hand, at higher ionization degree the polymer is aggregated into nanoparticles which can adsorb irreversibly at interfaces according to the Pickering mechanism [3], resulting in more stable emulsions with a higher energy input to achieve emulsification. The obtained emulsion drop size shows a dependence on the polymer concentration, a phenomenon which is known as limited coalescence [4]. The changes in size and polydispersity which are observed are very well related to the state of aggregation of the polymer. Besides, the type of emulsification device (microfluidizer, rotor-stator) also plays a role on the characteristics of the emulsion. Finally, the particles adsorption at the interface can be studied by tensiometry.

Keywords: Copolymers, Self-assembly, Emulsions, Pickering, Limited Coalescence

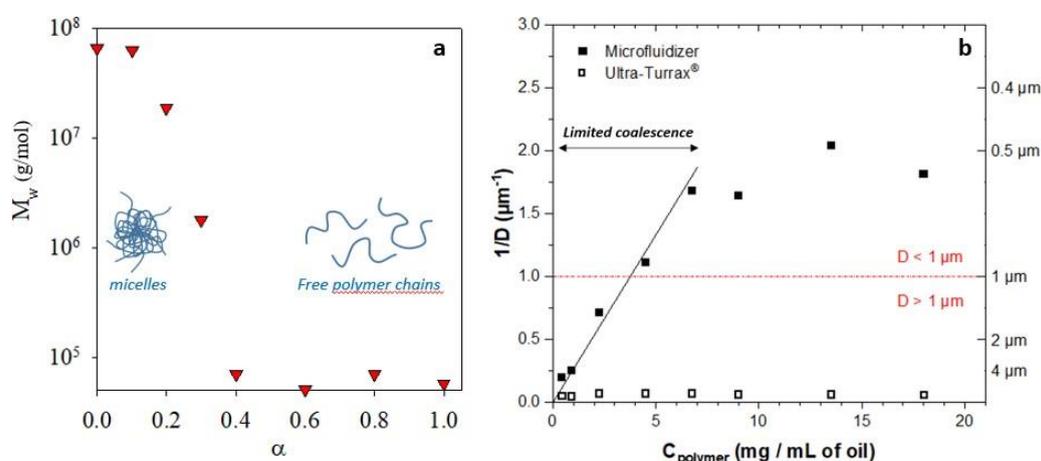


Figure 1. (a) Polymer aggregation as a function of the ionization degree α . (b) Relationship between the size ($1/D$) and the polymer concentration in a 10%vol dodecane-in-water emulsion prepared with two emulsification devices.

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Self-assembly of phospholipid systems at drying interfaces

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Land-living organisms face the challenge of drying out as the ambient air is drier than the interior of living cells. In nature, the interfacial layers have developed different strategies to prevent water evaporation and potential threat of drying out. For example, skin and alveolar interfaces of our lungs are covered with self-assembled lipid-protein structures which respond to the outer environment. [1-4] The overall goal of this study is to investigate the interfacial lipid-film formation in non-equilibrium conditions where the lipid film is maintained in controlled water gradient. We focus on the structural and compositional characterization of lipid model systems composed of non-evaporating components (lipid mixtures or mixtures of lipids and solutes) in water. In particular, we investigate if the water gradient may induce formations of other gradient in the systems. The distribution of lipid and solute components at the drying interface may result formation of new self-assembly structures which are not formed in equilibrium conditions of the same system. We use microfluidic capillary set-up [5] to strictly control boundary conditions and we characterize the interfacial layers as well as composition gradients by using X-ray scattering, Raman and light microscopy. As model systems, we mix phospholipids with different headgroup and hydrocarbon tail ratios, as well as add glycerol, which may act as osmolyte and protect self-assembled system against drying out conditions. In all cases, we observe that the formation of multilayer structures at the interface was associated with the compositional gradients of the lipid and solute components. Based on Raman data for the compositional gradient combined with X-ray scattering data in both non-equilibrium and equilibrium conditions, we can further analyze how water evaporation pushes the interfacial phases out of the equilibrium structures due to formation of multiple interfacial gradients.

Keywords: lipid film, air-water interface, self-assembly, non-equilibrium, Raman microscopy, X-scattering, microfluidics.

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Lightweight wood materials templated by wet foams

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Colloids assembled as lightweight materials, such as solid foams and aerogels, can absorb mechanical, sound, and heat energies very efficiently, with distinct performance over their respective condensed materials [1]. Polymer foams are typically produced by incorporating a gas phase in polymer fluids during synthesis (*e.g.* polyurethane (PU) foams) or in molten plastics (*e.g.* polyolefin foams) [2-3]. As wood cannot be processed as a fluid, we propose a route to prepare wood foams by oven-drying aqueous foams. The characteristic instability of wet foams was overcome by combining wood particles with poly(vinyl alcohol) (PVA) and sodium dodecyl sulphate (SDS), which reinforced the wet structure and enabled the foam to be dried without collapse. To assemble wood particles without chemical refining, PVA was added as a binder, holding the components together in a composite structure with dimensional stability. The wet foams were oven-dried, creating a lightweight material (0.13 g/cm³) with thermal conductivity (0.042 W/mK) close to PU foams and within the range of performance measured for nanocellulose gels and foams (0.013 - 0.075 W/mK) [4]. The wood foams could be fully recycled by re-dispersing and re-foaming the components in water, producing foams with the original density and performance. Foam recyclability without further processing was possible by dismantling water-soluble supramolecular structures of PVA and SDS. This route to produce lightweight solid structures from aqueous foams opens new opportunities for the creation of cellular bio-based materials by assembling particles and colloids at the air/water interface. Moreover, the application of water-soluble colloids allows for recovering pristine components and reassembling them into new structures, overcoming plastic disposal issues.

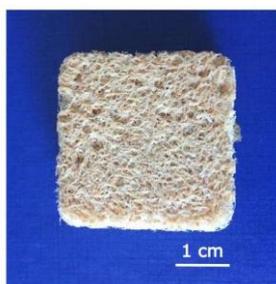


Figure 1. Wood foam prepared from aqueous wet foams.

Keywords: lightweight material, foam, wood, aqueous foam

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Mechanism of spontaneous emulsification at surfactantless liquid/liquid interfaces

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Conventional interface between two immiscible electrolyte solutions (ITIES) may undergo spontaneous emulsification without external polarization. It has been demonstrated that ITIES possessing a common-ion distributed between the both phases can form stable water-in-oil emulsion [1]. The first step in this process is the ion-pairs formation of a hydrophilic anion dissolved in the aqueous phase and a hydrophobic cation in the organic phase. Formation of ion-pairs is a driving force of the process. It decreases the equilibrium concentration of hydrophilic anions in the organic phase, enhancing thus their extraction from the aqueous phase. The extraction of anions proceeds as an electroneutral process where the transfer of anion is accompanied by the transfer of a common cation.

In this study we demonstrate that even in the absence of a common ion and without external polarization an intensive extraction of chloride ions from the aqueous phase occurs. To elucidate the mechanism of the chloride ions extraction and formation of ion-pairs clusters the open circuit potential (OCP) and potentiostatic pulses (PP) were employed in a four-electrode cell with ITIES. The electrochemical system under study comprises lithium chloride (LiCl) dissolved in the aqueous phase and bis(triphenylphosphoranylidene)ammonium tetraphenylborate (BATPB) in the organic phase. It has been found that the electroneutral extraction of chloride ions from the aqueous phase is accomplished by the transfer of TPB anion in the opposite direction. The both transfer reactions of anions are accompanied by the transfer of the cation BA. It makes them electroneutral and independent on each other.

Keywords: Liquid/liquid interface; Water clusters; Extraction.

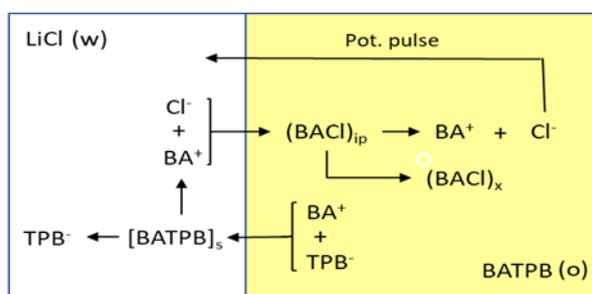


Figure 1. Cartoon depiction of the mechanism of interfacial processes at ITIES which leads to the formation of ion-pairs in the organic phase and their agglomeration into large clusters.

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Investigation of the Biophysical Interaction of Gold Nanoparticles of Different Geometries with Model Cell Membranes

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The cellular delivery of drugs and biomolecules is one of the focuses of interest in biomedical and pharmaceutical area. Recently, the development of biocompatible nanocarriers suitable for the cargo delivery into the cells is seen as a challenging yet exciting subject. Inorganic nanoparticles are seen as the promising nanomaterials that can be used for drug delivery due to their high functionality, high cell-targeting potential and adjustable geometry. Among metallic NPs, gold nanoparticles (AuNPs) are widely preferred, especially in biomedical applications due to their biocompatibility and bio-sensing ability [1]. It is well-known that the surface functionality is of vital importance in possible applications where AuNPs will be used. Besides that, even though the studies are very limited about that issue, the geometry of the AuNPs is also a significant parameter which can define the biophysical interaction of NPs with biological environments. Therefore, the effect of particle geometry on AuNP-cell interaction should be well understood, especially for the applications such as delivery of active pharmaceutical agents.

In this study, it's aimed to investigate the biophysical interactions and cellular uptake capacities of AuNPs of different geometries with the model membranes formed by Langmuir-trough (Figure 1). For this purpose, the variation of surface pressure (π) of lipids at the air-buffer interface with AuNPs injected from the subphase was investigated with time. In addition, the π -Area isotherms were collected and the cellular-uptake capacity of AuNPs into the model membrane was investigated. To get better understanding about the change in π , AuNPs interacting with the monolayer were visualized via AFM and TEM. The results show that AuNP geometry significantly affects its biophysical interaction with model membranes. In addition, the interaction studies were repeated with two different membranes (DPPC/endothelial model membrane) to reveal the role of the compositions of model systems used to mimic the cell membrane.

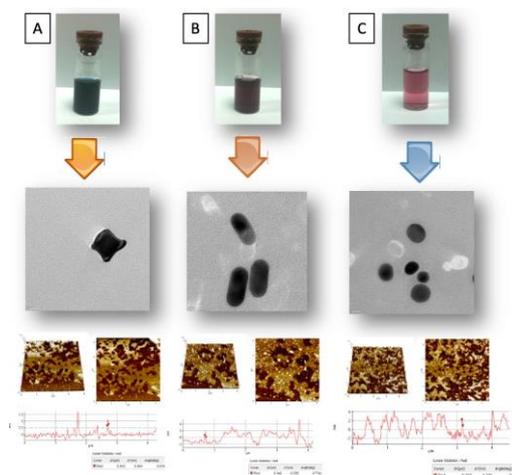


Figure 1. TEM and AFM images of A) cube, B) rod and C) sphere AuNPs

Keywords: Gold nanoparticles, biophysical interaction, endothelial model membrane, DPPC, rod AuNPs, cube AuNPs

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Essential oil micro and nanoemulsions formation, assisted by food grade preservatives

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Essential oils are a key ingredient in foods, beverages, personal care and home care products of various kind. Essential oils are often incorporated as micro or nanoemulsions to lower product costs and to achieve optimal delivery of a scent or a flavor, as well as to enhance their antimicrobial and antifungal activities.

In the current work, we study the formation and stability of micro and nanoemulsions originating from 8 different essential oils and 4 traditional food grade preservatives. Following our previous work [1], we prepared emulsions with lavender, chamomile, yarrow, melissa, tea tree, lemon, orange and rose oils in presence of citric acid, sodium citrate, potassium sorbate and sodium benzoate. Stable transparent nanoemulsions of lemon, lavender, melissa, rose and tea tree oils are formed when citric acid and sodium citrate present in the solutions. Model experiments revealed that bicontinuous phase is formed, which incorporates the essential oil upon heating and facilitates the formation of nanoemulsions upon rapid cooling of the mixture.

Keywords: essential oils, nanoemulsions, microemulsions.

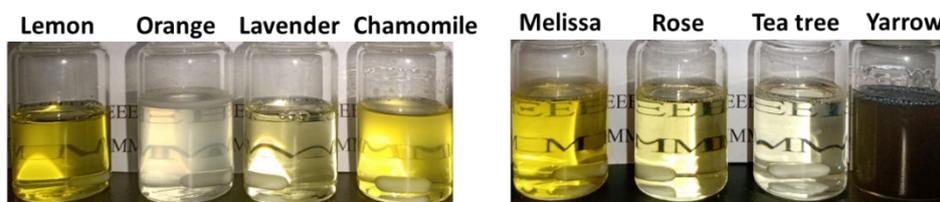


Figure 1. Pictures of emulsions containing different essential oils, stabilized with Tween 60 in presence of 40 % citric acid + 4.72 % sodium citrate.

Acknowledgements: This work was supported by Operational Program “Science and Education for Smart Growth” 2014–2020, co-financed by European Union through the European Structural and Investment Funds, Grant BG05M2OP001- 1.002-0012 “Sustainable utilization of bio-resources and waste of medicinal and aromatic plants for innovative bioactive products”.

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The interactions of trace amounts of ionic surfactants with saturated/unsaturated PC lipid model membranes

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Nowadays, surfactants are the basic ingredients of cleaning detergents, cosmetics and drug delivery systems. Due to the growing interest in liposomes as carriers for bioactive compounds, numerous studies are carried out in order to develop the liposomal drug delivery system. The beneficial effect of surfactants addition to the liposome suspension arises, among others, from their ability to modify the electrostatic charge of lipid vesicles [1]. However, surfactants influence not only the properties of the bilayer model of biological membranes but also those of the monolayer model [2].

The zeta potential, the surface pressure – molecular area isotherms, the penetration tests and the Brewster angle microscopy technique were used to demonstrate the interactions of the ionic surfactants with the DPPC, POPC and DOPC layers. The Langmuir monolayers and the SUV liposomes were studied. The obtained results showed that the addition of tiny amounts of surfactants affects the properties of model biological membranes due to their incorporation into the lipid membranes. This impact increases with the surfactant concentration, the alkyl chain length of the surfactant and the degree of lipid saturation. Moreover, this effect is greater for the anionic surfactant than for the cationic one of the same alkyl chain length. The π -A isotherms indicates that the ionic surfactant molecules are irreversibly integrated into the PC monolayers.

Keywords: ionic surfactants, liposomes, Langmuir monolayers, zeta potential

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Macro and nanoemulsions stabilized by phospholipids

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Emulsions are predominantly stabilized against coalescence by adsorbing amphiphilic species at oil/water interfaces. While their amphiphilic nature is evident from a biological standpoint, phospholipids are not commonly viewed as efficient surfactants to stabilize emulsions. Still, they are the main stabilizer of parenteral (nano)emulsions, which are used for intravenous nutrition at the hospital. Indeed, the large surface area of a nanoemulsion requires a large amount of stabilizer, which must then be innocuous. In this respect, phospholipids are advantageous compared to common surfactants. Nevertheless, these formulations are extremely sensitive to composition adjustments such as oil and lipid mixtures used, which calls for a mechanistic understanding in order to rationally choose composition.

Here, we unveil how oil and lipids intermolecular interactions and self-assembly control emulsion metastability, both for macro and nanoemulsions. To this purpose we probed the phase behavior of lipid/oil/water ternary systems, characterized oil/water interfaces with small-angle neutron scattering, quantified lipid location with Raman spectroscopy and assessed emulsion metastability over time with light scattering. We used two purified phospholipids (DOPC and POPC) and two oils (hexadecane, miglyol 812) to uncouple oil/lipid interactions. This systematic study of four model systems evidences all the relevant phenomena taking place when emulsifying and stabilizing these ternary systems. Notably, we highlight that an optimum exists for producing macroemulsions that corresponds to a narrow range of preferred curvature of the lipid layer, of the right sign but not too large. Nanoemulsions are then easily processed via high pressure homogenization and their metastability is enhanced by increasing preferred curvature. Therefore, the whole emulsification process can be rationalized and an adequate formation chosen based on measurable quantities. This opens interesting prospects for both the initial application of parenteral emulsions but also for other applications in which phospholipids could be advantageously used to replace common surfactants.

Keywords: emulsions, lipids, curvature, oil, formulation, parenteral

Investigating the ability of an hydrocolloid extracted from *Triumfetta cordifolia* to emulsify and stabilize emulsions

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Emulsions are colloidal dispersions which are thermodynamically unstable because of their high surface energy. Several industries are looking for efficient and sustainable substances capable of stabilizing such systems. Hydrocolloids able to modify interactions at the water/oil interface, are commonly used for this purpose.

This study aims to valorize the hydrocolloid from *T. cordifolia* (Malvaceae) as emulsifying and stabilizing agent in oil-in-water emulsions. The gum consisting of neutral sugars and two uronic acids [1-2] was reported to have an emulsifying and stabilizing activity toward cottonseed oil [1].

In this study, the gum was collected from fresh stem barks harvested in Yaoundé (Cameroon) according to a well-controlled protocol. After physicochemical and rheological characterization, the emulsifying and stabilizing properties of *T. cordifolia* gum were investigated on some low to high polarity oils namely paraffin oil, sunflower oil and myritol 331. Emulsions were formulated at room temperature and characterized using simple methods such as microscopy, lazer granulometry, rheology, and stability monitoring.

Globally, results revealed that *T. cordifolia* has an interesting potential in emulsifying and stabilizing simple oil in water emulsions (figure 1). These properties seem to be enhanced with the gum and fatty phase proportions.

Further characterizations of stabilized emulsions as well as the mechanisms governing the observed properties are in progress.

Keywords: hydrocolloid; *Triumfetta cordifolia* gum; emulsifying property; stabilizing property.



Figure 1. *Triumfetta cordifolia* gum stabilizing an emulsion with water and myritol 331 (80:20).

Acknowledgements: This work was partially supported by the SCAC French government fellowship. We are also grateful to Maëlle MOUZARD, Solène BOURVIER, Léa MARTEL and Camille VILA NOVA, four master's students who have contributed to this work as part of a tutored project.

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UV/Vis Spectroscopy in Distinction of Lipid Bilayers Structural Features

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The most distinctive quantities that describe structural features of lipid membranes are their phase transition temperatures which are usually determined by differential scanning calorimetry (DSC) [1]. Since the turbidity of lipid suspensions changes with temperature, it has recently been shown that UV/Vis spectroscopy can be used not only in the detection of phase transitions but also that low- and high-cooperative phase transitions can be recorded with almost equal sensitivity [2].

In this regard, we have examined suspensions of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) and 1,2-dipalmitoyl-*sn*-glycero-3-phosphoethanolamine (DPPE) in aqueous solution of NaCl ($I = 100$ mM) by temperature-dependent UV/Vis spectroscopy (Figure 1.), DSC and molecular dynamics simulations. Aside the main phase transition temperatures (T_m) of DPPC ($\square 41$ °C) and DPPE ($\square 63$ °C) lipids and pretransition temperature (T_p) of DPPC ($\square 34$ °C), multivariate analysis of acquired UV/Vis spectra of DPPE revealed certain changes in structural features on DPPE multilamellar aggregates about 10 degrees below T_m . Although this phenomenon does not appear in DSC curve of DPPE, the results of MD simulations imply that around this temperature the undulations of DPPE surface reach their maximum, but without formation of a ripple phase (like in DPPC).

The results of this research unequivocally show that full potential of UV/Vis spectroscopy, coupled with appropriate multivariate approach, has yet to show itself in its full light in exploration of lipid bilayers structural features.

Keywords: UV/Vis spectroscopy, lipid suspensions, melting point, surface undulations

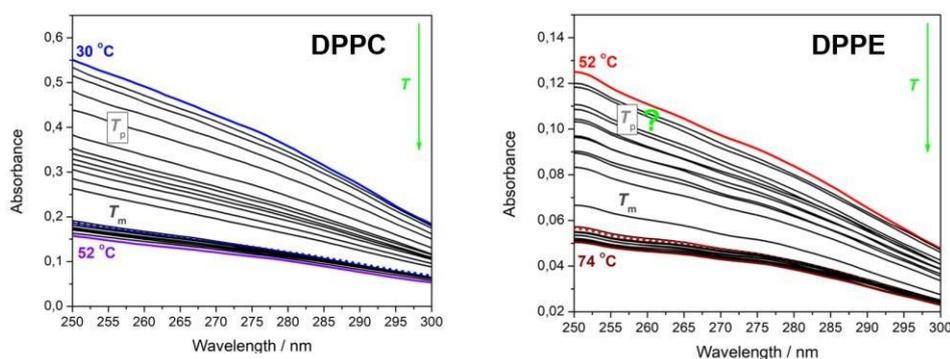


Figure 1. Temperature-dependent UV/Vis spectra of DPPC and DPPE suspension in NaCl ($I = 100$ mM).

Acknowledgements: This article was supported by the Croatian Science Foundation, Project No. UIP-2020-02-7669.

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Two-Dimensional Triblock Peptide Assemblies for the Stabilization of Pickering Emulsions with pH Responsiveness

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A variety of two-dimensional (2D) nanomaterials, including graphene oxide (GO) and clays, has been used to stabilize Pickering emulsions and demonstrate novel functions in the areas of biomedicine, cosmetics, food, etc. Here, we introduce a novel Pickering emulsion using spontaneously self-assembled amphiphilic triblock oligoglycine as the emulsifier. 2D self-assembled peptide amphiphiles are more responsive to environmental changes (e.g. pH, temperature, and ionic strength) than are inorganic 2D materials, which have a chemically rigid, in-plane structure. [1][2] This is because the non-covalent forces between the peptide molecules change with the environment, thereby tuning the self-assembly and corresponding morphology. In this work, we discovered that the oligoglycine, Gly₄-NH-C₁₀H₂₀-NH-Gly₄, self-assembles into a lamellar structure in solution at a neutral pH, according to small-angle X-ray scattering data and molecular dynamic simulations. We found that the 2D lamellar sheets adsorbed at the oil/water interface and stabilized oil-in-water emulsions. Upon reducing the pH, the protonation of the terminal amino groups of the oligoglycine induced structural changes in the peptide assembly that destabilized the emulsion. An unusual emulsion structure in which the oligoglycine stabilizer creates a thick interfacial layer was found after addition to a pH 9.2 buffer. This demonstration opens a new route to use synthetic peptide amphiphiles to stabilize Pickering emulsions, which can be significant for biomedical and pharmaceutical applications.

Keywords: Two-dimensional, peptide amphiphiles, Pickering emulsion, pH response

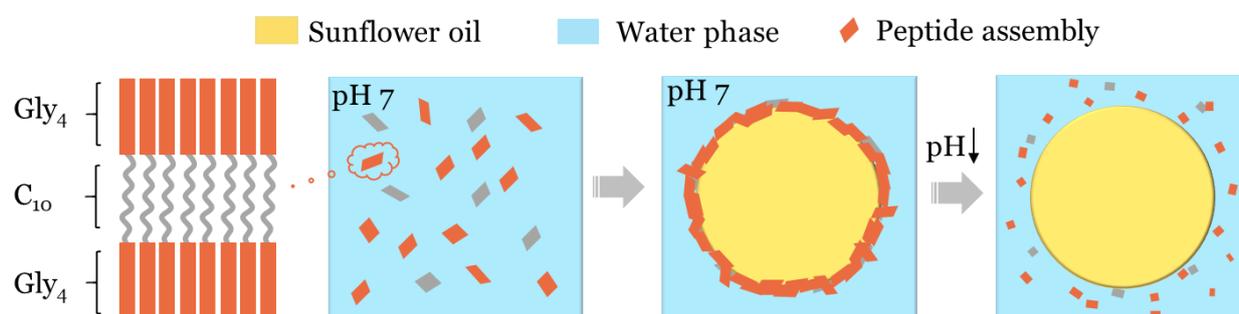


Figure 1. A schematic diagram showing how the peptide assemblies stabilize an oil drop in pH 7 buffer, and how the oil drop is destabilized when the pH is reduced.

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Preparation and properties of keratin foamer

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According to statistics, every year more than 40 thousand tons of wools, hooves and horns are got rid of as waste from slaughterhouse in Republic of Kazakhstan. The thrown away wastes from slaughterhouse such as wool, horn, hoofs cause the environmental pollution and it might be harmful to human's health. The aim of our work is - to synthesize keratin foam formers from this waste material and use it for human needs.

Liquid keratin is most widely known for its foaming ability which is very suitable for firefighting and construction and many other branches of science. As a result of research on the interaction of keratin and a base, a special condition of foaming and temperature has been made. Proteins from the different classes of wool keratins possess characteristics that give them unique advantages in specific applications [1]. Wool and hair are examples of hard α -keratin. All keratins are characterized by a high level of the sulphur-containing diamino-acid cystine, which acts as a cross-linking point between protein chains [2].

The obtained hydrolyzed liquid leveled to pH=6.8 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and some polymers are added to improve the foaming ability and the stability of foam surface tension, and lifetime. Foaming stability is measured in various concentrations of liquid. As a result, the keratin foam showed very good results and its foaming stability lasted for 5 hours. And it's proved that keratin foams which we synthesize can be used for fire-fighting and construction.

We also studied the infrared spectra of samples of hydrolysates. The expected structure of the sample corresponds to the presence of amino acids with a peptide bond. The advantage of this technology is that it is simple, cheaper, and that synthesized liquid has great foaming.

Keywords: environmental pollution, keratin, wool, foaming ability, foamer

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Quantifying the Bromide vs. Chloride Adsorption at Cationic Surfactant Interfaces

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Specific ion effects determine colloidal stability. The efficiency of Dioctadecyldimethylammonium (DODA⁺), a gene delivery agent, differs depending on the counterion, Cl (DODAC) or Br (DODAB) [1]. Here we quantified the preferential (Cl⁻/Br⁻) adsorption in cationic monolayers of DODA⁺ and of the shorter chain analog Dihexadecyldimethylammonium (DHDA⁺) at the air/water interfaces. DHDAC obtained by ion exchange from DHDAB. Pressure/Area isotherms of DHDAC and DODAB measured on aqueous subphases (2 mM) of NaBr, NaCl, or equimolar NaBr/NaCl. Brewster Angle Microscopy images (BAM) were taken. Total- reflection X-ray monolayer fluorescence (TRXF) was performed at the synchrotron beamline Po8 at PETRA III of DESY (Hamburg, Germany). Spectra were analyzed by fitting with multiple Gaussian functions [2]. Solvent-explicit molecular dynamics simulations (NPNyT)(GROMACS 2021.2) of monolayers at saline solution/vacuum interface were performed.

DODAB surfactant monolayer showed distinctive phases depending on the surface pressure, confirmed by BAM images. DHDAC exhibited only single fluid phase under all conditions. For DODAB, the isotherm on the equimolar NaBr/NaCl mixture subphase was similar to that on the NaBr subphase indicating that Br⁻ plays the dominant role in forming the electrical double layer. The x-ray fluorescence of bare salt solutions and that of the monolayer were determined. The fluorescence intensity of the anions increased in presence of the cationic monolayer, and 80% of the counterions at the interface were found to be Br⁻. Several simulation force fields were tested, and only GAFFlipids reproduced the monolayer organization observed experimentally. The simulations qualitatively reproduced the preferential adsorption of Br⁻ compared to Cl⁻ but to a lower extent than observed experimentally.

Experiments and simulations consistently showed that monolayers displaying cationic quaternary ammonium moieties preferentially interact with Br⁻. This preference is independent of the monolayer phase state.

Keywords: Cationic Surfactants, Ion Effect, Monolayers

Acknowledgements: FAPESP, Lichtenberg II cluster TUDa (Project ID 1544)

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Removal of perfluorinated alkyl substances (PFAS) from water using nanofiltration, foam fractionation and photochemical degradation

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Perfluorinated alkyl substances, PFAS, are a group of man-made chemicals used in various products such as aqueous fire-fighting foams (AFFF), water- and oil-repellent textiles; as well as in industrial processes such as fluoropolymer synthesis and electroplating. They are extremely difficult to degrade due to the strength of the C-F bond in their perfluorinated alkyl chains and are also highly soluble in water. Due to the persistence and mobility, they easily migrate and accumulate in water bodies and harm human health and natural ecosystems. In many countries, they are detected in drinking water, soil and food grown on fertilizers containing PFAS residues.

PFAS are typically found in 1-10 ng/L concentrations in drinking waters and at much higher concentrations near industrial facilities where they are produced or used. We aim at an integrated approach where PFAS is removed from the water source and concentrated via a combined nanofiltration-ion exchange process and then degraded under UV light with the Fenton reaction (Figure 1.a). We further aim to enhance the separation of PFAS from other micropollutants in water and its degradation efficiency by using foam fractionation during photodegradation.

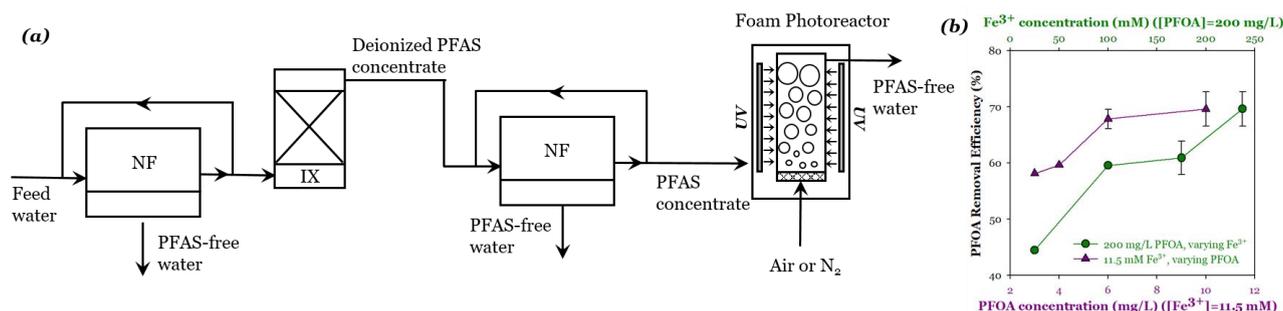


Figure 1. (a) Process scheme of nanofiltration-ion exchange for PFAS removal and concentration, followed by degradation in foam photoreactor, (b) PFOA removal efficiency via foam fractionation as a function of PFOA concentration and Fe³⁺ concentration.

Fractionation of perfluorooctanoic acid (PFOA), a common PFAS, into foam was observed in a 30-cm high column of 4 cm diameter, a diffuser of 25-50 μm pore diameter and at pH=1. The removal efficiency, i.e. the percentage of PFOA mass transferred into the foam, increased from 44% to 70% with increasing Fe³⁺ concentration from 3 to 11.5 mM. At 11.5 mM Fe³⁺, increasing PFOA concentration from 50 to 200 mg/L increased the removal efficiency from 58% to 70% (Figure 1.b).

Keywords: Perfluorinated alkyl substances, foam fractionation, UV-Fenton

Acknowledgements: This work received partial support from the SolarTwins project funded from the European Union's Horizon 2020 research and innovation programme under grant agreement No 856619.

Intraparticle Kinetics Unveil Crowding and Enzyme Distribution Effects on functionality of Cofactor-Dependent Heterogeneous Biocatalysts

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Understanding the interplay between enzymes and cofactors within the confined space of porous materials rationalizes the fabrication of self-sufficient heterogeneous biocatalysts. Multidimensional kinetic analysis of immobilized enzymes is essential to understand the enzyme functionality at the interface with solid materials. However, spatiotemporal kinetic characterization of heterogeneous biocatalysts on a microscopic level and under operando conditions has been rarely approached. As a case study, we selected self-sufficient heterogeneous biocatalysts where His-tagged cofactor dependent enzymes (dehydrogenases, transaminases and oxidases) are co-immobilized with their corresponding phosphorylated cofactors on porous agarose microbeads coated with cationic polymers. These self-sufficient systems do not require exogenous cofactor addition to function, thus avoiding the extensive use of expensive cofactors. To comprehend the microscopic kinetics and thermodynamics of self-sufficient systems we performed fluorescence recovery after photobleaching measurements, time-lapse fluorescence microscopy and image analytics at both single-particle and intraparticle levels^[1]. These studies reveal a thermodynamic equilibrium that rules out the reversible interactions between the adsorbed phosphorylated cofactors and the polycations within the pores of the carriers, enabling the confined cofactors to access the active sites of the immobilized enzymes. This work unveils the relationship between the apparent Michaelis-Menten kinetic parameters and the enzyme density in the confined space, eliciting a negative effect of molecular crowding on the enzyme performance. Finally, through studies at the sub-micrometric level, we demonstrate that the intraparticle apparent enzyme kinetics are significantly affected by the enzyme spatial organization. Hence, multi-scale characterization of immobilized enzymes serves as an instrumental tool to better understand the in-operando functionality of enzymes within confined spaces^[2].

Keywords: protein immobilization, confined kinetics, heterogeneous biocatalysis, polyelectrolytes

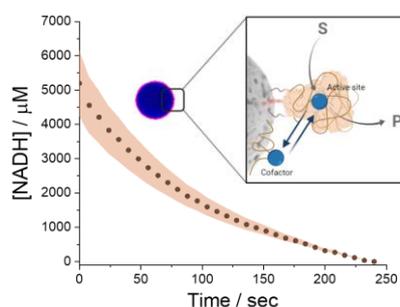


Figure 1. Schematic representation of the real-time enzyme kinetics derived from single-particle analysis of self-sufficient heterogeneous biocatalysts.

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Solvent Modification in (Photo-)Catalysis Regarding Structuring and Solubilization Power

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Catalysis is known to play a crucial role when performing chemical reactions in the sense of Green Chemistry. However, many applications require the use of possibly toxic heavy metal catalysts. In addition, organic solvents are used instead of water due to lacking solubility of reaction components. In order to overcome the problem of solubility, the usage of complex designer surfactants is often the method of choice. Though, their synthesis and recycling are time- and material-consuming, and may not meet the criteria of sustainable chemistry. [1-4] We present different approaches to overcome these problems. By combining physical and organic chemistry with the principles of Green Chemistry, we enable demanding organic reactions in simple green solvent systems.

In our research, we focus on surfactant-free microemulsions (SFMEs) consisting of a green oil, water, and a simple hydrotrope (see Fig. 1, left). Achieving great solubilization power in such systems, they are applied as reaction media for challenging organic reactions that are currently performed in either micellar solutions or organic solvents. In doing so, we can perform Heck reactions as well as, for example, the addition of 3-bromophenylboronic acid to cyclohexenone in green and predominately aqueous systems at room temperature (see Fig. 1, right).

In addition, detailed solubility studies on the organic photocatalyst 1,8:1,4-naphthalenetetracarboxdiimide are part of our research. The metal-free catalyst has a promising redox potential, however, its poor solubility limits applications. By the addition of glucamine derivatives and other amines, we could dissolve the catalyst in water. In addition, solubility and absorbance properties can be adapted by changing pH and by introducing mesoscopic structuring through an SFME. Several C-C coupling reactions are performed in the presence of visible light at room temperature.

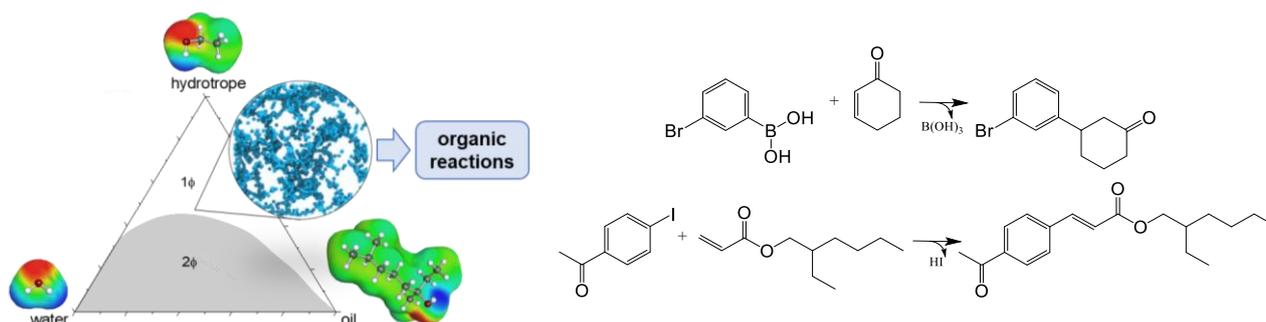


Figure 1: Schematic representation of a ternary phase diagram consisting of water, hydrotrope, and oil with a snapshot from molecular dynamics in mesoscopic structured SFME (left) and reactions performed in green solvents (right).

Keywords: Organic Reactions, Catalysis, Green Chemistry, Surfactant-Free Microemulsions, Mesoscopic Aggregation, Solubilization

Acknowledgments: E. Hofmann thanks the Fonds der Chemischen Industrie (FCI) for her scholarship.

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Innovative antimicrobials from facial steroidal surfactants

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Antimicrobial resistance represents an increasing threat to public health and makes urgent the need for new-generation antimicrobials.

Natural antimicrobial peptides (AMPs) have been widely regarded as a promising solution for fighting multi-drug resistant bacteria, due to their broad-spectral bactericidal activity, rapid killing rate, and a membrane targeted mechanism of action that gives them low susceptibility for developing resistance. Indeed, AMPs adopt a facial amphiphilic structure when in contact with bacterial membranes, by winding into α -helix or β -sheet structures with positive charges and lipophilic groups arranged on opposite sides. This facial amphiphilicity allows AMPs to efficiently bind to negatively charged bacterial membranes and penetrate inside them leading to cell death [1].

In the fight against antimicrobial resistance, the development of new antimicrobials able to reproduce the main structural feature of AMPs, such as peptide amphiphiles (PAs), is a major strategy.

In this work we present the synthesis, physical-chemical properties and antimicrobial activity studies of a new class of antimicrobials obtained by joining the facial amphiphilic skeletons of bile acids [2] to cationic peptides. The influence of structure, net charge, and self-assembly behavior on the antimicrobial activity of these unconventional PAs was investigated through multiple experimental techniques, such as Dynamic and Static Light Scattering, Electrophoretic Mobility, Small-Angle X-ray Scattering, Nuclear Magnetic Resonance, Circular Dichroism, Fluorescence Spectroscopy, cryo-Transmission Electron Microscopy and Quartz Crystal Microbalance with Dissipation measurements. The antimicrobial activity was tested against model bacteria such as Gram-positive *Staphylococcus aureus* and Gram-negative *Pseudomonas aeruginosa* by the broth microdilution assay through turbidimetric measurements, together with direct microscopic count, with very promising results.

Keywords: antimicrobials, peptide amphiphiles, bile acids

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Self-assembled mesostructure in an aqueous dispersion of the drug propranolol hydrochloride: a multi-scale approach combining experiment and simulation

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Some amphiphilic drugs behave like surfactants and self-assemble in aqueous solution when their concentration exceeds their critical micelle concentration (cmc) ¹. Such micellar behaviour can significantly affect the solubility, membrane permeability and ultimately the therapeutic activity of the drug ^{2,3}. In the study presented here, we sought to understand, at the molecular level, the structure of the aggregates formed in aqueous solution by the β -blocker, propranolol hydrochloride (propHCl), and thereby to gain insight into the impact of such phenomena on the drug's therapeutic activity.

Small angle neutron scattering (SANS) in combination with contrast variation and ¹H-NMR were performed for a series of propHCl concentrations to determine the nature of the aggregation and the aggregate structures. Both SANS and NMR indicated that the self-assembly of propHCl is a continuous process, with small aggregates being formed at concentrations lower than the experimentally determined cmc, and which continue to grow above the cmc. SANS experiments also showed that the core of the micelle was dry and composed entirely of naphthalene rings while the shell comprised highly hydrated aliphatic side chains, suggesting that interactions between the aromatic rings provide the driving force for aggregation. This observation was confirmed by the NMR experiments where the chemical shifts of the protons indicated that there was close interaction between the naphthyl moieties. All atom molecular dynamics simulations and the predicted SANS profile obtained from the simulation data were wholly consistent with the measured SANS profile and NMR spectra, confirming that the self-assembly of propHCl is a concentration dependent continuous process, resulting in the formation of core-shell structures and driven by hydrophobic effects and close interaction between the aromatic rings.

Keywords: amphiphilic drug, self-assembly, continuous association, simulation

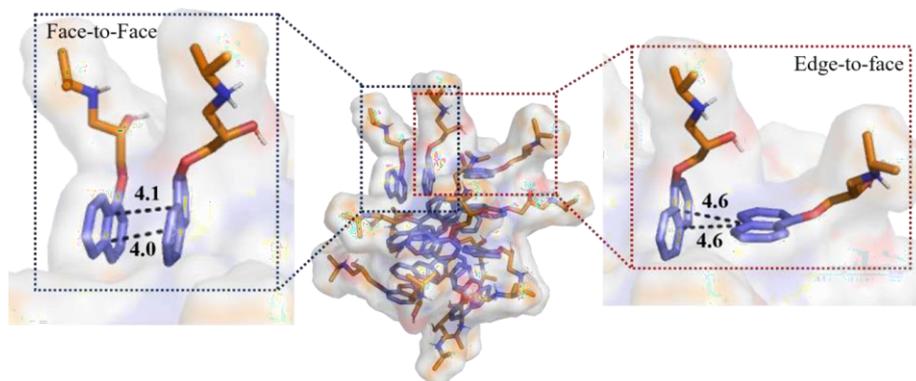


Figure 1. Snapshot of one picked aggregate ($N = 15$) from 200 mM simulation of propHCl.

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Poly(ethylene glycol) as surfactant reduces conformational change of adsorbed proteins on nanoparticles.

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In the nanomedicine field, the surfaces of nanoparticles are always covered by proteins after contact with the biological medium. These adsorbed biomolecules constitute the so-called protein corona and influence on the biological behavior. Initially, it was observed that nanomaterials functionalized with PEG chains showed a generally decrease on protein adsorption promoted by the stealth effect. Further studies suggested that the presence of PEG not only reduces the overall unspecific protein adsorption in blood plasma but can also promote the enrichment of particular proteins.¹ Although the literature has reported information about PEG-protein interaction, more accurate and sophisticated structure and dynamics analysis are needed to understand the interaction processes in detail. This work is focused on studying the PEG-protein interaction using model polystyrene nanoparticles stabilized with the PEG-based surfactant (LutAT50) or a non-PEG-based surfactant, sodium dodecyl sulfate (SDS). The interaction with the most abundant protein in human blood plasma, human serum albumin (HSA), was studied using neutron scattering techniques. The parameters obtained by small angle neutron scattering (SANS) yielded information about the adsorbed protein layer thickness on the angstrom scale. Additionally, via nano differential scanning fluorimetry (nanoDSF) measurements and elastic neutron scattering, structural changes of the protein can be detected. The combination of these techniques gives a better insight into the PEG-protein interaction to contribute to the physico chemical characterization and biological behavior prediction of nanomaterials for medical applications.

Keywords: protein adsorption, PEG, proteomics, nanoparticles, SANS

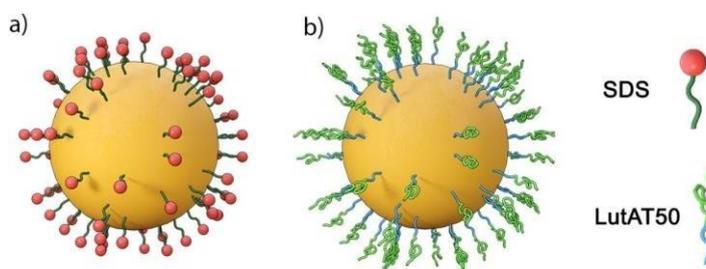


Figure 1. Schematic illustration of surfactant distribution (a) SDS and (b) LutAT50 on of PS-NPs surfaces

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Inhibition effect of statins on HMG-CoA reductase reconstituted in model lipid rafts

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Hypercholesterolemia is associated with a significant health risk - it promotes cardiovascular diseases, such as heart attack or atherosclerosis [1]. The key protein in the process of cholesterol synthesis is 3-hydroxy-3-methylglutaryl coenzyme A (HMG-CoA). It is a liver enzyme located in the membranes of the endoplasmic reticulum (ER) which are rich in cholesterol and sphingolipids forming lipid rafts [2]. Statins are widely used to prevent cardiovascular diseases by inhibiting the catalytic site of HMG-CoA reductase.

The reductase has been reconstituted in the model of lipid rafts (DOPC:Chol:SM) [3,4]. For this purpose the method of proteoliposomes formation was used. Thanks to Langmuir method, dynamic light scattering and fluorescent microscopy methods has been proved effectiveness of HMGR incorporation into the lipid raft system. However, in presented studies, the most important aspect was to obtain a model showing the activity attributed to catalytic site of HMG-CoA reductase. Using the UV-Vis spectrophotometry and linear sweep voltammetry methods based on oxidation of NADPH to NADP⁺ reaction [1], we showed that reductase did not lose its properties in the process of incorporation of the protein into the lipid membrane.

The present studies show the inhibitory effect of the HMGR catalytic site by selected statins (pravastatin, fluvastatin, cerivastatin) using a combination of the above-mentioned methods. It has been shown that the degree of HMGR inhibition depends on the location of the drug in the lipid model, which is closely related to the hydrophobicity of statins [5].

Our experiments allowed us to determine the optimal method of HMG-CoA reductase incorporation into the model lipid rafts. Moreover, we showed the specific nature of interaction of statins with model lipid membranes and, what is more important, that the reconstituted protein can also be inhibited by selected statins.

Keywords: lipid rafts, statins, HMG-CoA reductase, model biological membranes, Langmuir method

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Topical siRNA therapy for diabetic-like wound healing using copolymer-grafted nanodiamonds

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The wound healing delay (chronicity) observed in diabetes mellitus can be triggered via different pathological mechanisms. Targeting these triggers can serve as an efficient tool for the faster treatment of chronic diabetic wounds, which represent a heavy burden on the public healthcare system. Matrix metalloproteinases (MMPs) are responsible for the degradation of damaged extracellular matrix during wound healing, and their increased levels represent one of the known triggers causing chronicity. Currently, the most common treatment of chronic diabetic wounds is based on the affordable conventional dressing (gauzes, hydrocolloids, etc.) with only limited availability to bring the chronicity triggers back to normal levels. The aim of this study is to design bioactive and biodegradable dressing for wound healing, which allows effective topical delivery of siRNA molecules downregulating MMP levels and thus facilitating the wound to heal faster. The presented approach combines the advantages of hybrid electrospun polyvinyl alcohol/poly-ε-caprolactone nanofiber mesh (NF) embedded with copolymer-grafted nanodiamonds (Cop⁺-ND) delivering the siRNA against MMP-9 mRNA in the wound cells – NF{Cop⁺-ND:siRNA} composite. In addition, recently developed cationic copolymer coating (poly{(2-dimethylaminoethyl methacrylate)-co-[N-(2-hydroxypropyl) methacrylamide]}) used for modification of the embedded nanodiamonds was already proven as an effective *in vivo* platform for siRNA delivery [1]. Healing of the wounds (scar formation) for diabetic-like mice treated with NF{Cop⁺-ND:siRNA} composite became comparable with non-treated diabetes-free mice. In other words, the wound delay typical for diabetic-like mice was not observed after application of NF{Cop⁺-ND:siRNA} composite. Thus, the restoration of MMP-9 balance in damaged tissue seems to be a promising way that may ease the translation of topical gene therapy into the clinic.

Keywords: nanodiamond, wound healing, siRNA therapy

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Co-treatment with Daptomycin and Bacteriophage K liposomes realizes superior *in vitro* activity compared to free actives

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The overuse of antibiotics has led to serious resistance, requiring urgent development of innovative treatments. Herein we developed liposomal daptomycin (D-lips) and bacteriophage K (P-lips) [1] and studied *in vitro* activity against *staphylococci*. Thin-lipid film hydration method was used for liposomes; D was measured by HPLC, while P-lips titer was assessed by plaque assay. D-lips and P-lips were characterized for % encapsulation, size distribution and zeta-potential (Zetasizer, Malvern). Antibacterial activity was evaluated in two strains, of *S. aureus* (71406 and 71221) and *S. epidermidis* (9817 and 783). Inhibitory concentration (IC) of free or liposomal actives was determined by microdilution method, and synergistic activity of D and P (free or liposomal) was measured by checkerboard assay [2]. Results were verified with the LIVE/DEAD bacterial viability assay (by FACS). Biocompatibility of liposomal formulations was evaluated in HEK-293 and hCMEC cells (MTT assay). D-lip and P-lip were uniformly sized with high D or P encapsulation. PC/Chol (1:1) D-lips and PC/Chol/Stearylamine (1:1:0.17) P-lips had higher activity compared to free antimicrobials. Encapsulation of D and P in liposomes decreased their ICs by 21% and 47.7%, respectively for *S. aureus* strains, while the reduction for *S. epidermidis* 9817 was ~ 17% and 90%, and for MRSA 783 stain, 40% and 99.7% (Fig.1). Furthermore, synergy was revealed between liposomal forms of antimicrobials for the three strains. Finally, both, D-lips and P-lips were non-cytotoxic at concentrations that completely inhibit bacterial growth. Concluding, the current results are extremely promising, justifying further exploitation of this innovative antimicrobial strategy

Keywords: *Staphylococci*, Daptomycin, Bacteriophage, Liposomes

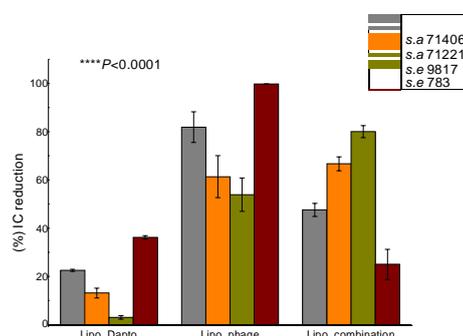


Figure 1. IC reduction (%) of bacteria by D-lips, P-lips and combination compared to free forms.

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The effect of Liposome Preparation Method on Physicochemical Properties and Antimicrobial Activity of Liposomal Moxifloxacin

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Two different liposome (LIP) preparation methods were used, the DRV and the active loading (AL) [1] methods to study their effect on antimicrobial efficacy (AE) of MOX-LIPs. LIPs were compared for MOX encapsulation (EE%), release kinetics, physicochemical properties (DLS, Cryo-TEM, XRD) and antimicrobial efficacy. LIP AE towards planktonic & biofilm bacteria was investigated.

AL method conferred liposomes with higher MOX EE%, that retained MOX for significantly longer periods compared to DRVs. All MOX LIP types (DRV & AL) had spherical morphology in nano-scale (100-150 nm), while most AL liposomal formulations and especially the ones with high EE% revealed some MOX crystallinity (XRD experiments).

Interestingly, AL LIPs demonstrated significantly higher AE towards planktonic *S. epidermidis* growth (Figure A,B) and biofilm susceptibility of the same bacterial strain, compared to corresponding DRV LIPs, indicating the importance of MOX retention in LIPs for their activity.

In conclusion, the liposome preparation method/type determines the rate of MOX release from LIPs and modulates their antimicrobial potential, a finding that deserves further *in vitro* and *in vivo* exploitation.

Keywords: *S. epidermidis*; active loading; DRV; antibiotic; antimicrobial activity; release.

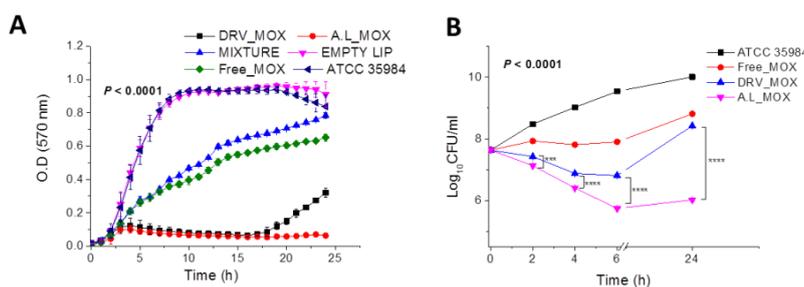


Figure 1. Effect of DRV and AL (MOX) LIPs on *S. epidermidis* Growth (A) and number of colony-forming-units (B)

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Interactions between molecules of oleic and oleanolic acid in the pharmaceutical formulations - physicochemical perspective

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Oleanolic acid (OLA) and oleic acid (OA) are among the natural substances with significant therapeutic potential. Both substances are ubiquitous in the plant kingdom and are components of numerous pharmaceutical formulations. Due to the limited bioavailability of the OLA, nanotechnology-based drug delivery systems (like nanostructured lipid carriers or liposomes) are of particular interest nowadays.

The amphiphilic properties of OLA (a representative of triterpenic acids) and OA (unsaturated fatty acid) enable the use of the Langmuir monolayer technique for the physicochemical analysis of the mixed OLA-OA biomimetic system.

Our research aimed to determine the surface properties (morphology, miscibility, and rheological properties) of OLA-OA monolayers in various molar ratios to finally evaluate the influence of the film composition on the character of intermolecular interactions.

We confirmed that the OLA-OA monolayers exhibit intermediate features compared to pure substances and the surface properties of the mixed systems strongly depend on their composition. We proved that the system with significant domination of OLA over OA is characterized by the best miscibility, due to the attractive intermolecular interactions presence. This, in turn, contributes to the increased monolayer stability. We have formulated a theory that in a system containing a small amount of OA, fatty acid molecules can penetrate between terpenoid molecules, affecting their orientation. On the other hand, the lack of miscibility between the film components in different molar proportions may result from the OA molecules exclusion from the monolayer and, consequently, phase separation [1,2]. This phenomenon causes film inhomogeneity and can make pharmaceutical formulations unstable.

The results obtained may contribute to the development of drug delivery systems and the design of therapeutic systems with optimal properties.

Keywords: mixed monolayers, phase separation, excess free energy of mixing, interface stability

Acknowledgements: This work was financially supported by the National Science Centre, Poland by project no 2021/41/N/ST4/01289.

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Rheological characterization of camphene-based capillary suspensions for bone implants fabrication

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Capillary suspensions represent a newly emerging field but despite their promising capabilities, are still relatively underexplored. They are three-phase systems composed of a solid fraction dispersed in a mixture of two liquids: a bulk fluid and a secondary fluid with a concentration smaller than 4-5%. The liquids are chosen to be immiscible and usually the secondary liquid is chosen to preferentially wet the particles. This liquid forms capillary bridges between individual particles, leading to the formation of a sample-spanning three-dimensional particle network inside the bulk fluid [1]. This particle network can then be used in the formation of porous materials [2].

In the present work, we use capillary suspensions as a favourable precursor for the fabrication of bone implants. The system consists of tricalcium phosphate suspended in camphene to which either a sucrose solution or a nano-suspension of silica are added as secondary liquids. After structuring, bioactive porous implants can be obtained by debinding the camphene and sintering the green body originally made from this capillary suspension. The bioactivity given by the use of tricalcium phosphate is enhanced by the porosity coming from the capillary suspension three-dimensional particle network resulting in encouraging bone reconstruction. The capillary suspension pastes are rheologically characterized to study the network formation and processability as a function of the nature and concentration of the secondary liquid. Processing temperature is also a key parameter where the yield stresses, moduli and performances between 47-60°C are typically of interest (Figure 1). The suspensions prepared with sucrose as a secondary fluid form networks with higher moduli than the ones with silica nano-suspension. The rheological results are also compared to the structure of the resulting ceramic.

Keywords: Capillary suspension, rheology, bioactive implants

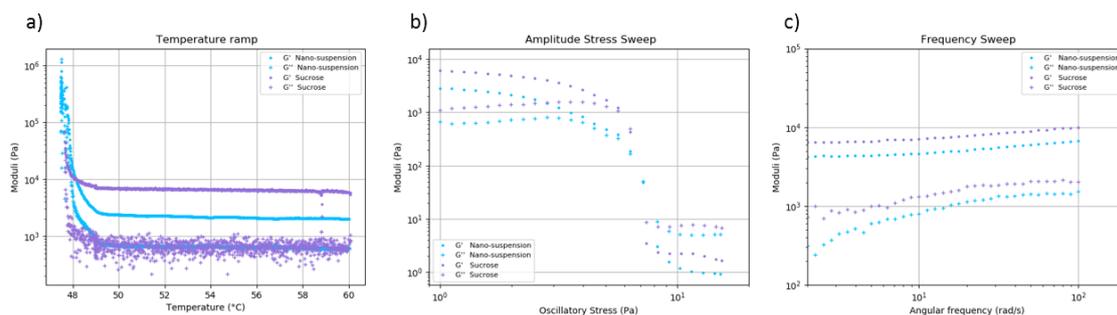


Figure 1. a) Temperature sweep, b) Amplitude sweep and c) Frequency sweep demonstrating the higher strength of the capillary suspension when the sucrose is used over the nano-suspension as a secondary fluid.

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Freeze-dried liposomal formulations loaded with Cefuroxime

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The aim of this study was the development of cefuroxime (CEF)-loaded liposomes (LIPs) for intraocular sustained release. CEF is a cephalosporin antibiotic with limited shelf-life in aqueous solutions¹ and therefore lyophilized forms of these liposomes are required.

Various CEF LIPs were prepared (by microfluidic mixing) with different lipid compositions (both, PEG and non-PEG). CEF encapsulation and particle size/polydispersity were measured (before-FD, BFD), and LIP were submitted to freeze-drying (FD) using sucrose as a cryoprotectant at different suc:lipid ratios. After reconstitution to their initial volume (AFD) changes in particle size and CEF loading were investigated (figures 1A & 1B).

By comparing results from all samples it became clear that PEG presence on LIPs significantly hindered the cryo protective effect of sucrose.

Thereby, a post-PEGylation (PP) protocol was applied after FD, by incubating reconstituted non-PEG liposomes for 30 min and 60 min with PEG-lipid micelles at 37°C; CEF % and size/dispersity of LIPs were measured. In order to verify if this approach could be used for shipping of samples to partner labs post-PEGylated liposomes were stored at 4°C for 60 days and physical (LIP) & chemical (CEF) stability were measured. Approximately 90% of cefuroxime was intact (figure 1C) and only a slight increase in liposomal size and polydispersity index, were noticed.

Keywords: liposomes, lyophilization, antibiotic, cefuroxime, chemical stability

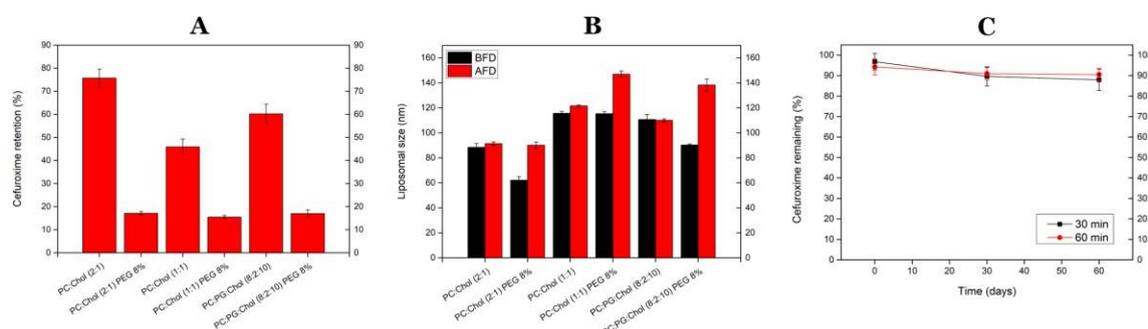


Figure 1. CEF retention from liposomes after FD (A) Liposomal size before and after FD (B) PP-liposomes stability (C)

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Moxifloxacin liposomes prepared by a novel active-loading-microfluidic-mixing method demonstrate increased loading and sustained release kinetics.

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For sustained release Moxifloxacin (MOX) liposomes (lip) as intraocular therapeutics, three methods were compared: the Dehydration-Rehydration (DRV) method [1], the “conventional” Active Loading method (AL) [2], and a newly developed Microfluidic mixing method (MF). Numerous lipid compositions were studied to determine potential effect on MOX loading and release from lips. Vesicles were characterized for drug encapsulation (EE%)/release, and also by DLS, Cryo-TEM and XRD.

All MOX lips had nano-size & spherical morphology, while encapsulated MOX in AL and MF lips, and especially in lips-types with high EE%, revealed some crystallinity (XRD/Cryo-TEM) (Fig1). MF method conferred liposomes with higher/similar MOX EE% compared to AL method, while MOX EE% in DRVs was lower (Fig1A). Furthermore, AL & MF retain MOX more (Fig 1B)

Concluding, a novel MF method for high-MOX-loading and sustained release lips was developed, and also found to have high antimicrobial activity compared to free drug and DRV lips.

Keywords: Liposomes; DRV; Active loading; Microfluidic mixing; antibiotic; encapsulation; release.

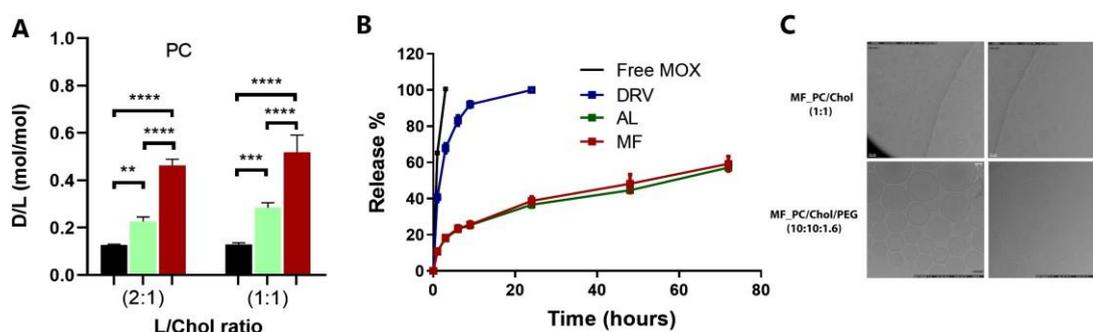


Figure 1. A. Encapsulation (D/L) and **B.** release of MOX from Lips; **C.** Cryo-TEM micrographs

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Electrokinetic, viscoelastic and optical properties of the biocompatible multilayers based on polysaccharides - the impact of the films on the cell adhesion

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Macroion multilayer adsorption on silica was studied by streaming potential measurements (SPM), quartz crystal microbalance (QCM-D), and optical waveguide lightmode spectroscopy (OWLS). Poly(diallyldimethylammonium chloride) (PDADMAC) (synthetic macrocation) and polysaccharides: chitosan (CHIT), of a cationic type, and heparin (HEP), of an anionic type, were used in our studies. Bulk characteristics of the macroions were determined by measuring diffusion coefficients and electrophoretic mobilities for various pHs. These data allowed a proper interpretation of adsorption kinetics of the macroions as well as the multilayer formation from low macroion concentration (5 mg L⁻¹). Periodic variations in the apparent zeta potential between positive and negative values were observed for all multilayer types fabricated. The stabilities of macroion films against time (reaching 48 h) were determined using the SPM. It was demonstrated that in all systems the 6th and 7th layers were considerably more stable, compared to the 1st and 2nd layers. Subsequent adsorption kinetics measurements and in situ multilayer formation were carried out under flow conditions by applying QCM-D and OWLS. The successive adsorption of oppositely charged macroions on silica led to a progressive increase of dry and wet mass of the multilayers. The solvation of the macroion layers was evaluated. The experiments confirm the successful formation of the (PDADMAC/HEP)₅ and (CHIT/HEP)₅ multilayers. The utility of the multilayers in preosteoblast cell attachment was determined. The microscope imaging and microplate analysis revealed that cells adhere the best on the (PDADMAC/HEP)₃ multilayers. It is concluded that the polysaccharide-based multilayers can be considered as versatile systems for medical applications.

Keywords: Polyelectrolyte multilayers, polysaccharide layers, streaming potential, OWLS, resonant waveguide grating, cell adhesion

Acknowledgements: This work was financially supported by the National Science Centre, Poland, Opus Project, 2018/31/B/ST8/03277.

The biological part was supported by the Hungarian Academy of Sciences [Lendület (Momentum) Program], the National Research, Development and Innovation Office (NKFIH) [KKP 129936 and TKP2021-EGA-04 Programs].

Nanomedicines based on Polypept(o)ides

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The enormous potential of polymeric nanoparticles, in particular polymeric micelles, arises from the possibility to combine desirable material properties with compartmentalized functionalities within one distinct system.[1] Synthetic complexity is an enormous hurdle or maybe the major drawback for cost-effective industrial production or clinical translation and can prevent even the most effective polymeric systems from entering the market or becoming approved drugs, since it complicates up-scaling and can affect reproducibility of materials.[2] Therefore, a major task for polymer chemists is –besides the synthesis of new materials– the development of synthetic methods, which intrinsically reduce chemical complexity, while preserving the desired functionalities. With respect to these needs, we have introduced polypept(o)ides (polypeptoid-block-polypeptide copolymers), which can be synthesized by living ring opening polymerization providing precise control over molecular weights, low polymer dispersities and high end group integrities. Furthermore, this class of materials is completely based on endogenous amino acids and combines the stealth-like properties of polysarcosine with the multi-functionality of polypeptides.[3,4] This toolbox enables the synthesis of core cross-linked micelles [5] & nanohydrogels [6], bottlebrush [7] & star-like polymers [8], polymersomes [9] and polyplexes[10]. Either bottom up-synthesis or directed self-assembly provide control over particle morphology and function. Besides, the secondary structure formation of polypeptides can be used to direct the self-assembly process of polypept(o)ides in aqueous solution. The combination of secondary structure directed assembly and functionalities beyond nature's possibilities within these polymers leads to novel materials for a multitude of applications.

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Understanding the toxicity of drug-loaded metal-shell microcapsules.

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Targeted delivery of cytotoxic molecules is vital for the advancement of cancer therapy. Cytotoxic molecules are highly efficient at inhibiting cell growth but have limited use due to their wide distribution in the body once administered [1]. This leads to low dosages used clinically, which therefore tend to have low efficacy and repeated treatments are required. Nanomedicines that provide increased targeting have had little success clinically as they have not shown the expected increased patient prognosis as compared with cytotoxic molecules alone [2]. Encapsulation of the molecules in polymeric capsules or micelles has been explored but often suffers similar dosage issues due to leaching of the cytotoxic molecules, which then affects healthy cells.

Long term retention of small molecules within microcapsules has been shown through the growth of an impermeable gold metal film on a Pickering emulsion core containing the drug to encapsulate [3]. These capsules can be remotely fractured using ultrasound [4] and can be produced using FDA-approved oils as their core [5], which can allow for localised release of the encapsulated cytotoxic drugs within the body. However, before such core-metal shell capsules can be used therapeutically, their toxicity needs to be studied both as the initial colloidal objects and when fragmented with ultrasound to facilitate drug release.

Therefore, this work investigates the toxicity of all aspects of the metal shell capsules, including that of their individual components. Initial in-vitro data show that, at concentrations similar to those that would be used in treatment, there is minimal toxicity from the capsule components. In addition, these studies also suggest that the capsules themselves bear minimal toxicity.

Keywords: Cancer treatment, Encapsulation, Drug delivery

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Scalable Production of Silica-coated Magnetic Nanobeads and their Applications in Viral Diagnostics

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In December 2019, a novel coronavirus SARS-CoV-2 was identified in Wuhan, China that led to a subsequent global pandemic. This led to a massive shortage of RNA extraction kits among others, worldwide, heavily affecting the testing capacity of infected people.[1] To help alleviate the shortage, an interdisciplinary collaboration between the Departments of Chemical Engineering and Clinical & Molecular Medicine led to the development and upscaling of nanoparticle (NP) production, lysis buffer production, extraction protocol optimization and implementation on liquid handling systems for large scale diagnostics. The method was approved for corona virus diagnostics in Norway.[2]

The synthesis of these beads involves a two-stage process, where, in the first step, 10-12 nm iron oxide nanoparticles (IONPs) are synthesized via co-precipitation followed by silanization of the cores using a modified Stober's method, leading to monodisperse nanobeads of 580 ± 25 nm. (Figure 1(a)) The size, morphology and magnetic properties of the silica coated IONPs were optimized by varying the solvent, mass ratio of silica precursor to IONPs, catalyst concentration among other parameters. The optimized protocol was scaled up and this scaled-up process has been licensed to Lybe Scientific A/S, an NTNU based startup that sells these nanobeads under the trade name NAXtra.

Our results demonstrate that NAXtra has a very broad application range, including RNA (Figure 1(b),(c)) and DNA viruses both with protein and lipid layer envelope. Additionally, NAXtra is efficient for extraction of nucleic acids from bacteria and mammalian cells and tissue. In conclusion, NAXtra is a sensitive, robust, fast, simple, flexible and inexpensive method for nucleic acid extraction in research and diagnostics.

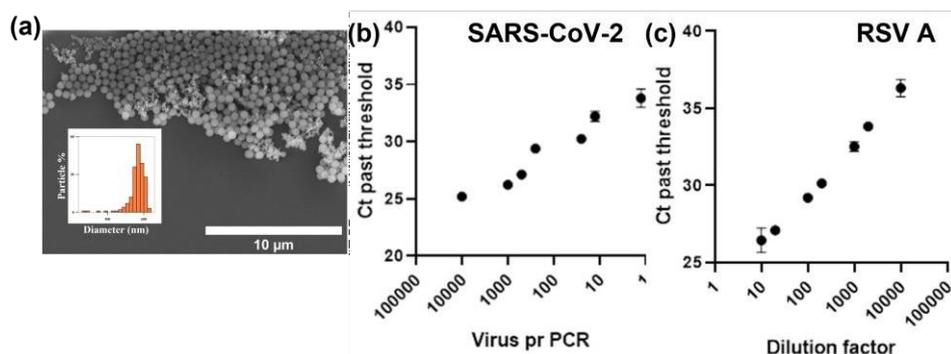


Figure 1. (a) Representative SEM image of NAXtra. (b)(c) Results from NAXtra method on various Qnostics analytical panels. Elution product analyzed on qPCR. Error bars show the standard deviation.

Keywords: Iron oxide nanoparticles, diagnostics, virus, lysis buffer, magnetic nanobeads

Acknowledgements: The authors would like to thank all members of the Corona Project Team that contributed to the production of close to 20 million test kits during the pandemic.

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Surfactant interactions with feline Coronavirus

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The recent pandemic of COVID-19 challenges the current disinfection technologies to a level never afforded before. Surfactants are low-cost chemicals that could be used in aqueous solutions to inactivate viruses (especially enveloped viruses). However, there is a lack of mechanistic understanding of coronavirus inactivation by surfactant molecules. To fill such a gap, we have undertaken a detailed investigation of the interactions between the feline coronavirus (FCoV) and different types of surfactants.

FCoV belongs to the same family of the human SARS-CoV-2, Coronaviridae, but can be handled safely. We characterized the effects of surfactant type and concentration on the FCoV using dynamic and electrophoretic light scattering to follow possible aggregation or disruption of the virus, and fluorescence spectroscopy to probe possible protein denaturation. A parallel study was conducted on phospholipid vesicles (SUV) mimicking the charge of the virus envelope, probing the damage on the bilayer by following the leakage of entrapped calcein by fluorescence measurements. Finally, the virucidal activity of selected surfactants was tested on cultured Crandell Reese Feline kidney cells, where FCoV induces fast cytopathic effects. We tested the effect surfactant type, choosing representative cationic (CPC), anionic (SDS), and nonionic (C₁₀E8) surfactants.

There is an effect on both dimension and protein denaturation upon loading with ionic surfactants around their cmc. However, no sign of protein denaturation is seen for the nonionic surfactant, and only a considerable increase in the size is seen after its cmc. We conclude the main mechanism of FCoV inactivation with nonionic surfactant involves the disruption of the lipidic envelope, while the ionic surfactants also induce the denaturation of proteins (Figure 1). The virucidal activity assay confirms the surfactant-induced aggregation corresponds to coronavirus inactivation. The fundamental understanding and control of these interactions will aid in practical formulations for coronavirus inactivation and removal from contaminated surfaces.

Keywords: coronavirus, surfactants, protein denaturation, biomedicine

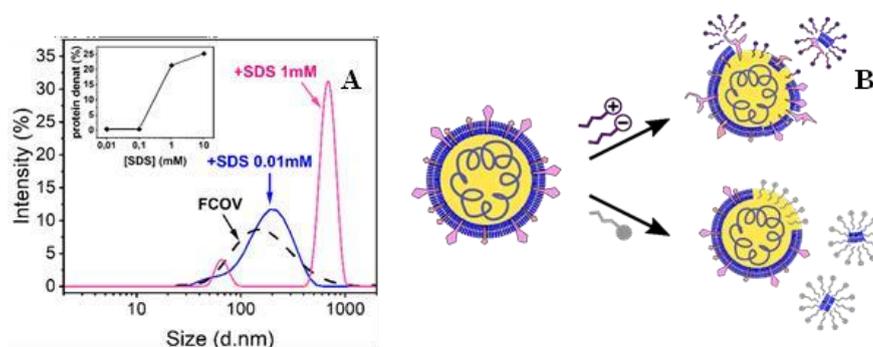


Figure 1. A) Effect of SDS on the dimension and protein denaturation of FCoV at increasing concentrations and B) sketch of the mode of action of the three types of surfactants on the virus.

Encapsulation and Sustained Release of Octenidine Dihydrochloride from PLGA Microcapsules

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Chronic wounds are often associated with conditions like vascular disease and diabetes mellitus and are becoming more common with an ever-increasing human lifespan. One of the main factors leading to non-healing chronic wounds is bacterial colonization in the wound, which is often prevented by topical antibiotics. In commercial topical treatments, like ointments or impregnated wound dressings, there is usually an initial fast and excessive release of the antimicrobial which leads to rapid loss of antimicrobial functionality. To extend the efficacy, we have in this work formulated poly(D,L-lactide-co-glycolide) (PLGA) microcapsules loaded with the antimicrobial agent octenidine dihydrochloride (OCT) for slow and sustained release of the active.

To enable control and prediction of the release, the effects of release medium composition and temperature on the release rate were studied. It was found that the release of OCT into pH-buffered aqueous solution— despite its significant aqueous solubility – was hindered by the partitioning between microcapsule and release medium. Through the addition of nonionic surfactant to the release medium, the partitioning was shifted towards the aqueous phase.

This resulted in a slow OCT release over several months at ambient temperature, described mathematically by appropriate diffusion models. Strong electrostatic interactions between cationic OCT and anionic PLGA end groups were observed by infrared spectroscopy, explaining the slow sustained release of OCT. At physiological temperatures (37 °C) a 200 times higher diffusivity was observed, leading to release over weeks instead. This dramatic change in diffusivity was due to being above the glass transition temperature of PLGA, at around 30 °C in its hydrated state. At longer times, it was instead the increased PLGA degradation rate and microcapsule erosion at elevated temperature that was rate-limiting. These results illustrated how the combination of both internal interactions within the microcapsule as well as external factors affected the release kinetics.

Keywords: microencapsulation, sustained release, antimicrobial.

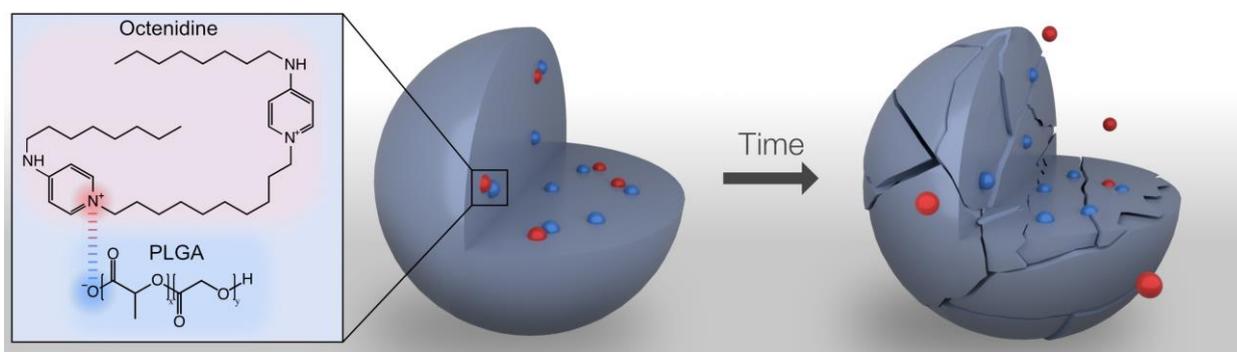


Figure 1. Schematic illustration of the strong PLGA-OCT interaction as well as the time-dependent microcapsule degradation.

In situ Characterization of Viruses Colloidal Systems for Design of Antiviral Solutions

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Viruses are a class of pathogens that have a high burden on humanity. Waterborne viruses, such as rotavirus and norovirus, have their biggest toll on young infants in developing countries. Whereas airborne lipid enveloped viruses, such as influenza virus and SARS-CoV2, have worldwide consequences. Viruses are self-assembled colloidal particles. To design antiviral solutions, the interactions and effects of such solutions on their self-assembled structure need to be understood. Bacteriophages Qbeta and Phi6 were used as surrogates respectively for non-enveloped and enveloped virus pathogens. Their interactions and structures were characterized by small angle X-ray scattering, dynamic light scattering and cryogenic transmission electron microscopy.

This allowed to show, (i) the pH-dependent adsorption of viruses on cationic modified nanocellulose as well as the viruses' structural integrity upon interacting, subsequently allowing to design a regenerable virus adsorption filter for water purification. [1] (ii) The mechanism of ethanol inactivation of enveloped viruses is via the separation of the outer lipid envelop from the inner nucleocapsid, hence separating the host-cell recognition function from the genetic material. [2] *In situ* characterization of the virus colloidal systems allows a bottom-up design of effective antiviral solutions.

Keywords: Virus, SAXS, disinfection, filtration, ethanol, nanocellulose

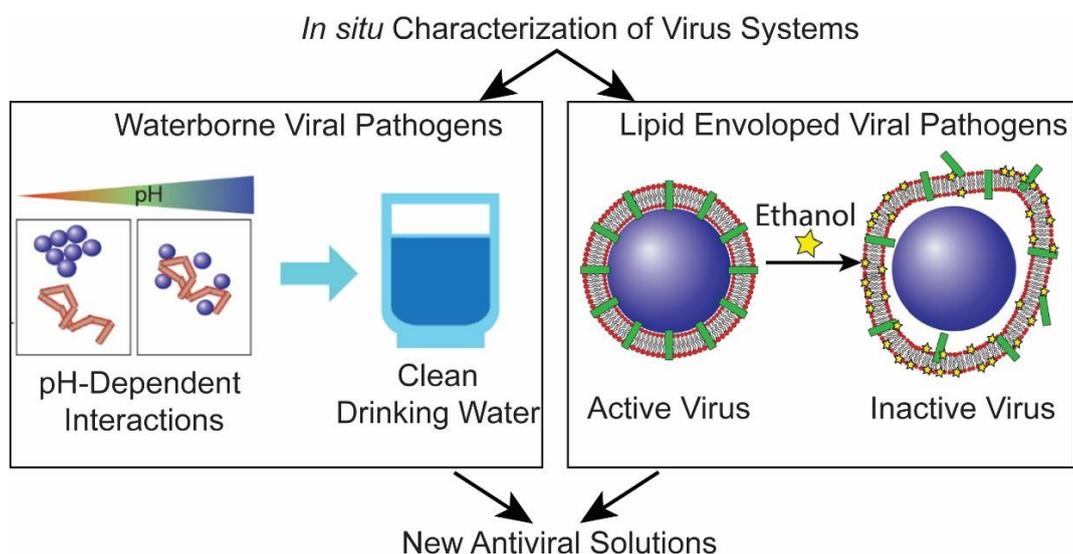


Figure 1: Graphical abstract.

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Specific interactions of ionic boron clusters with proteins

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Ion Specific Effects (ISE) are involved in a wide variety of physicochemical and biological phenomena such as on protein solubility.^[1] Low charge density ions with nanometer size, such as ionic boron clusters, were called "superchaotropes" because it was found that they exhibit a "salting-in" effect on non-ionic surfactants.^[2]

We focus here on the cobalta-bis-(dicarbollide) anion, COSAN [Co (C₂B₉H₁₁)₂]⁻, (Fig. 1a). Besides its superchaotropic character, COSAN has surfactant properties, although lacking the classical amphiphilic structure: surface activity, self-assembly^[3a] and formation of lyotropic lamellar phases.^[3b]

This work aims to understand COSAN-protein interactions and to make the comparison between COSAN and SDS, a classical anionic surfactant. We investigated the interactions of COSAN with myoglobin (Mb), carbonic anhydrase (BCA), and trypsin inhibitor (SKTI), which have different dominant secondary structures that are α -helix, twisted β -sheet, and a mixture of both, respectively. These specific interactions were characterized by (i) using UV, fluorescence, and circular dichroism (CD, Fig. 1b) spectroscopy to obtain information on the local environment of COSAN and on the proteins secondary structures and folding; and (ii) using dynamic light scattering (DLS, Fig. 1c) to obtain information on the hydrodynamic diameter and protein aggregation. We observed preferential interactions of COSAN with BCA whereas COSAN interferes with Mb through its haeme and to a lesser extent (i.e. at higher COSAN/protein molar ratios) with SKTI. The strong interactions between COSAN and the two proteins, BCA and Mb, induced substantial changes in their structural features. By comparing Apomyoglobin and Hemin interactions with COSAN separately, we were able to find the interacting part of Mb with COSAN. The present work shines light on the complex interplay of molecular interactions acting between COSAN and proteins, opening opportunities for a better understanding of the biological effects of COSAN.

Keywords: proteins, COSAN, nano-ions

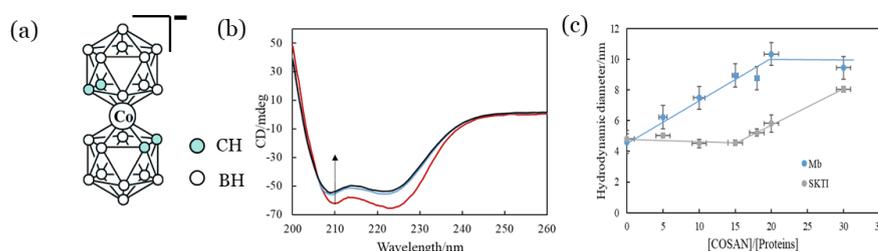


Figure 1. (a) Chemical structure of COSAN, (b) Far UV-CD spectra of 0.01 mM Mb in presence of different COSAN/Mb molar ratios: 0 (red), 5 (light blue) and 20 (blue) and (c) Hydrodynamic diameter as a function of different COSAN/Mb (light blue) or SKTI (grey).

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Bioactive Films Based on Chitosan and Polypyrrole

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The fabrication of biologically active biomaterials with appropriate biological and material qualities is one of the most critical parts of efficient tissue engineering. Here, films based on modified soluble chitosan (SCN) crosslinked by dialdehyde cellulose were prepared [1,2]. The films' bioactivity was further enhanced by the incorporation of conducting polypyrrole colloidal dispersion stabilized with polyvinylpyrrolidone (PPy) [3]. Such films were tested in terms of material properties (rheology, electrical conductivity). Furthermore, the NIH/3T3 mouse fibroblast cell line was used to evaluate the cytotoxicity and scratch assay. Also, immunogenic tests were performed. SCN/PPy films showed good biocompatibility, conductivity, antimicrobial activity and *in vitro* wound healing properties and it is therefore assumed that they could be used in the area of biomedical applications.

Keywords: Chitosan, Dialdehyde Cellulose, Polypyrrole, Films, Cytocompatibility



Figure 1. Chitosan films based on polypyrrole.

Acknowledgements: This research was supported within the project OP RDE Junior Grants of TBU in Zlín, Reg. No. CZ.02.2.69/0.0/0.0/19_073/0016941 (JUNG-2020-001).

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Conducting film prepared in colloidal dispersion mode, the efficient way of surface functionalization

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Biointerface is a critical place, where the interactions between the biological/artificial systems occur. This is the reason why the surface properties of biomaterial are one of the main factors that affect its applicability *in vivo*. The chemical and physical characteristics of the biomaterial surface can affect many of cellular functions. To reach the desired cell reaction, the surfaces could be functionalized. There is a number of techniques of surface functionalization but here we describe the innovative approach for preparing both the electrically-conducting and cytocompatible coating based on conducting polymers and biopolymers. The technique is based on the preparation of polymer films in a colloidal dispersion mode [1], where the natural biopolymers are used as stabilizers [2]. In this arrangement, the conducting polymer contribute with electroactivity and biopolymers provide cytocompatibility. The proper function of natural tissue is aided by its electrical and ionic conductivity, therefore conductive polymers are a promising material for tissue engineering. Moreover, the surfaces prepared in this way are bioactive.

Polyaniline (PANI) is one of the few conductive polymers that can be used in biomedical fields. However, PANI environment itself does not provide appropriate cell response, thus the biocompatible polysaccharides lead to improvement of cell instructive properties.

In this research, PANI based coating were prepared, where sodium hyaluronate, sodium alginate or chitosan were used as stabilizers. Cytocompatibility of films were determined by interaction with mammalian cells. e.g. NIH/3T3 or stem cells. In addition, surface energy (measured by sessile drop technique) and electrical conductivity (determined by four-point probe) of functionalized surfaces were investigated.

Keywords: Polyaniline, Surface Modification, Cytocompatibility

Acknowledgements: This research was supported within the project OP RDE Junior Grants of TBU in Zlín, Reg. No. CZ.02.2.69/0.0/0.0/19_073/0016941 (JUNG-2020-001).

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Cytocompatibility of Polypyrrole Thin Layers Synthesized *In Situ* with Polyurethane Electrospun Mats

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Looking back throughout the last few years, polymers have been completely dominating as a suitable material for medical devices and accessories and yet, their potential is far from being exhausted. Polyurethane is one of the polymers that have uncountable variations in forms and properties and thus it can be also widely used in medicine, including the currently often researched regenerative medicine [1]. In this presented research, electrospinning was chosen to prepare various polyurethane scaffolds since it is a cost-effective method of creating nanofibrous mats mimicking the structure and guiding function of the natural extracellular matrix.

Depending on the intended applications, the engineered biomaterial should be adapted to aimed tissue. For many of them, the electrical conductivity of the substrate serves as an important cell-instructive cue. For the cardiac and neural tissues, it is especially advantageous. Therefore, the here-presented polyurethane mats were further functionalized by coating with conductive polypyrrole. Polypyrrole, as well as other conductive polymers, is at the center of attention due to its combined electron and ion-based conductivity. In addition, its synthesis is quick, facile, and adaptable and results in relatively cytocompatible products which can have positive or desired effects on cell behavior, including stem cell differentiation [2]. Coating of electrospun polyurethane fibers was carried out by *in situ* polypyrrole polymerization.

In addition to the morphology characterization, which was done by scanning electron microscopy, cytocompatibility with fibroblasts and more importantly with embryonic stem cells was studied. This research focuses on deepening current knowledge about cell/polymeric biomaterial interactions with a special concentration on material properties mimicking *in vivo* environments.

Keywords: polypyrrole, coating, conductivity, stem cells.

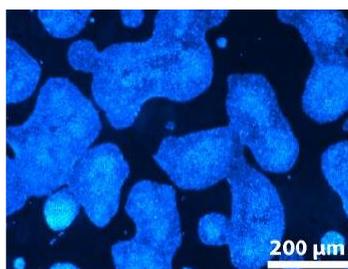


Figure 1. The fluorescence microscopy image of mouse embryonic stem cells R1 cultivated on the prepared composite based on the electrospun polyurethane mat coated with polypyrrole (blue color: Hoechst - DNA).

Acknowledgements: Support for this research was provided by the project OP RDE Junior Grants of TBU in Zlín, Reg. No. CZ.02.2.69/0.0/0.0/19_073/0016941.

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Reactive Microgels as Platform for Design of Complex Cell-culture Substrates using Microcontact-Printing and Post-Modification

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Various studies have shown that the adhesion and proliferation of cells is determined to a high degree by the properties of the substrate they are cultivated on.^[1,2,3] Hence, the design of bio-compatible and interactive surfaces, which integrate various possible stimuli, are of high interest for application in tissue culture.

The present work combines surface structuring techniques with reactive (post-) modification to design complex interfaces providing structural, chemical and mechanical cues on the basis of poly(*N*-vinylcaprolactam) microgels carrying reactive groups. Soft lithography techniques were employed to create micrometer-sized line patterns on glass surfaces. The successful transfer of the printed patterns was proven by light and atomic force microscopy.

Functionalities such as epoxy or carboxylic acid groups in the microgels enabled covalent binding to the surface as well as post-functionalization. Coupling of reactive fluorescent dyes to microgel arrays was performed to demonstrate reactivity on the surface. Surface chemical gradients were created *via* dip-coating and analyzed with confocal microscopy. The dipping speed and dye concentration were varied to adapt the slope and intensity of the gradient. Microgel-structured surfaces were successfully employed as cell culture substrates to guide the growth and movement of cells.

Keywords: Microgels, Microcontact Printing, Lithography, Cell Culture, Surface Gradient

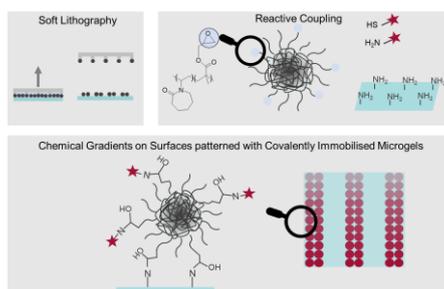


Figure 1. Combination of soft lithography and click chemistry allow for the design of stable micro-patterned microgel-modified substrates with surface-chemical gradients.

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Polysaccharide-functionalized iron oxide nanoparticles for mRNA delivery

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mRNA is a very promising tool for the development of a new generation of vaccines for the treatment of various diseases/disorders including infectious diseases, cancer, heart and brain disorders and others [1]. Herein, we present a new hybrid mRNA delivery system comprising an inorganic core, based on Fe₃O₄ nanoparticles (NPs), functionalized with chemically modified natural polymers, which can either interact electrostatically or chemically bind mRNA, thus protecting it from hydrolysis and increasing its penetration through the cell-membrane [2].

The polysaccharides used in this study are chitosan and dextran, two non-toxic natural biopolymers. Chitosan was modified using glycidyl trimethyl ammonium chloride to afford quaternized chitosan (Q-Chi), which bears cationic groups and can interact with the negatively charged mRNA to form polyelectrolyte complexes. In the second approach, the hydroxyl groups of dextran were oxidized (Ox-Dex) into aldehydes moieties, which can rapidly react with the amine groups of mRNA forming a pH-labile Schiff base. The successful modification of the polymers was verified by ¹H NMR and ATR-FTIR spectroscopies. Bare and citric acid (CA) coated Fe₃O₄ NPs were synthesized through the co-precipitation method and were next coated with the polymers to obtain different hybrid carriers: Ox-Dex-NPs, Ox-Dex-CA-NPs, Q-Chi-NPs and Q-Chi-CA-NPs. The hybrid materials were characterized by FTIR spectroscopy and TGA analysis. Moreover, the morphology, size and surface charge of the polysaccharide modified NPs were determined by transmission electron microscopy, dynamic light scattering and zeta potential measurements. The hybrid carriers were studied in terms of their toxicity against T47D breast cancer cells. Their *in vitro* transfection efficiency was investigated using *in-vitro*-transcribed mRNA trastuzumab (IVT-mRNA) to produce the antibody trastuzumab, which is widely used for the treatment of breast cancer in women.

Keywords: biopolymers, iron oxide nanoparticles, mRNA, hybrid materials

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Tumour microenvironment-responsive polymer-based nanomedicines for therapeutic applications in cancer

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Systemic use of chemotherapeutic agents is often accompanied with severe side effects, mostly related to lack of cellular and tissue selectivity of these drugs for tumours over healthy tissue.[1] Over the past years breakthroughs have been made in the development of advanced drug delivery systems with the aim to obtain precision medicine to fight cancer.[2] A strategy that has successfully been applied is to use the chemistry of the tumour microenvironment to induce the more specific release of therapeutic cargo at the site of the tumour.[3] Herein, several polymer-based nanomedicines (polymer-drug conjugates, polymer nanoparticles – polymersomes)[4-6] were designed to display tunable oxidative triggered degradation in the presence of physiologically relevant reactive oxygen species (ROS)-concentrations or low pH, as well as multiresponsive systems able to respond to multiple different chemical triggers.[7] The chemical approaches, polymers' characterization, their in vitro degradation and their potential application is demonstrated in in vitro and in in vivo models and critically compared to marketed nanoparticulate chemotherapeutics for cancer applications.

Keywords: nanomedicines; stimuli-responsive; polymers; tumour microenvironment, chemotherapy

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Novel drug delivery system based on multifunctional PEO-*b*-polyacetal diblock copolymers nanoparticles

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Nanoparticle-based drug delivery systems are considered a promising therapeutic platform because of their potential to enhance the efficacy of drugs in anticancer and antiviral therapy. Modern nanomedicine combines therapeutic and bioimaging modalities in a single entity known as theranostic nanoparticles, which allow the simultaneous diagnosis and therapy [1-3]. Herein, we present a novel theranostic platform based on degradable nanoparticles comprising self-assembled poly(ethylene glycol)-*b*-polyacetal diblock copolymer chains (figure 1). The response of the nanoparticles to four different external stimuli, which induce their disassembly following the main chain scission of the polyacetal block, is demonstrated. The degradation of the polymer by (i) UV (365 nm) photolysis, (ii) ultrasound (1 MHz) irradiation, (iii) a redox environment and (iv) acidolysis at mildly acidic pH (ca. 5.2) was monitored using size exclusion chromatography. Micelles loaded with the model anticancer drug camptothecin (CPT) were prepared in aqueous media. Their ability to serve as MRI contrast agents was evaluated using NMR spectroscopy, while the drug release profile, upon application of the four external stimuli, was determined by UV-Vis spectroscopy.

Keywords: Theranostic nanoparticles, polyacetals, multi-sensitive polymer, MRI contrast agent.

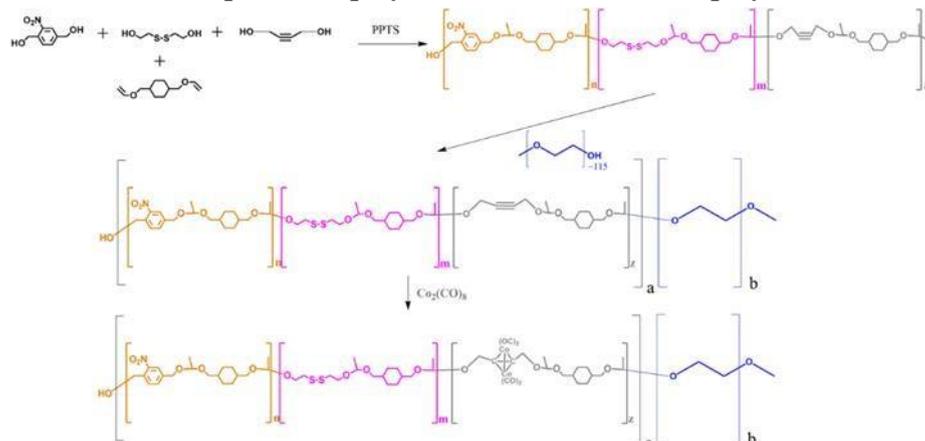


Figure 1: Synthetic procedure followed for the preparation of the polyacetal-*b*-PEO diblock copolymer.

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pH-responsive giant polymer vesicles for biomedical applications

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Currently, giant vesicles are among the most promising candidates to mimic the structure and function of cell behavior. Specially, giant unilamellar vesicles (GUVs) have become increasingly popular model systems in bottom-up synthetic biology because they can be manufactured from lipids and/or amphiphilic block copolymers to match the dimensions and basic functions of eukaryotic cells. Herein, microfluidics was used for preparation of stimuli-responsive GUVs based on the pH-responsive poly[2-(diisopropylamino) ethyl methacrylate-*b*-poly(ethylene-glycol) block copolymer. pH-responsive GUVs are formed from the amphiphilic block copolymers by water-in-oil-in-water (W/O/W) double emulsion method using a microdroplet generator that allows the production of monodisperse GUVs under strict control. The presence of the pH-responsive polymer block in GUVs promotes the physical changes at specific pH, that caused polymeric membrane disruption (Figure 1). This behavior was well-studied by confocal laser scanning microscopy (CLSM). The obtained results demonstrated pH-controlled GUVs disruption under simulated relevant physiological conditions. Cytotoxicity studies were performed with pH-responsive GUVs, revealing great biocompatibility, which is important feature for biomedical application. The presented GUVs could find application in pH-responsive drug and gene delivery, microreactors and as a model of artificial cell studies.

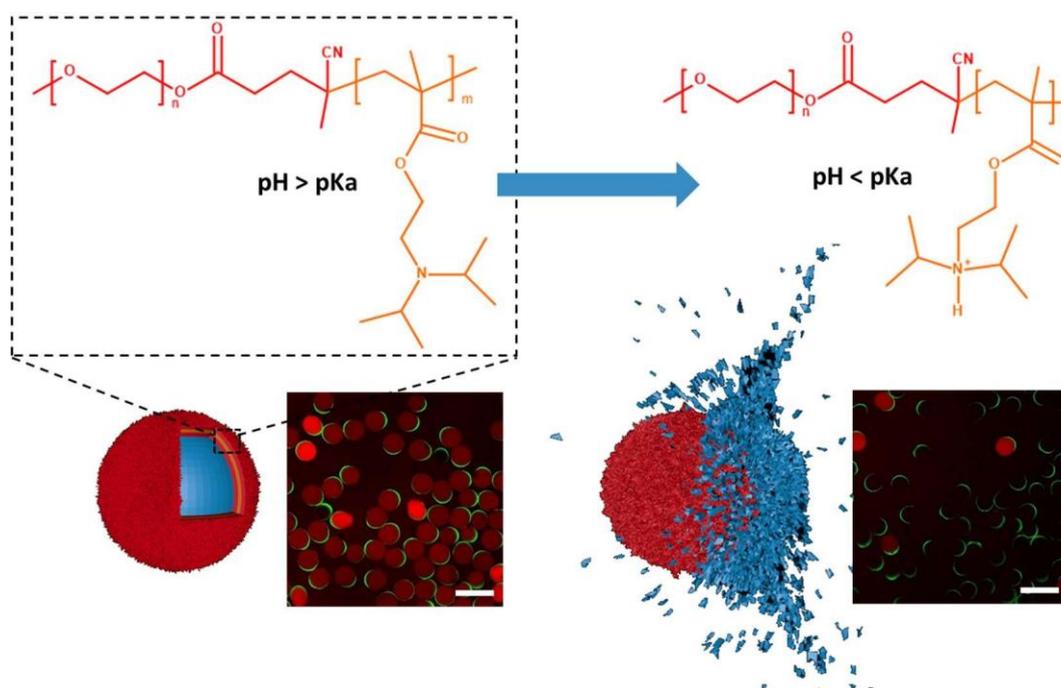


Figure 1. Illustration scheme of pH-responsive GUVs triggered explosion with CLSM images (scale bar 100 μm).

Keywords: GUVs, microfluidics, pH-responsive

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Liquid crystalline nanoparticles for encapsulation of pharmaceutically active compounds from marine algae

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Biomass of marine algae is a widely available raw material in a large part constituted by bioactive pigments and their derivatives, including chlorophylls, pheophytins and carotenoids [1]. These compounds have been studied as potential natural photosensitizers in photodynamic therapy and they also exhibit anti-cancer activity [2,3]. However, they are intrinsically unstable because of high sensitivity to temperature, light and oxygen [1]. Moreover, given their hydrophobic character, once exposed to aqueous media they can quickly aggregate or degrade, losing their biological properties. Thus, for the proper delivery of these hydrophobic agents to pathological tissues in their photoactive monomeric form there is a need to find relevant delivery carriers able to assure their solubilization as well as protection against degradation.

In this work, we explored the potential of liquid crystalline nanocarriers known as cubosomes and hexosomes, endowed of high colloidal stability and high entrapment efficiency of compounds with variable hydrophobicity, for the encapsulation, protection, and release of bioactive agents extracted from marine algae: *Ulva Rigida* or *Caulerpa Cylindracea*. In this investigation, we will discuss how modern, efficient, and green extraction techniques (microwaves, ultrasounds) makes the process of obtaining chlorophylls and pheophytins from algae fast, relatively cheap, and environmentally friendly. Particularly, the physicochemical features of the nanoparticles encapsulated with chlorophylls and pheophytins will be presented along with the biocompatible aspects of these formulations [Fig. 1].

Keywords: seaweed, chlorophyll, pheophytine, cubosome, hexosome, nanoformulation

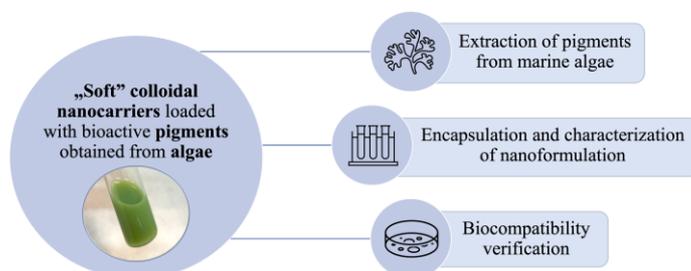


Figure 1. General scheme of the investigation

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Superfluorinated nanoprobes for T Lymphocytes tracking by ^{19}F Magnetic Resonance Imaging

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In the field of oncology, adoptive cellular therapy, as the use of chimeric antigen receptor T-cells, has shown promising results in various tumour types. However, several drawbacks are still limiting their routinary use in clinics. Therefore, the development of a non-invasive imaging protocol to track engineered cells in the body is an unmet clinical need. In this regard, MRI is a promising non-invasive imaging tool [1], and PERFECTA molecule is a promising superfluorinated probe, with 36 equivalent ^{19}F atoms and a symmetric structure, which assure a single and intense magnetic resonance peak [2-3]. Since PERFECTA is highly hydrophobic, in this work we optimized a PERFECTA-loaded nanoformulation (NP) for T cells labelling.

For this purpose, we developed a positively charged biocompatible NP with improved physico-chemical properties to maximize its uptake by non-phagocytic cells [4]. In this perspective, optimized NPs showed an optimal size for cellular uptake and high colloidal stability in cellular culture media together with stealth properties.

Notably, the high PERFECTA encapsulation efficacy allowed the use of these NPs as ^{19}F -MRI tracking agents on a model of T-cells showing a promising labelling efficacy in terms of ^{19}F /cell without affecting cellular viability.

Keywords: Nanoparticle, self-assembly, ^{19}F MRI, cell therapy

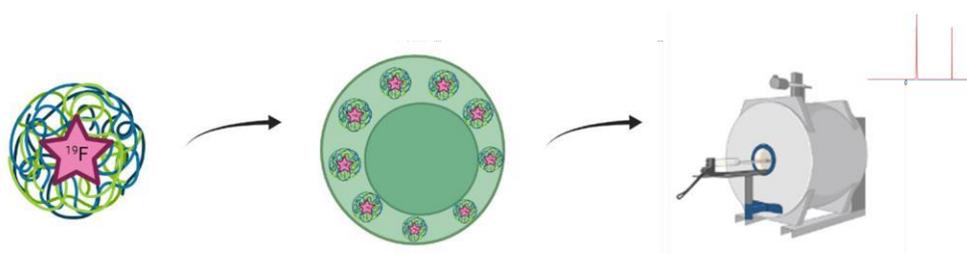


Figure 1. Schematic representation of PERFECTA-loaded nanoparticles labelling T cells for in vivo ^{19}F MRI imaging.

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Liquid Crystalline Nanoparticles for Photodynamic Therapy

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Photodynamic Therapy (PDT) can be considered an emerging tool for cancer treatment, whose application is also approved by the US Food and Drug Administration. Basically, PDT requires a photosensitizer (PS) molecule that, after low energy light activation, produces Reactive Oxygen Species (including the highly cytotoxic singlet oxygen, 1O_2) that cause cell death, microvascular damage and, later, an inflammatory reaction that can lead to the development of systemic immunity. However, most of PSs possess a highly hydrophobic character, therefore must be loaded into appropriate vehicles for their systemic administration, also to favor their escape from the Mononuclear Phagocyte System.

Here, lipid-based non lamellar liquid crystalline nanoparticles loaded with commercial or newly synthesized PSs engineered for systemic or topical applications will be discussed. Particularly, here will be presented the physicochemical properties as well as the PDT features of classical PS-loaded cubosomes alternatively stabilized against flocculation in water solutions by the block copolymers Pluronic F108, Pluronic F127, or polymer free stabilized cubosomes. The cytotoxicity features of these formulations will be also presented.

Keywords: Cubosomes, Hexosomes, Nanomedicine, Cytotoxicity

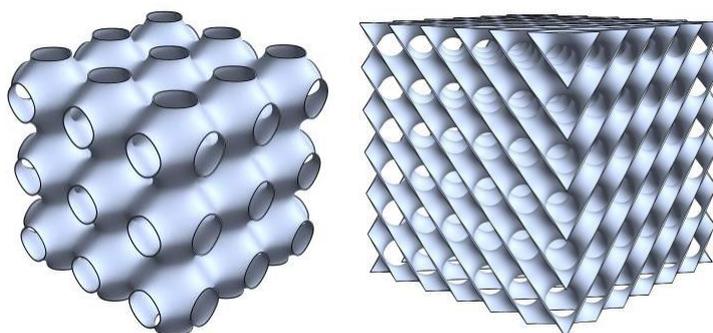


Figure 1. Schematic illustration of the primitive ($Im3m$, left) and double diamond ($Pn3m$, right) Infinite Periodic Minimal Surfaces, characteristic of cubosomes nanostructure.

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Targeted drug delivery system based on bulk nanostructures formed by two-antennary oligoglycines

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The interest in the scientific area for exploration of different nanocarriers for hydrophobic medicines has continued its growth over the last two decades. However, the higher lipophilicity of these drugs is still a significant challenge for their introduction and targeted delivery in biological systems.

A relatively new class of biocompatible compounds, called two-antennary oligoglycines are promising candidates for hydrophobic drug delivery systems. They possess the so-called bola-amphiphilic structure, and are obtained by preliminary molecular design. Each molecule consists of two equal hydrophilic oligoglycine antennae attached to a central hydrophobic alkyl core [1]. Different lengths of the core, and/or of the antennae, alter the size, the shape, and the amphiphilic properties. In aqueous solutions, they form well-defined and stable self-assemblies named tectomers [2]. The structure of the tectomeric aggregates is directly dependent on their molecular design [3] and is also crucial characteristics in the process of controlled entrapment of a hydrophobic drug and its further release in the human body.

In the present study we have investigated the formation of bulk nanoaggregates based on a type of two-antennary oligoglycine which is capable to capture the slightly soluble medicine indomethacin. By applying several complementary physicochemical techniques, the effects of concentration, pH, temperature, and ethanol presence are evaluated.

Keywords: amino acids; bola-amphiphiles; hydrogen bonding; oligopeptides; tectomers

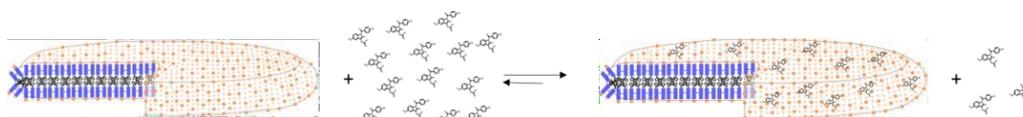


Figure 1. Indomethacin entrapment and formation of stable biocompatible nanoaggregates with tectomers.

Acknowledgements: The present investigation is financially supported by Bulgarian National Fund for Scientific Research through Project “Design and Characterization of Soft Nanostructured Materials Based on Antennary Oligoglycines”, No. КП-06-H39/5. The authors are thankful to Pharmaceutical Development and Characterization Laboratory of Research, Innovation and Development Consortium at Sofia Tech Park, Sofia Bulgaria for the possibility to use their laboratories for UV-VIS spectroscopy.

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Polyelectrolyte polymer networks for the uptake of charged short-chained polyamides

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Anyone who wants to live healthily needs a clean environment. To do so, there are already a variety of different cleaning products which can remove the coarse mass of all impurities. Nevertheless, especially in sensitive areas, such as medical rooms, special detergents are needed that specifically remove certain types of contamination. For this purpose, it is necessary to develop new and more efficient detergents. Polymer networks show a high potential in the absorption of contaminants with ionic charges or with acidic/basic groups. [1] In our research, we deal with the uptake of charged chains, such as polyamides, in polyelectrolyte macromolecular networks. An important factor here is the immobilization, which describes how much charged polymers can be accommodated per polymer network. For example, polyelectrolyte networks with a basic group can immobilize polymers with acid groups through electrostatic interactions. However, determining the amount of polymers incorporated into a network is challenging. In this work, isothermal titration calorimetry (ITC) is used to determine the immobilization of polyamides in macromolecular networks. During the immobilization of polyamides with acid groups into a polymer network with basic groups, a temperature difference occurs due to the chemical reaction, which is measured by ITC. In our experiments, the polyamides are titrated into a polymer network solution using a special syringe. As soon as no further temperature difference is measured in the sample chamber, the exact number of immobilized polyamides per macromolecular network can be calculated from the volume used up to this point. In order to achieve the highest possible uptake, polymer networks with differently adjusted proportions of basic groups and different cross-linking densities are investigated. In addition, networks with different architectures are also considered.

Keywords: polyelectrolyte polymer networks, isothermal titration calorimetry, uptake/release

Acknowledgements: This work was carried out as part of the cooperative project Bio4MatPro: Boostlab-1-3 Bio4Clean "Functional diols and diamines as building blocks of new sustainable functional polymers based on regionally available sustainable raw materials for use in detergents and cleaning agents, TP A" funded by the German Federal Ministry of Education and Research (BMBF).

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In vitro study of triglyceride lipolysis: cholesterol lowering by phytosterols and Quillaja saponaria extract

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High plasma concentrations of cholesterol are associated with high risk of myocardial infarction and other cardio-vascular diseases. One of the strategies for reduction of plasma cholesterol is to replace unhealthy fats with healthy ones, and increase dietary fiber by emphasizing whole grains, fruits, vegetables and legumes. To work to its fullest potential, this strategy can be combined with cholesterol-lowering functional ingredients.

Phytosterols are a group of naturally occurring compounds found in plant cell membranes. Since phytosterols are structurally similar to cholesterol, they compete with cholesterol for intestinal absorption. According to the US Food and drug administration (FDA), phytosterols block cholesterol absorption, resulting in a decrease of blood cholesterol levels. In the same time, Quillaja saponin extracts are also known to reduce plasma cholesterol [1,2] and are approved to use in foods (E999). Here we explore the impact of the combination of phytosterols and Quillaja Dry saponin extract (QD) on cholesterol bioaccessibility and we compare the results to the single-component systems. In vitro model of triglyceride lipolysis is used [1] to quantify the effect of phytosterols on the fraction of bioaccessible (viz. solubilized) cholesterol and of the lipolysis products (fatty acids and monoglycerides) in the dietary mixed micelles (DMM). We found that phytosterol decreases significantly the cholesterol (from 100% to 60%) and even more so if combined with QD (from 100% to 35%) solubilized in DMM. The experiments prove that both phytosterols and QD may act by direct precipitation of cholesterol and displacement of cholesterol from the DMM and subsequent precipitation.

We found that the solubilized cholesterol increases linearly with the concentration of free fatty acids which is evidence for co-solubilization of these two components in the bile micelles.

In conclusion, the combination of phytosterols and Quillaja extract is a promising approach for formulation of cholesterol lowering functional foods and nutraceuticals.

Keywords: cholesterol, phytosterol, in vitro, triglyceride lipolysis

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A comparison between Lutrol F-127 and β -casein micelles using Calorimetry and Cryo-EM

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Amphiphilic block copolymers are in extensive use in a wide range of domains such as the food, pharma, and cosmetic industries. The main reasons for this broad application are their strong emulsification properties and the ability to self-assemble and form core-shell micelles that can encapsulate hydrophobic bioactives. In this study, we present differential scanning calorimetry (DSC), and isothermal titration calorimetry (ITC) [1] results of two amphiphilic block copolymers micellar systems: the protein β -casein (β CN) and the polymer Lutrol F-127, in absence and presence of drugs. The model drug used is Celecoxib (Cx), which is characterized by low solubility and high permeability, and via encapsulation, we increase its bioavailability.

DSC heating experiments of unloaded β CN micelles did not present any phase transition. In contrast, experiments of β CN/Cx complexes disclosed irreversible and distinctive exotherms. We identified a critical temperature related to drug release, defined as T_r , which changes as a function of the scan rate [2].

DSC exotherms of Lutrol were different: the polymer alone showed reversible and distinctive peaks in the heating and cooling cycles, however, Lutrol/Cx complexes presented a phase transition, though small compared to the one detected for the protein/drug system under similar conditions. The irregular thermotropic behavior of the Lutrol/Cx complexes found by DSC required an additional investigation to understand the interaction between the block copolymer and the drug. ITC titration experiments of this system showed a classical sigmoidal graph. However, in the drug-loaded polymeric system, the inflection point shifted to a much higher concentration which we interpret as strong adsorption/binding between the polymer and the drug, leaving less polymer available for micellization. The Calorimetry data is supported by cryo-EM and light microscopy analysis.

Keywords: Lutrol, β -casein, DSC, ITC, cryo-EM

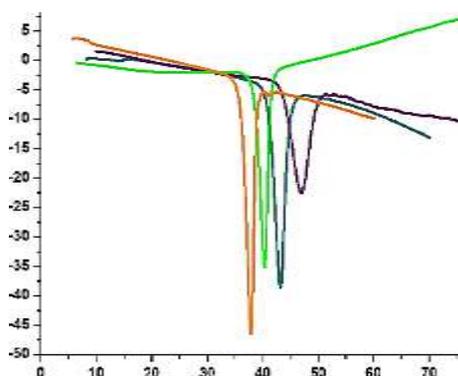


Figure 1. DSC exotherms of Celecoxib loaded β -casein micelles.

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Lipid nanoparticles using cationic ionisable lipids: Effect of cargo on structure

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DLin-MC3-DMA (MC3), currently the most potent cationic ionisable lipid in research, is widely used in the most popular formulation for lipid nanoparticles (LNPs) for mRNA delivery, along with cholesterol, the neutral helper lipid DSPC and the PEG lipid DMPE-PEG2000 [1]. Although many reports have investigated the *in vitro* efficacy of these LNPs, less is known about the behaviour of the MC3 lipid and the LNP structure, especially with respect to its dependence upon the LNP cargo. In this work, we have investigated the structure and stability of LNPs formulated with three different cargos, double stranded DNA (dsDNA) and the model mRNAs polyadenylic acid (polyA) and polyuridylic acid (polyU), at two different concentrations.

Dynamic light scattering (DLS) was used to characterise the size distribution of the LNPs over time in order to determine their colloidal stability. For all samples, the size increased with cargo concentration and initial PDI was reasonable. In the case of the polyU LNPs, aggregation was observed within 24 hrs after preparation, whereas the other LNPs remained stable over the 41 day measurement period. Small angle x-ray and neutron scattering (SAXS and SANS respectively) measurements were performed to investigate the LNP structure, highlighting their core-shell structure. In the SAXS patterns, the peak corresponding to the internal structure is in a similar position for all the cargos, however different in shape for the polyU loaded LNPs. Through *in situ* SAXS measurements of the microfluidic mixing process, we were able to follow the formation of the LNP internal structure and observe the appearance of the corresponding peak.

In conclusion, we have characterised the effect of different cargos on the particle structure in order to contribute to the understanding of the cargo's role, aiming to link this to LNP efficacy.

Keywords: drug delivery, lipid nanoparticles, cationic ionisable lipid, scattering techniques

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Fluorescent Nanodiamonds Modified with Biocompatible Polymers

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In the past decade, sentinel node(s) mapping became the standard procedure used in cancer diagnostics. However, agents commonly used in these applications, mostly molecular dyes, and radiotracers, still have several disadvantages. Fluorescent nanoprobe currently show the most promising results as potential alternatives. Fluorescent nanodiamond (FND) is a biocompatible material exhibiting unique optical properties. The origin of the nanodiamond fluorescence is based on artificially created nitrogen-vacancy (NV) centres. The emission maximum of NV centres is in the near-infrared region (approximately 700 nm), which belongs to the tissue imaging window. NV centres are extremely resistant towards photobleaching. These properties make FND a promising candidate for bioimaging applications.

This work is focused on the preparation of FNDs coated with D-mannosylated polyglycerol for sentinel node(s) visualization. Polyglycerol coating overcomes the limited colloidal stability of FNDs in the biological environment and enables surface modification. D-mannose targets macrophages, which are abundantly present in the sentinel nodes. The functionalization with D-mannose was achieved using click chemistry (azide-alkyne cycloaddition). First, treatment with glycidyl propargyl ether provided alkyne-modified polyglycerol, which was connected with azidated D-mannose via click reaction. The optimal polymerization and click reaction conditions were extensively studied. The resulting particles (both mannosylated and non-mannosylated) were highly stable in the high-salt condition (1 M NaCl), and non-specific protein binding in FBS was completely eliminated. The mannosylated particles interacted specifically with macrophages and showed enhanced retention in mice lymphatic nodes, providing a clear imaging contrast.

Keywords: fluorescent nanodiamonds, polyglycerol coating, CuAAC click, mannose targeting, sentinel lymph node visualization

Acknowledgements

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Study of Interaction between Cationic Ion Pair Amphiphile Vesicles and Hyaluronan

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This contribution is focused on the study of interaction between positively charged cationic vesicles and the oppositely charged biopolymer, hyaluronan. Cationic vesicles have very similar structure to liposome. Unlike them, cationic vesicles are formed from so called ion pair amphiphile (IPA), which was prepared by mixing two oppositely charged single-chain surfactants – HTMAB (hexadecyltrimethylammonium bromide) and SDS (sodium dodecylsulphate), after removal of their counterions. The resulting IPA can be written as HTMA-DS. Due to positively charged vesicles surface [1]. Due to the positively charged surface, the vesicles may interact with oppositely charged polymers. Hyaluronan appears to be very suitable for this purpose. This polymer is present in human body, it is fully biocompatible and biodegradable and therefore can increase the biocompatibility of cationic vesicles [2].

Cationic vesicles were prepared from ion pair amphiphile HTMA-DS and were doped with positively charged dioctadecyldimethylammonium chloride (DODAC) and cholesterol for higher physical stability. Hyaluronan of four molecular weights (16; 418; 750, and 1 670 kDa) was used for interaction with vesicles and these interaction were studied by using the light-scattering technique, specifically using size and ζ -potential titrations. It was possible to observe interactions independently of the molecular weight of hyaluronan. With increasing addition of hyaluronan, the ζ -potential decreased exponentially. The formation of larger aggregates were observed during higher polymer additions and visible aggregates (larger than 1 000 nm) were made around the point of charge equilibration (0.9–1.0). Behind the point of charge equilibration, these aggregates disintegrated. It was dependent on the choice of molecular weight of hyaluronan.

Keywords: ion pair amphiphile, cationic vesicles, hyaluronan, light-scattering techniques

Acknowledgements: This work was supported by the University Specific Research, project No. FCH-S-22-7870.

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Physicochemical Study of Interactions between Catanionic Vesicles and Hyaluronan

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Catanionic vesicles were formed from an ion pair amphiphile (IPA). Their stability was increased by the use of cholesterol (43 mol.%) and the addition of the double-chain surfactant dioctadecyldimethylammonium chloride (DODAC).

The vesicles thus formed have a spherical shape which allows them to encapsulate both hydrophobic and hydrophilic substances. In order for vesicles to be used as a cheaper alternative to liposomes, it is necessary to reduce their cytotoxicity. Hyaluronan was chosen as the body's own biocompatible polymer for this task. Hyaluronan has been found to have a positive effect on the toxicity of positively charged surfactants [1, 2]. At the same time, it carries the opposite charge compared to vesicles, which should allow them to interact with each other.

High-resolution ultrasonic spectroscopy (HR-US) and visual observations were used to study these interactions. Basic information about the system was obtained by visual observations using hyaluronan with molecular weights of 16 and 1670 kDa. The result was several concentrations (charge ratios) at which visual changes occurred in the solution.

In the case of using HR-US, it was possible to monitor the titration of hyaluronan into the vesicles in a much higher resolution. The results varied depending on the molecular weight of the hyaluronan. The smallest change in the normalized relative velocity parameter indicating the presence of interactions occurred in the case of the lowest molecular weight of hyaluronan (16 kDa), while the decrease was highest in the case of the highest molecular weight of hyaluronan (1670 kDa). The hyaluronan conformation probably also plays a role here, because while 16 kDa is rod-like, the longer molecular weights examined are coiled [3]. Depending on the concentration (charge ratio), several different regions were identified during the titration.

Keywords: hyaluronan, catanionic vesicles, HR-US

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Aptamer biosensor for LPS using F-doped ZnO nanoparticles

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Bacterial infections cause numerous risks to human health. Gram (-) is a major source of infection, due to the inside of their outer membrane of endotoxins, such as lipopolysaccharides (LPS) [1]. For this reason, it is important to develop a biosensor that can specifically detect and quantify Gram (-) pathogens [2]. Biosensors combine a biological recognition mechanism with physical transduction, leading to selective and sensitive recognition of analytes. The aim of this project is to develop a biosensor by optimizing the matrix, consisting of F-doped zinc oxide nanoparticles (F-ZnO NPs) [3,4], and choosing the appropriate biomolecule (the aptamer LA-27). In this way, the aptamer labeled with a fluorescence probe (i.e., FAM or ROX) should act as the energy donor and the NPs as the energy acceptor, analyzing the optical response of the aptasensor will be able to detect the presence of LPS and their quantification [5]. Therefore, we have synthesized and characterized F-ZnO at different F-concentration NPs in solution to choose the best sample, in terms of size, morphology, and optical properties, to create the matrix. On the NPs matrix surface was linked an LPS sensible aptamer for the detection and quantification of LPS of Gram (-) pathogens. Here the developing of the system and the preliminary results will be discussed.

Keywords: Biosensor, aptamer, nanomaterial, zinc oxide, LPS, physico-chemical characterization.

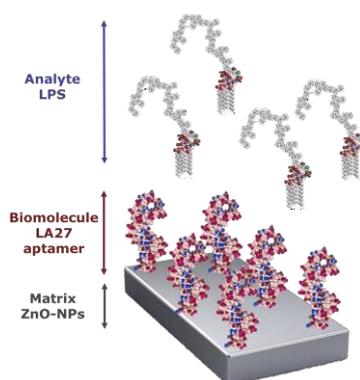


Figure 1. Schematic representation of aptasensor

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Spontaneous Vesicle Formation in Mixture of Phospholipid and Amphiphilic Drugs

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Amphiphilic drugs interact with phospholipids and expected to influence properties related to pharmacological activity, toxicity and function of a drug delivery agent in release mechanisms and transport of drug molecules across cell membranes [1].

The stabilization of vesicles is expected to depend on the chemical composition of different molecular species (phospholipid and drug) in the vesicles. In certain systems, vesicles may even form spontaneously, and the size of them may be determined and tuned by the choice of phospholipid, surfactant and their compositions.

We have observed small vesicles (15-20nm in diameter) to form spontaneously in mixtures of the phospholipid DOPC and the amphiphilic drug surfactant amitriptyline-hydrochloride (AMT). This is among the smallest vesicle ever reported. From a theoretical point of view, the vesicles are predicted to be stabilized by the uneven distribution of the molecular components, so that the surfactant is preferably located in the outer leaflet and the phospholipid in the inner leaflet of the vesicles [2]. We have observed that the size of vesicles is depending on the length of the lipid tails. To the best of our knowledge, this is the first time that spontaneous vesicles formation has been reported in the mixture of lipids and amphiphilic drugs.

Keywords: vesicles, amphiphilic drugs, phospholipids, bending elasticity

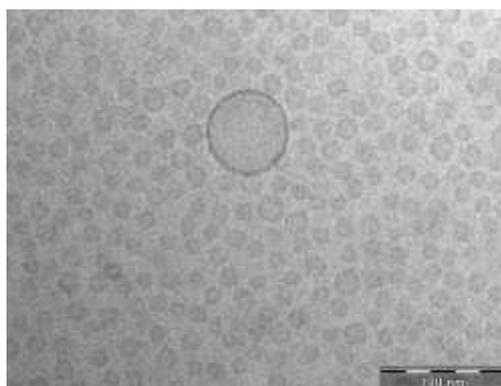


Figure 1. Cryo-TEM image of 25% DOPC, 75% AMT in physiological salt concentration. The sample mostly consist of small vesicles with average diameter of 16 nm.

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Techno-functional properties of lecithin in the context of cosmetic formulation

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In cosmetics, lecithin acts not only as an emulsifier but also an emollient, moisturizer and penetration enhancer [1]. The multifunctionality of lecithin is a result from its high content of phospholipids, essential fatty acid and other substances. Because of the amphiphilic structure of phospholipids, it possesses surface active properties as emulsifying, solubilizing, dispersing and wetting properties. Furthermore, the presence of fatty acids and lamellar forming capacity allow lecithin to reinforce the skin barrier and to transport actives into the deeper layers of the skin [1, 2].

The aim of this study was to understand lecithin behavior in different oil and their performances in cosmetic formulation as well as textural and sensory properties of final formulas. To deal with this challenge a complex methodology was developed including macroscopic and microscopic observation and laser diffraction granulometry for evaluating the dispersibility of lecithin in oil. Obtained results suggest that lecithin concentration, lecithin type and oil polarity are the most three important factors that influence their dispersibility. The dispersibility of lecithin in oil can be facilitated by the increase in hydrophobic part in its structure, the rise in concentration and the decrease in oil polarity.

The results showed a great importance for choosing the most suitable phase to incorporate the lecithin in formulation process. In fact, oil polarity has a significant impact on emulsion stability and lamellar formation. Effectively, polar oil can facilitate the formation of liquid crystals while non-polar oil can disrupt the structure. These results allow choosing the right mixture of oil with suitable oil polarity to enhance the lamellar formation and ensuring emulsion stability. Finally, textural and sensory analysis showed that lecithin has a crucial role in the outstanding sensory signature of cosmetic emulsions.

Keywords: lecithin, functional properties, formulation, sensory signature

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A physicochemical and spectroscopic characterization of novel erlotinib conjugates with platinum nanoparticles

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Anticancer drug conjugates with metal nanoparticles are in the centre of research interest due to the promising application potential in modern medicine. It was proved that plasmonic metal nanoparticles are not only drug carriers and amplifiers of biological effect but also sensors for tracking the fate of the drug in organisms and cells.

The formation of drug conjugates with gold (AuNPs) and silver nanoparticles (AgNPs) are widely described in the literature whereas less attention was paid on the formation of anticancer drug conjugates with platinum nanoparticles (PtNPs). These studies were conducted to verify the main hypothesis that conjugates of erlotinib (ERL), belonging to drugs used in non-small cell lung cancer (NSCLCs) treatment, with PtNPs can be formed in electrostatically-driven self-organization process.

PtNPs were prepared using a seed-mediated growth method. PtNPs exhibited quasi-spherical shape and an average size equal to 108 ± 11 nm. The formation of ERL-PtNP conjugates was carried out under mild acidic conditions, at pH 4.9 and ionic strength 7×10^{-3} M. The spectroscopic analysis of formed conjugates was performed with the use of surface-enhanced Raman spectroscopy (SERS) and surface-enhanced infrared adsorption spectroscopy (SEIRA). The spectroscopic investigation was carried out for positively charged conjugates.

The performed SERS and SEIRA studies indicate that the prepared PtNPs provide effective surface enhancement in visible and infrared regions, respectively, ensuring the possibility to perform detailed characterization of the adsorption process on these metal nanostructures. The considered ERL indicates strong interaction with the PtNPs mainly through the quinazoline and the amino moieties. Also, the ethylene bridge takes part in the conjugates formation, while methoxy moiety and phenylacetylene ring remain at a certain distance from the metal surface.

The comparison of obtained results with available literature data showed that the adsorption pattern of ERL strongly depends on the type of plasmonic nanoparticles because the phenylacetylene ring of ERL plays a crucial role in the formation of conjugates with AuNPs and AgNPs.

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Effect Of Surfactants on Biocompatible And Biodegradable Poly (N^5 -2-Hydroxypropyl-L-Glutamine) – Based Nanogel Preparation And in Vivo imaging of Nanogel Biodistribution

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Nanogels are internally crosslinked hydrogel particles in the nanoscale size range. They are soft, porous, able to swell in aqueous media, biocompatible. Some nanohydrogels may possess stimuli-responsive behavior and biodegradability. These properties, as well as ability to modify nanogels with different functional groups, make them attractive for use in bio- and nanomedicine and modern nanotechnologies, such as the drug delivery and diagnostics systems, biosensors, bioimaging, etc. In the present research, we used a new approach of the synthesis of nanogel from a biocompatible and biodegradable hydrophilic poly(N^5 -2-hydroxypropyl-L-glutamine)-based polymer precursor containing tyramide units (P2HPG) by horseradish peroxidase/ H_2O_2 crosslinking in inverse miniemulsion. We investigated the effects of various surfactants (SPAN 80, TWEEN 85 and AOT) with different concentrations (5, 10, 15, 20, 25% relative to dispersed phase) on nanogel diameter and morphology characterized by dynamic light scattering, nanoparticle tracking analysis and transmission electron microscopy. Finally, the nanogel with tuned properties was radiolabeled with ^{125}I and tested in a non-tumor mouse model *via* single-photon emission computed tomography/computed tomography with two mice. The results showed that nanogel were non- cytotoxic, well-biodistributed, continuously degraded and removed in the urine.

Photochromic surfactant/monoolein nanovectors for the smart delivery of nucleic acids

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There has been a strong interest in the development of nanocarriers of genetic material for its effective delivery into cells, as demonstrated by the recently developed anti-SARS-COV-2 mRNA-based vaccines from Pfizer-BioNTech (Comirnaty®). Smart nanocarriers have also been intensively investigated due to their ability to controllably release their bioactive cargo via stimuli application [1-3], thus potentially increasing therapeutic efficacy. This work involves the development of DNA-compacting nanocarriers that controllably release the cargo via light irradiation (with or without acidification). The carriers are composed by a cationic chalcone derivative and the helper lipid monoolein (with stabilizing and fusogenic properties [3]). The chalcone surfactant acts both as the compacting agent, by electrostatic condensation of DNA, and as the stimuli-sensitive element, since chalcone compounds are part of the multistate chemical network of flavylum compounds [4]. We investigated different chalcone/monoolein molar ratios for the bare vectors and different chalcone/DNA +/- charge ratios for the ternary lipoplexes. The experimental toolbox includes dynamic/electrophoretic light scattering, tensiometry, microscopy, fluorescence and UV-Vis spectroscopy. Results show that chalcone/monoolein mixtures form cationic vesicles that are monomodal and highly stable, able to efficiently compact DNA. Further results concerning lipoplex cytotoxicity and the photo-stimulated DNA release will be shown and discussed.

Keywords: Photosurfactant, Lipoplexes, Stimuli-responsiveness, Nucleic acid delivery

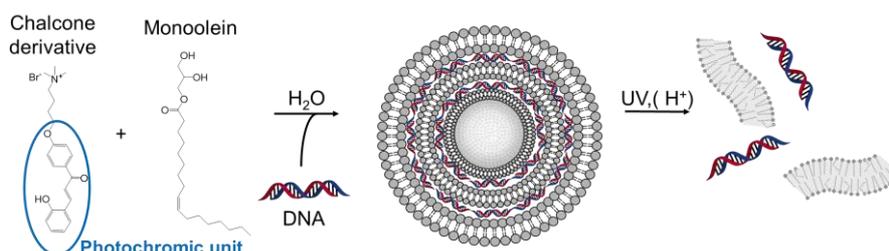


Figure 1. Rationale for the DNA compaction and release by the photoresponsive nanovectors.

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Thermal transport in self-assembled materials: From high anisotropy to high temperatures

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Thermal transport can be significantly influenced by the presence of nano- and mesostructures and the interfaces that exist in such materials. This structuring can be employed to realize super-insulation properties as well as efficient heat spreading. Consequently, nanoscale thermal transport has attracted a lot of research interest for the past 20 years.[1]

Colloidal materials represent an ideal platform to access well-defined devices structured on hierarchical length scales. Colloidal superstructures, which can be amorphous or crystalline, cover size ranges from a few nanometers up to micrometers and beyond. Additionally, one can quickly implement different kinds of materials and fabricate heterostructured composites and hybrid materials.

In this contribution, I will focus on two extreme cases of thermal transport derived from colloiddally self-assembled materials. The first example will cover extremely anisotropic thermal conductors based on 1D crystalline Bragg stacks.[2] Spray-coating of nematic dispersions of 1 nm thick clay dispersions with a distinct amount of water-soluble polymers leads to strictly hard-soft alternating layers. The ratio between in-plane and cross-plane thermal conductivity reaches up to 38 in such fully dielectric materials.[3] Based on a complete mechanical tensor analysis, we can also assess the influence of the nanostructure on the phonon mean free path in such systems.

The second example comprises an isotropic, thermally insulating material based on colloidal ensembles of hollow silica nanoparticles. The combination of low density, disorder, and interparticle constriction results in ultralow thermal conductivities at room temperature.[4] When using such particle packings at high temperatures, the thermal insulation is compromised by an increasing amount of thermal radiation. Laser flash analysis allowed us to directly measure the temperature-dependent transition from purely conducting to radiative transport mechanisms. Combined with a detailed optical and theoretical characterization of the colloidal assembly structures, we work out the relevance of their mid-infrared optical properties.[5]

Keywords: nanoscale thermal transport; colloidal superstructures; anisotropy; radiative transport

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Rare earth liquid-liquid phase transfer facilitated by hydrotropes for intensified processes

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We illustrate here the practical wins in intensification of recycling processes of rare earths leached from electronic waste obtained by advanced formulation of the solvent based on the oil-phase as formulated complex fluids.

The standard theory of liquid-liquid extraction of metals between a concentrated ionic solution and a complex fluid close to water-poor microemulsions at supramolecular scale relies the Gibbs energy of transfer between a water and a solvent phase used in all hydrometallurgic processes to a combination of a large number of identified processes. The “*ienaic*” decomposition [1] takes also into account the Gibbs energy terms that act as quenchers of the transfer towards solvent: i.e. solvent reorganization and polar core cohesion enthalpy, as well as interfacial terms linked to extractant film entropy [2].

We compare here the yields of extraction obtained by replacing the industrially used branched alkane by a standard short chain amphiphile that is used in advanced solubilization of sparingly soluble molecules. All quantities being equal, the replacement of the solvent should have limited effect on the yield of extraction according to the multiple complexation model. However, we observe a stunning increase of extraction yield, by a factor of ten to hundred in distribution coefficients.. This increase in performance in advanced formulation could be used to reduce by a factor of at least ten the environmental cost of rare earth extraction from waste.

We first determine the structures present by small angle X-ray scattering and the Gibbs energy of transfer by fluorescence analysis in specific points of the ternary phase diagram [3]. Then, we will demonstrate this increase in extraction yield of rare earth transfer is independent of stoichiometric complexation, but due to the strong variation of colloidal terms linked to solvent, film and polar core cohesion entropy combined to the supramolecular complexation.

Keywords: reverse micelles, Gibbs energy of transfer, liquid-liquid extraction, hydrotrope

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Assembly of polymer donor: acceptor nanoparticles for high-performance optoelectronic applications

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Water dispersed organic semiconductor nanoparticles (NPs) are considered promising for optoelectronic applications due to their environmentally friendly process. However, deposition of these water-dispersed NPs is inefficient, and control of layer morphology is full of challenges. This work presents a facile and quick approach to preparing self-assembled donor:acceptor NP monolayers for the first time. The nanoparticle arrays are on a large scale (10 cm²) on the water surface and then transferred to various substrates. Notably, the packing pattern can be well controlled from the net-like structure to the close-packed structure.

Furthermore, this approach is suitable for donor:acceptor NPs in various internal structures proved through energy-filtered transmission electron microscopy (EFTEM). Janus particle consisted film shows efficient charge generation and fast charge transfer properties. An outstanding performance of polymer solar cells with over 5% efficiency is achieved by applying this Janus NP film. Ultimately, this work provides a new protocol for processing water-dispersed organic semiconductor colloids and future optoelectronic devices fabrication.[1]

Keywords: donor:acceptor nanoparticles, air-water interface, self-assembly, close-packed monolayer, Janus structure, charge transfer, opto-electronic applications

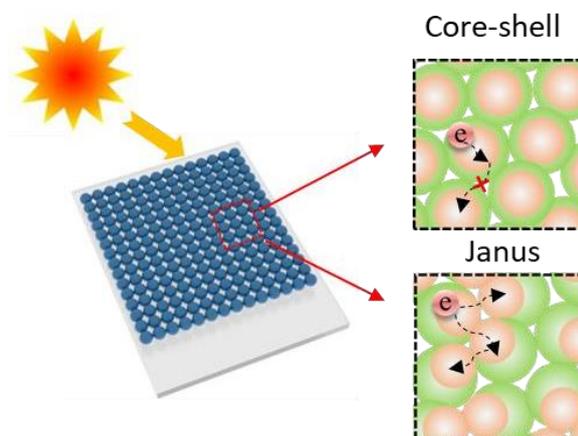


Figure 1. Scheme of the electron transport inside of PTB7:PC₇₁BM NP films.

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Polysaccharide-based microparticles as delivery systems for cosmetic actives: design, stability, interactions with cosmetic formulations

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Colloidal systems (e.g polymeric micro/nano particles, lipid based nanocarriers) are suitable technologies for the encapsulation and delivery of sensitive active compounds (e.g antioxidant, anti-aging, anti-inflammatory, anti-microbial, photo-protective), in various fields including cosmetic [1,2]. The use of microparticles as delivery systems for cosmetic actives allow to maintain the stability and efficacy of these ingredients by protecting them against degradation [3,4] and ensure their controlled release [2] over time and onto the desired target site.

The aim of our project is to design microparticles as carriers for cosmetic actives for skin applications. Active microparticles were prepared using polysaccharides (e.g alginate) as encapsulating agent and polyphenols (e.g gallic acid) as actives molecules (antioxidant). Extrusion-dripping technique has been selected as the encapsulation method to elaborate two kind of systems : microspheres and microcapsules [5], varying in term of morphology. Active microparticles were developed under optimised preparation conditions and characterised in terms of physico-chemical (size, morphology, drug loading) and mechanical properties using different techniques (microscopy, UV spectroscopy, texture analyser). Then, the developed microparticles were incorporated into cosmetic formulations such as emulsions and gels.

The formulations with and without active microparticles were characterized regarding their physico-chemical properties, the colloidal stability and rheological characteristics in order to better understand the interactions of active microparticles with the cosmetic formulations. Furthermore, antioxidant properties of active microparticles were evaluated by using 2,2-Diphenyl-1-picrylhydrazyl (DPPH) method.

Keywords: polysaccharide, microparticles, cosmetic actives, encapsulation, formulations

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Cold atmospheric plasma technology as a versatile approach for producing rhenium nanostructures of catalytic properties

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Organic compounds, such as 4-nitrophenol (4-NP), are common pollutants of wastewaters and have a negative impact on the natural environment [1]. As it is difficult to remove these contaminants by common methods used in sewage treatment plants, development of effective and low-cost methods intended for degradation of these by-products is still of particular importance. A very promising approach to removal of 4-NP is application of colloidal suspensions of metallic nanoparticles (NPs) such as *e.g.* AuNPs and PtNPs [2] that efficiently catalyze their hydrogenation. Very recently, a special attention has been paid to the usage of colloidal suspensions of ReNPs [3]. Among different methods applied for synthesis of NPs of catalytic properties, a very favorable one is this based on cold atmospheric plasma (CAP) interactions with liquids. Because CAP is a rich source of Reactive Oxygen and Nitrogen Species (RONS), synthesis of NPs is driven only by these species, without any need for additional reducing or capping agents [3].

Here, we show a high-throughput CAP-based system developed for production of colloidal suspensions of ReNPs for effective (catalytical) hydrogenation of 4-NP in aqueous solutions. In this approach, the direct current atmospheric pressure glow discharge (dc-APGD) was used as a CAP source and its operating parameters were appropriately selected [4]. After subjection of a ReNPs precursor solution to the CAP action, the post-plasma liquid was gathered and analyzed in view of optical, granulometric, and catalytic properties of the resultant ReNPs. By using transmission electron microscopy (TEM) supported by an energy dispersive X-ray scattering (EDAX) and selected area electron diffraction (SAED), it was found that operation of CAP under these conditions leads to the production of colloidal suspensions of spherical ReO_x NPs of 4.97 ± 3.82 nm in size [4]. Afterwards, ReO_x NPs were applied as catalysts for hydrogenation of 4-NP to 4-aminophenol, and established to be responsible for 85% removal of the targeted compound within 10 mins (with $k_{\text{app}} = 2.66 \times 10^{-3} \text{ s}^{-1}$ [4]).

In a view of the performed experiments, it was confirmed that 4-NP is easily reduced to 4-aminophenol. The suggested method might be a tempting alternative to traditional degradation methods.

Keywords: colloids, 4-nitrophenol, non-thermal plasma

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Conductive hydrogel beads: New generation of flowable electrodes

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Electrically conductive hydrogels (ECHs) are arising types of hydrogels synthesized either by using conductive polymers or dispersing conductive particles in their matrix. These composite hydrogels have been widely used as electrodes [1]. Flowable electrodes, or suspension electrodes, open up new horizons for energy and water technologies [2]. Here, we propose a method to shape conductive hydrogels as microspheres that are flowable due to their deformability. This introduces a new type of electrodes that can be substituted and discharged continuously underflow in capacitive deionization-based water desalination devices.

We developed a high throughput method based on suspension polymerization (inverse emulsion) allowing the production of a large amount of polyacrylamide hydrogel beads as required for their further use (Fig 1. a). A carbon nanotubes (CNTs) network inside these hydrogel beads can provide electronic conductivity, yet their synthesis faces many challenges. Hydrophobic CNT can be dispersed in the aqueous medium with the assistance of surfactant which can then be removed by dialysis in order to provide contact between the particles after gelling [3]. The first challenge is to stabilize the emulsion and prevent coalescence while the beads are polymerizing. Thus, it is necessary to choose a surfactant with a proper nature and sufficient concentration to disperse CNTs. A concomitant issue is the potential adhesion between neighbouring droplets since hydrophobic particles can adsorb at their interface. Additionally, the concentration of surfactant in the continuous phase is also limited to prevent a high number of micelles that cause emulsion polymerization which competes with polymerization inside the droplets. A strategy to overcome these issues is to isolate all the single aqueous droplets while polymerizing (Fig 1. b). This is possible by using a surfactant-free viscoelastic continuous phase to disperse the droplets while avoiding polymerization in micelles and droplet coalescence. Along that, an improved way is to use a microfluidic device to generate calibrated double emulsion droplets that act as microreactors.

Keywords: Conductive hydrogel, Flowable electrodes, Microfluidic, Inverse emulsion polymerization, Double emulsion

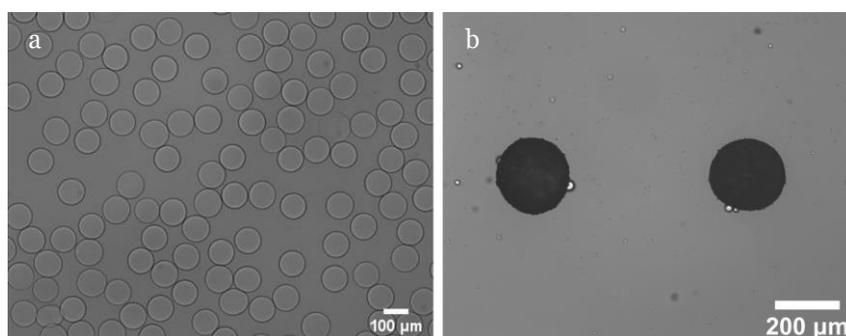


Figure 1. (a) high throughput synthesis of polyacrylamide beads (b) Isolated composite polyacrylamide beads.

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Preparation of colourful solar reflective coatings via sol-gel method

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The sun's rays hitting the Earth's have a wide spectrum of wavelengths, from ultraviolet to infrared. The absorption of near-infrared (NIR) rays, which constitute 53% of the sun's total rays, is responsible for the heating of objects [1, 2]. The amount of NIR rays increases during the summer season, causing the walls and roofs of buildings to overheat. To reduce the discomfort felt in warm buildings, the usage of air conditioning increased. Buildings coated with a solar reflective paint absorb less energy, resulting in a 20% - 40% energy saving through reduced use of air conditioning systems [3, 4]. In this study, different colour solar reflective coatings have been prepared by sol-gel reaction of tetraethoxysilane, methyltrimethoxysilane, and inorganic solar reflective pigments. The coatings morphology and spectral reflectance were investigated by SEM and UV-VIS-NIR spectrophotometry, respectively. Total solar reflectance (%) performance of coatings was calculated to examine the effect of pigment concentration on reflectance performance. The coatings showed a maximum of 86% total solar reflectance.

Keywords: Solar reflective, sol-gel, spray coating

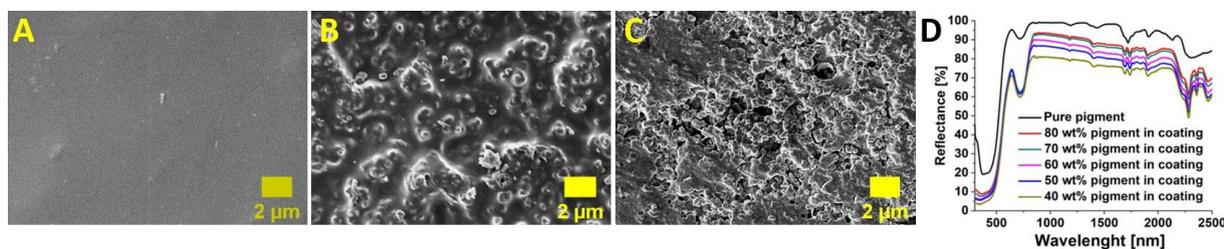


Figure 1. Surface morphologies for different yellow pigment concentrations in the coating (A) 40 wt%, (B) 60 wt% and (C) 80wt%) and spectral reflectance curves (D).

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Water sorption behaviour of commercial furcellaran

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Furcellaran is sulphated polysaccharide extracted from the red seaweed *Furcellaria lumbricalis*. It is a hybrid of κ - and β -carrageenan [1], and is used in the food industry as a gelling and stabilising agent.

The physical and chemical properties of biopolymers are strongly dependent on their temperature and moisture histories. The high temperatures during production of furcellaran and the interaction between water can change the hydrocolloid structure and may make it sensitive to ambient humidity. To understand the water sorption characteristics among biopolymers and atmosphere the water sorption isotherms are usually determined. Every food has its own special isotherms and there is no available isotherm information on furcellaran. The isotherms are important in order to optimise drying parameters, determine packaging requirements and estimate shelf life [2-4].

The aim of the work was to determine the water sorption isotherms of commercial furcellaran at different temperatures (20, 35 and 50 °C) using a gravimetric method under different levels of relative humidity (19–95%). The experimental data obtained have been interpreted in the terms of various isotherm models and it was found that the best results were obtained with the Peleg model. The obtained isotherms followed the type II pattern and, in all cases, the sorption capacity increased with increasing water activity and decreased with increasing temperature. The net isosteric heat of sorption decreased exponentially with increasing moisture content and it was slightly lower during adsorption than during desorption. The developed mathematical relationships can be used to optimize the drying processes and storage conditions of furcellaran.

Keywords: furcellaran, sorption isotherm, modelling, net isosteric heat of sorption

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Glossy Surfaces: Metal Flake Alignment in Printed Liquid Films

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Metallizing surfaces by printing and hereby producing glossy surfaces and patterns for consumer product packaging is a challenging process in contemporary graphical arts and industries. The option to design glossy surfaces by liquid-based production methods has continuously acquired attention with the trend to more sustainable and resource-saving production, because it offers opportunities and substitutes for low margin printing product markets.

Metallic printing inks are dispersions of metallic platelet pigments in a printing ink. For instance, the metallic flakes can be dispersed in UV inks. They can be processed with an e. g. flexographic printing press. After printing on foil, paper or cardboard, the gloss changes in the short time between application and the solidification of the ink by UV curing. Platelet relaxation is driven by capillary forces between the platelets and on the liquid surface, and by imbibition of the volatile ink components. Gloss development depends on ink rheology and on the size distribution of the platelets, features which can be tailored by deliberate ink formulation and printing process design.

As a matter of fact, “gloss” or “glossy appearance” is a matter of human perception [1]. Gloss meters have been developed to perform physical measurements of the reflectance of a surface. The dynamic change of measurements over time of the gloss measurements after printing give insight into the liquid film relaxation and behavior of metal flakes in the liquid film. Systematic studies of the printed liquid film relaxation give interesting insight into fundamental physics of colloid and dispersion dynamics such as surface leveling and particle size distribution dependent Kohlrausch behavior of particle ordering.

Keywords: printing, liquid film, platelet pigments, gloss

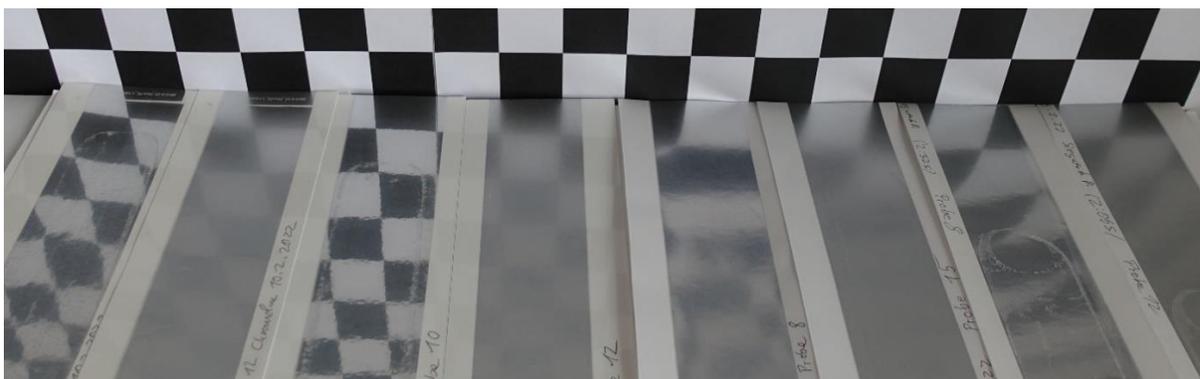


Figure 1. Mirror images of a checkerboard pattern in printed glossy surfaces of different qualities

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Role of particles size on the cohesive strength of non-sintered (green) ceramics

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Preparation of particle-loaded foams, followed by drying, sintering and/or cross-linking are widely explored routes for developing lightweight ceramics with high mechanical strength. The non-sintered foams are less studied due to their intricate production (complex foam generation and long-term stabilization), possible cracking upon drying, and the assumed poor mechanical strength of the obtained "green" bodies after drying. Here we produce and evaluate the mechanical strength of non-treated lightweight ceramics, composed of spherical silica particles with diameters varied between 7.5 nm and 26 μm . We produced wet foams in the presence of cationic surfactant and dried them at ambient conditions, thus obtaining porous materials with mass density between 100 and 700 kg/m^3 . The materials containing smaller particles exhibited much higher strength (up to 2000 times), approaching that of sintered materials. We explain the higher strength via increased van der Waals attraction between the particles per unit area of the materials.

Keywords: green strength, mechanical strength, foamed ceramics, particles size, grain size

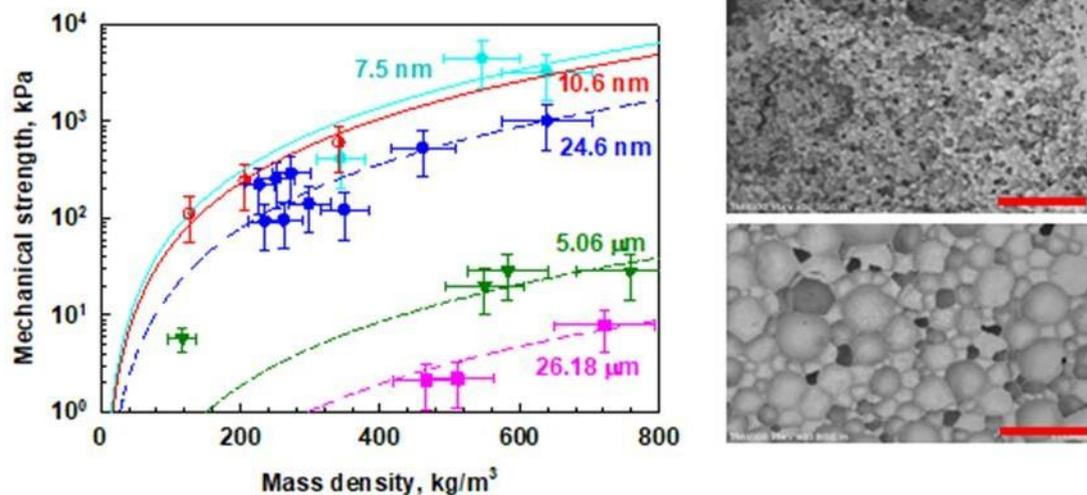


Figure 1. Mechanical strength of green materials, as function of their density

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Polymeric Capsules with VOCs for Controlled Emission

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Micro-(nano-)encapsulation technology involves building of a barrier between the core and the environment and offers a number of benefits to preserve the functional and physicochemical properties of core material. Tremendous progress has been made in synthesizing well-defined capsules to achieve desired properties such as particle size, chemical composition, and controlled release of the payload.

Encapsulation of volatile organic compounds (VOCs) that could evaporate with a defined rate is of immense interest for application in emission reference materials (ERM). These are urgently needed for quality assurance and quality control purposes (QA/QC) required by test standards for the determination of chemical emissions of construction and other materials for interior use. As such ERMs are hardly available on the market, the EU-funded EMPIR project MetrIAQ [1] was started to fill this gap by developing a material with temporally constant emission of VOCs typically found in indoor air.

Different capsules in a size range between 5 and 50 µm were synthesized through an interfacial polyaddition/polycondensation reaction in direct (water-in-oil) system. As VOC several types of hydrophobic liquid materials were used. After synthesis, the morphology and physicochemical properties of capsules were characterized by electron microscopy, FTIR and DSC/TGA. An encapsulation efficiency up to 90% could be reached. The emission kinetic of volatile agents was studied in emission test chambers at 23 °C and 50% RH for 14 days. First results indicate that variation of the cross-linking grade of the shell material is one important parameter to adjust the desired emission rate. The overall aim is to achieve a consistent emission profile that decreases by less than 10 % over a target period of at least 14 days.

Keywords: capsules, volatile organic compound, polymer, material emissions, QA/QC, reference materials.

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Phase separation of saturated micellar network and its potential applications for nanoemulsification

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Phase separation of saturated micellar network, as a result of cross-linking of branched micelles, is established in mixed solutions of the anionic surfactant sodium lauryl ether sulfate (SLES) and the zwitterionic cocamidopropyl betaine (CAPB) in the presence of divalent counterions: Ca^{2+} , Zn^{2+} , and Mg^{2+} . The saturated network appears in the form of droplets, which are heavier than water and sediment at the bottom of the vessel. In the case of Mg^{2+} , the sedimented drops coalesce and form a separate multiconnected micellar phase – a supergiant surfactant micelle. For this phase, the rheological flow curves show Newtonian and shear-thinning regions. The appearance/disappearance of the Newtonian region marks the onset of the formation of a saturated network. The addition of small organic molecules (fragrances) to the multiconnected micellar phase leads to an almost spontaneous formation of oil-in-water nanoemulsion. The nanoemulsification capacity of the multiconnected micellar phase decreases with the rise of the volume of the oil molecule. A possible role of the network junctions in the nanoemulsification process can be anticipated. The properties of the multiconnected micellar phases could find applications in extraction and separation processes, in drug/active delivery, and for nanoemulsification at minimal energy input.

Keywords: Multiconnected micellar phase; Saturated network; Nanoemulsions

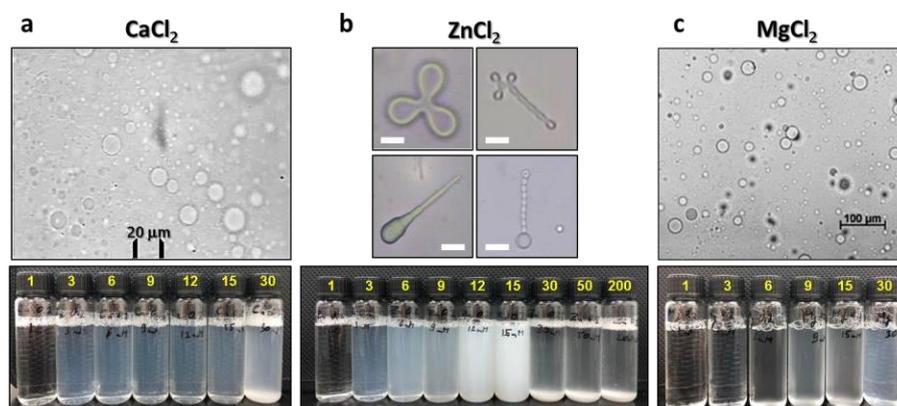


Figure 1. Photographs illustrating the phase behavior of 0.2 wt% 1:1 w/w CAPB:SLES solutions with the rise of the concentration (mM) of added salt given on the caps of the vials

Acknowledgements: The authors acknowledge the financial support of the Operational Programme “Science and Education for Smart Growth”, Bulgaria, project No. BG05M2OP001-1.002-0023.

PMMA nano-encapsulated phase change material colloids for heat management applications

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Phase change material emulsions (PCMEs) and nano-encapsulated PCMs have risen interest in recent years as potential heat transfer and heat storage fluids. These systems consist of a base fluid, a suitable heat transfer fluid, and an emulsified or an encapsulated PCM, which should be immiscible with the base fluid. The idea is to exploit the latent heat of melting and crystallization of PCM to increase the thermal energy storage capacity of the base fluid. The continuous phase, the base fluid, confers greater thermal conductivity and lower viscosity than PCM. The emulsified or encapsulated systems have also the advantage to be pumped through a heat transfer circuit independently from the state of PCM. In this work, RT21HC, a commercial PCM material with transition temperature at 21 °C provided by Rubitherm Technologies GmbH, has been successfully nano-encapsulated with Poly(methyl methacrylate) by an emulsion polymerization process after the selection of proper surfactant and synthesis parameters in order to obtain complete encapsulation and stable colloidal dispersions. Water-based colloidal dispersions at 10 wt% PCM have been obtained and characterized from colloidal stability point of view, rheological properties, apparent heat capacity and thermal conductivity. The effect of PMMA nano-encapsulation and the presence of nucleating agents within the capsules on PCM supercooling has also been studied.

Keywords: nano-encapsulation, PCM, emulsion polymerization

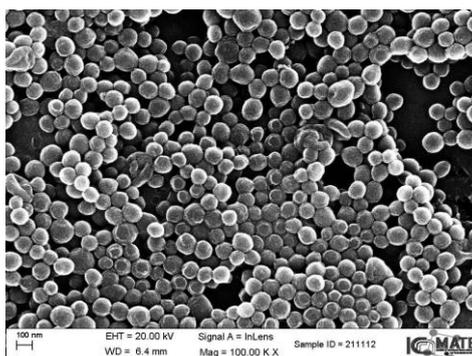


Figure 1. SEM micrograph of PMMA nano-encapsulated PCM.

Acknowledgements: The authors would like to acknowledge the financial support of CNR through the project@CNR "Phase change material nano-emulsions for energy efficient cooling".

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Rational formulation of a more sustainable household cleaning product

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Because of the new cleaning routines assessed during the SARS-CoV-2 (COVID-19) pandemic, the global surfactant market turnover is expected to grow to \$58.5 billion by 2024. The main portion of this market is devoted to fossil fuel-based chemicals but nowadays several European manufacturers are trying to switch to more sustainable products involving the use of novel green surfactants [1]. This is not only a message of environmental awareness but also a way to orient the constant growth of surfactant market on a sustainable route. Other strategies to reduce the environmental footprint of the cleaning product market imply the use of more sustainable organic solvents and reducing packaging materials. To do so green solvents are now used in many formulations and the use of more concentrated refill products has been assessed as a clever tool to reuse packaging materials, these more concentrated formulations are also known as juice.

In the present work we try to handle all these tasks in the formulation of a hard surface cleaning spray: novel glucamide surfactants with a high renewable carbon index (RCI=95%) have been applied; limonene has been used as solvent but also as perfume; the possibility of formulating a juice is eventually considered. To do so a partial phase diagram has been developed as starting point, small angle X-Ray scattering (SAXS) and rheology allowed us to individuate the more suitable dilution line for the development of our product [2]. Scattering and optical microscopy were essential to individuate and characterize the liquid crystal phases which are to be avoided in many cases but wanted in others. In the end we tested our product efficiency in a full performance review comparing it with other products on the market.

Keywords: formulation, biosurfactant, cleaning

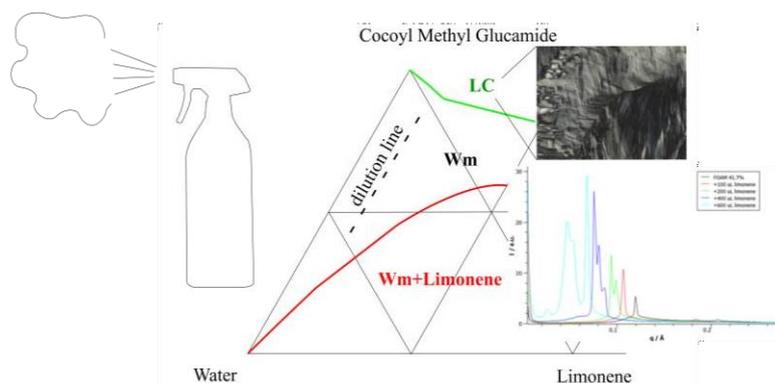


Figure 1. Partial phase diagram of a cocoyl methyl glucamide/water/limonene system.

Acknowledgements: D.S. was funded from the Italian Ministry of research MUR under the program “PON Ricerca e Innovazione 2014–2020” project DOT1302393.

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Local Zeta Potential correction in Dead-end Pore

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Chemically induced transport methods open up new strategies for colloidal transport in dead-end pore geometries[1]. Diffusiophoresis, a chemical gradient transport mechanism, describes particle movement under chemical energy differences resulting from a concentration gradient. Particles can enter a dead-end pore when it contains a salt gradient[1-2]. These particles experience both a diffusiophoretic motion and convective flow induced by the analogous action of a concentration gradient on a charged pore wall. The particle velocity is influenced by the electrokinetic parameters of the particle and the wall, ion valance, and diffusivity contrast of cations and anions (Figure 1). Although it is known that some of those parameters are affected by concentration, e.g., zeta potential, the research to date reduced to averaged values in theoretical expressions. Here, we point out that using concentration-dependent zeta potentials is essential for identifying the particle transport inside dead-end channels. We simulate the particle transport numerically based on the Stokes equation and species transport, including phoretic and osmotic contributions, and the simulation results agree with the experimental observations when the concentration-dependent zeta potential is used. Moreover, a modified particle tracking method was developed to determine the velocities to characterize the particle movement experimentally. Our study shows that experiments and models match better when using the concentration-dependent zeta potential.

Keywords: Diffusiophoresis, diffusio-osmosis, dead-end pore

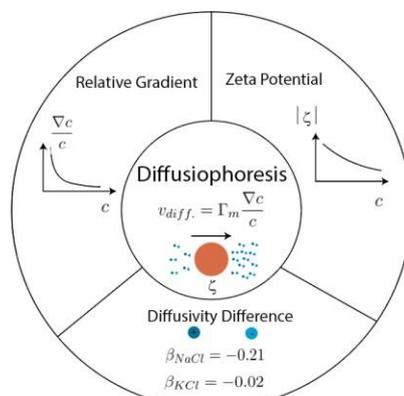


Figure 1. Origins of the electrolyte diffusiophoresis.

Acknowledgements: This work was supported by the Netherlands Center for Multiscale Catalytic Energy Conversion (MCEC), an NWO Gravitation programme funded by the Ministry of Education, Culture, and Science of the government the Netherlands. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 801359.

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Enhanced solubility of methyl ester sulfonates below their Krafft points in the presence of nonionic cosurfactants

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Many ionic surfactants with wide applications in personal-care and house-hold detergency show limited water solubility at lower temperatures (Krafft point). This drawback can be overcome by using mixed solutions, where the ionic surfactant is incorporated in mixed micelles with another surfactant, which is soluble at lower temperatures [1].

The solubility and electrolytic conductivity for a binary surfactant mixture of anionic methyl ester sulfonates (MES) with nonionic alkyl polyglucoside and alkyl polyoxyethylene ether at 5°C during long-term storage were measured. Phase diagrams were established; a general theoretical model for their explanation was developed and checked experimentally.

The binary and ternary phase diagrams for studied surfactant mixtures include phase domains: mixed micelles; micelles+crystallites; crystallites, and molecular solution (Figure 1.). The results could be used to increase the range of applicability of MES–surfactants with relatively high Krafft temperature, but with various useful properties such as excellent biodegradability and skin compatibility; stability in hard water; good wetting and cleaning performance.

Keywords: Methyl esters sulfonates; Alkyl polyglucoside; Alkyl polyoxyethylene ether; Surfactant mixtures – phase diagrams; Lowering of the Krafft point; Micelle–crystallite coexistence

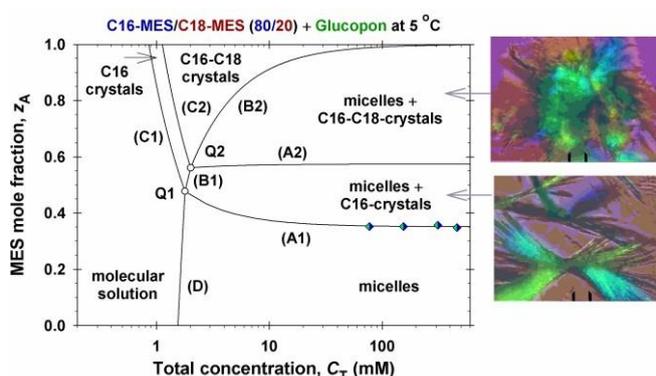


Figure 1. Phase diagrams of C16/C18 (80/20) MES in Glucopon micellar solutions.

Acknowledgements: The authors gratefully acknowledge the support from the National Science Fund of Bulgaria, Grant No. KP-06-PN 49/5/2020.

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Diffusion of pharmaceuticals in agarose hydrogels enriched by humic acids

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The use of many different pharmaceuticals in medicine can result in potential dangerous behaviour in soil and aqueous environments [1]. Drugs are not completely eliminated in human body, therefore their residues can leave the body and pass into water, sediments and soils [2,3]. The potential degradation of drugs depends on their chemical character and physicochemical properties of their environment as e.g. soil properties and quality of organic matter. The migration ability and toxicity of pharmaceuticals in nature can be significantly affected by their interactions with soil components.

Sulfonamides are one of the most commonly used antibiotic in human and veterinary medicine. Their overuse and misuse led to their widespread occurrence in nature [4,5]. In this contribution, sulfamethoxazole and sulphapyridine were used as representative of them. Diffusion experiments in agarose hydrogels and the hydrogels enriched by humic acids were realized. Pharmaceuticals diffused from saturated solutions into hydrogels and (in the case of enriched hydrogels) interacted with humic acids. A part of drugs such was immobilized which influenced the value of diffusion coefficients. Diffusion coefficients were determined for pure agarose hydrogels as well as for hydrogels containing humic acids and compared. The portion of free movable and immobilized pharmaceuticals and apparent equilibrium constant between free and bound drugs were calculated.

Keywords: pharmaceuticals, diffusion, agarose, hydrogel, humic acid

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Using the HLD_N equation to design direct and reverse emulsions stabilized by highly effective dodecylglycerylether surfactant

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The well-defined surfactant 1-O-dodecyl diglycerol ether ($C_{12}Gly_2$, see Fig. 1a) yields highly stable emulsions at low concentration (1 wt.%). In this work, the amphiphilic behaviour of $C_{12}Gly_2$ is quantified within the Normalized Hydrophilic-Lipophilic-Deviation (HLD_N) framework (Eq. 1), allowing to design $C_{12}Gly_2$ /Oil/Water macro-, micro- or nano-dispersed emulsions with desired features.[1,2]

$$HLD_N = PACN - EACN + \tau \cdot (T - 25) + \delta \cdot S \quad (1)$$

Where PACN expresses the hydrophilic/lipophilic ratio of the surfactant, EACN is the oil hydrophobicity, T the temperature ($^{\circ}C$) and S the salinity (wt.% NaCl) τ and δ reflect the surfactant sensitivity towards temperature and salinity respectively.

Thus, the Winsor phases formed at equilibrium and the dynamic phase inversions of $C_{12}Gly_2$ /*n*-Alkane/Water systems were investigated to determine the characteristic parameters of the surfactant in the HLD_N equation (PACN, τ , δ).

Either direct O/W or reverse W/O emulsions were formed by varying the oil hydrophobicity in the $C_{12}Gly_2$ /Oil/Water system. Droplet size (see Fig. 1b) was measured and emulsion stability was monitored using a Turbiscan device. Typical curves are shown in Fig. 1b. Results show that there exists a minimum in droplet size and emulsion stability matching the $HLD_N = 0$ value. In these particular conditions, the surfactant affinity for both the aqueous and the oil phases is identical and the curvature is close to 0.

Keywords: Normalized Hydrophilic-Lipophilic-Deviation, Phase Inversion, Microemulsion, Emulsion, Turbiscan.

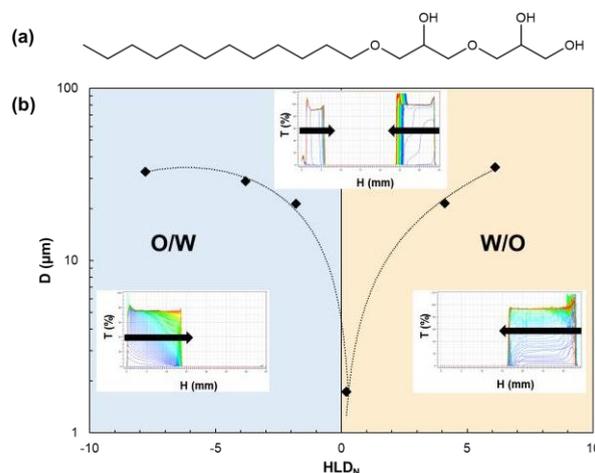


Figure 1. (a) 1-O-dodecyl diglycerol ether ($C_{12}Gly_2$) structure and (b) droplet diameter evolution with HLD_N values and Turbiscan-monitored stability showing creaming/sedimentation for SOW systems yielding O/W emulsions ($HLD_N < 0$), W/O emulsions ($HLD_N > 0$) or Winsor III microemulsion ($HLD_N \approx 0$).

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Poly(2-oxazoline)s as smart PEG-alternatives: high tunability and versatility for an easy access to a wide range of hydrophilic emulsion stabilizers

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In the past decades, polyoxazolines (POx) have seen a resurgence of interest due to their biocompatibility, low (cyto)toxicity and higher tunability compared to polyethylene glycol ethers (PEG) [1]. Although their use as an alternative polymeric surfactant to PEGs has been shown, studies concerning the ability of these amphiphilic (co)poly(2-oxazoline)s to stabilize emulsions remains unexplored and even non-existent in the case of Pickering emulsions [2].

In this work, we show how to take advantage of the high tunability of POx to synthesize a series of amphiphilic copolymers based on 2-methyl-2-oxazoline (hydrophilic moiety) and 2-phenyl-2-oxazoline (hydrophobic moiety) with variable hydrophilic/lipophilic balance (HLB), degree of polymerization (DP), and monomer distribution, capable of stabilizing either conventional emulsions when the copolymers are soluble or Pickering emulsions when it is insoluble.

Remarkably, very stable (> 2 months at 60 °C) oil-in-water and high internal phase emulsions (both conventional and Pickering) can be obtained with 0.5 wt.% copolymers. Their texture and rheological properties can be adjusted from the nature of the amphiphilic copolymers used based on HLB values and DP, concentration or water/oil ratio. Interestingly, the physical-chemical properties of the emulsions prepared with gradient copolymers show similar behavior compared to their block counterparts, thus offering easy access to efficient new emulsifiers for pharmaceutical, cosmetic and food applications.

Keywords: Polyoxazoline; Polymeric surfactant; Amphiphilic particle; Emulsion; High internal phase emulsion; Pickering emulsion

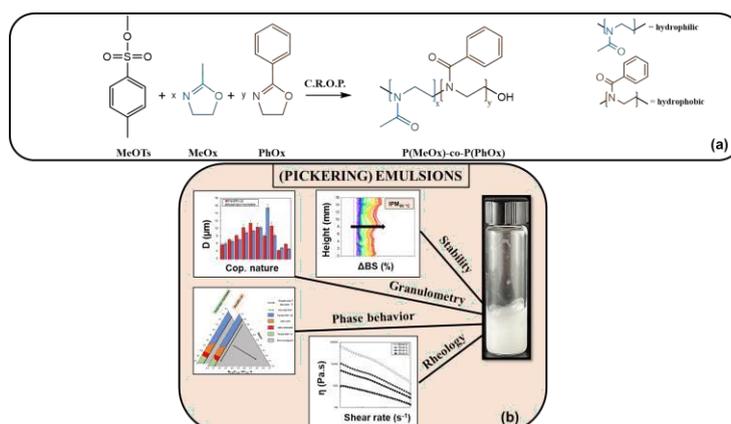


Figure 1. (a) Schematic representation of the synthesis strategy of amphiphilic P(MeOx)-co-P(PhOx). (b) Physical-chemical characterizations of emulsions.

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Scalable Production of Silica-coated Magnetic Nanobeads and their Applications in Viral Diagnostics

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In December 2019, a novel coronavirus SARS-CoV-2 was identified in Wuhan, China that led to a subsequent global pandemic. This led to a massive shortage of RNA extraction kits among others, worldwide, heavily affecting the testing capacity of infected people.[1] To help alleviate the shortage, an interdisciplinary collaboration between the Departments of Chemical Engineering and Clinical & Molecular Medicine led to the development and upscaling of nanoparticle (NP) production, lysis buffer production, extraction protocol optimization and implementation on liquid handling systems for large scale diagnostics. The method was approved for corona virus diagnostics in Norway.[2]

The synthesis of these beads involves a two-stage process, where, in the first step, 10-12 nm iron oxide nanoparticles (IONPs) are synthesized via co-precipitation followed by silanization of the cores using a modified Stober's method, leading to monodisperse nanobeads of 580 ± 25 nm. (Figure 1(a)) The size, morphology and magnetic properties of the silica coated IONPs were optimized by varying the solvent, mass ratio of silica precursor to IONPs, catalyst concentration among other parameters. The optimized protocol was scaled up and this scaled-up process has been licensed to Lybe Scientific A/S, an NTNU based startup that sells these nanobeads under the trade name NAXtra.

Our results demonstrate that NAXtra has a very broad application range, including RNA (Figure 1(b),(c)) and DNA viruses both with protein and lipid layer envelope. Additionally, NAXtra is efficient for extraction of nucleic acids from bacteria and mammalian cells and tissue. In conclusion, NAXtra is a sensitive, robust, fast, simple, flexible and inexpensive method for nucleic acid extraction in research and diagnostics.

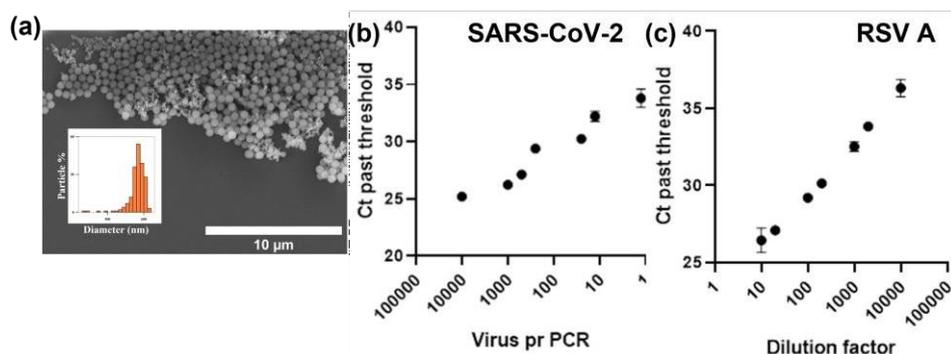


Figure 1. (a) Representative SEM image of NAXtra. (b)(c) Results from NAXtra method on various Qnostics analytical panels. Elution product analyzed on qPCR. Error bars show the standard deviation.

Keywords: Iron oxide nanoparticles, diagnostics, virus, lysis buffer, magnetic nanobeads

Acknowledgements: The authors would like to thank all members of the Corona Project Team that contributed to the production of close to 20 million test kits during the pandemic.

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Microgels as lubricants and rheology modifiers

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Oral tribology has emerged as a key paradigm in the tribology field to quantify friction in soft sliding oral contact surfaces such as tongue-palate, tongue-food etc [1,2] and is recently providing fundamental insights into the physics of oral processing and sensory perception. In particular, biocompatible microgels have been recently demonstrated to act as excellent lubricants in oral tribological contacts, with applications in dry mouth therapy and designing fat mimetics [3]. Using a combination of experimental techniques and theoretical considerations, case studies [3-6] will be covered on tribology of soft elastomeric surfaces (with different wetting properties and surface roughness) in the presence of proteinaceous microgels with well-defined deformability, composition, cross-linking densities, degree of conjugation and particle sizes. Some of these microgels show aqueous 'ball-bearing' abilities depending upon their volume fraction [4]. A case study [6] will be presented on how these proteinaceous microgels can act as viscosity modifiers of the continuum, where the lubrication performance can be quantitatively described using the Newtonian plateau value (η_{∞}). Also it will be discussed on how proteinaceous microgels can be combined with non-microgelled free protein to provide combined viscous and thin-film lubricity [7]. In summary, we will demonstrate that microgels act as viscosity modifiers directly influencing the tribological performance, depending upon a subtle interplay of mechanics of the particles as well the continuum in which the microgels are dispersed.

Keywords: soft tribology; oral; microgel; viscosity; continuum; particle size

Acknowledgements: The European Research Council is acknowledged for its financial support (Funding scheme, ERC Starting Grant 2017, Project number 757993) for this work.

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Effect of alkali activators on pore size of geopolymers – A comparative study

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Geopolymers are alumina-silicate polymeric, porous materials that are a promising green alternative to cement thanks to the facile and low-temperature synthesis. For applications as construction materials or in nuclear waste treatment, the pore structure is of central interest: large and open pores are disadvantageous with respect to mechanical stability and adsorption capacity. We investigate the influence of the alkali activator (K- or Na-based) on the pore size of the geopolymers. A comparative study of characterization techniques (mercury intrusion porosimetry (MIP), N₂ adsorption and small angle x-ray scattering (SAXS)) is presented. Results show that K activators lead to smaller pore sizes. By combining the three measurement methods it is possible to characterize the overall pore structure including open (MIP and N₂, SAXS) and closed (SAXS) pores.

Reinforced hydrogels: polymer cross-linking by emulsion droplets

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Hybrid materials of a polymer network with inclusions of lyotropic liquid crystalline droplets can provide versatile transport of both hydrophilic and hydrophobic substances through aqueous media. Therefore, such systems have a great potential for biotechnological and food science applications. However, weak mechanical strength of the hydrogel skeleton significantly limits the use of such composites. Haraguchi *et al.* [1] proposed to prepare hydrogels with improved mechanical properties by free radical polymerization in an aqueous suspension of Laponite clay particles. In this case, the polymer chains adsorb at the surface of the particles so that the cross-linking density of the resulting physical gel network is largely increased. We combine this effect with Pickering stabilization of droplets by Laponite particles [2] to prepare hydrogel/emulsion composites. Due to the droplets acting as multifunctional cross-links, the materials demonstrate an enhanced elastic modulus in comparison with Haraguchi hydrogels. Moreover, we prepare emulsion droplets using L2 liquid crystal phase composed of inverse micelles of phytantriol in dodecane medium [3] (Figure 1), which allows to functionalize the resulting hybrid materials both with hydrophilic and lipophilic agents.

We correlate the mechanical properties with the structure by studying the multi-scale organization of the materials with electron microscopy, X-ray Scattering and Small Angle Neutron Scattering (SANS).

Keywords: hydrogel, Pickering emulsion, hybrid materials

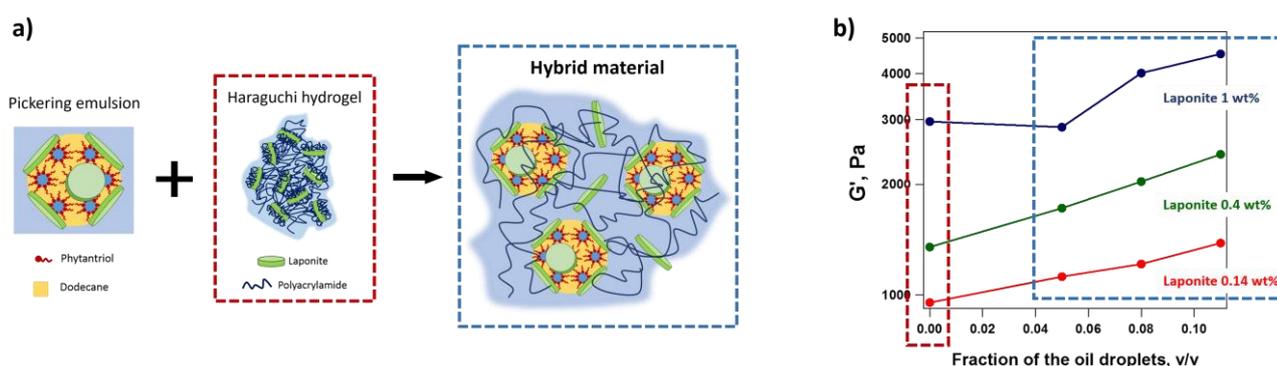


Figure 1. Sketch of the hydrogel/emulsion hybrid material structure (a) giving improved mechanical properties (b).

Acknowledgements: AM acknowledges financial support from LABEX MMCD.

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Thin layer of organosilane having specific functionality for the understanding of rare earth extraction

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In the context of rare earth element recycling by solid-liquid extraction, silica-hybrid materials are found to be a promising approach. In this study, we have used functionalized plane surface associated to specific surface characterization techniques to quantify the interactions between the REE and the extractive group of the molecule.

In a first part, we have followed the grafting process of molecules having a diglycolamide functional head group, known to have complexing properties regarding REE [1]. Combining *ex situ* technique such as contact angle, X-ray reflectivity analysis and peak force measurements using atomic force microscopy with *in situ* techniques using Attenuated Total Reflection coupled to Infrared spectroscopy (ATR-FTIR), we have evidenced a monolayer of 2 nm presenting polycondensed molecules with Si-O-Si network forming cage-like structure.

In a second part, the evolution of the grafted molecules in contact with NdCl_3 and $\text{Nd}(\text{NO}_3)_3$ solutions at 0.1 M and pH comprised between 1 and 4 was investigated by *in situ* ATR-FTIR and hard X-ray reflectivity measurements at ESRF. The results showed that the highly hydrated Nd^{3+} cations diffuse inside the grafted layer and then are complexed by the DGA head group. This complexation raises with a pH decrease and leads to Nd^{3+} dehydration associated with a measurable deformation of the surface brush. Apparent Gibbs energy of binding can be also calculated.

Keywords: REE extraction, organosilane, grafting, complexation, hard X-ray reflectivity, infrared spectroscopy

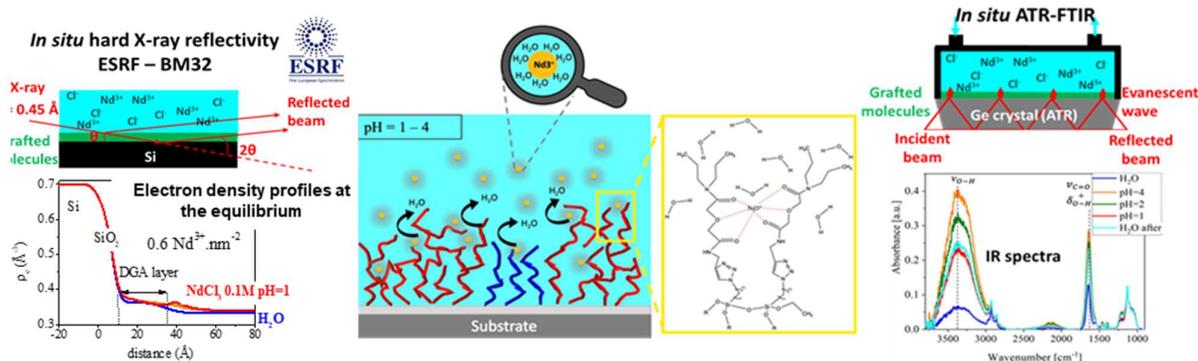


Figure 1. Illustration of the method used to characterize the interactions of grafted organosilane having a diglycolamide headgroup for the understanding of REE extraction.

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Templating the Growth of Bi_2MoO_6 with Clay-like Materials toward Sorbent Photocatalytic Composites

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Bi_2MoO_6 is the simplest member of the Aurivillius group and has been lately studied for its photocatalytic activity. An anionic discoidal nanoclay was organically modified and used to template the growth of Bi_2MoO_6 . The organically-modified clay interface templated Bi_2MoO_6 crystal growth along the $[010]$ direction, resulting in the formation of clay- Bi_2MoO_6 hybrids terminating in $\{100\}$ -facets of Bi_2MoO_6 . These $\{100\}$ -faceted Bi_2MoO_6 -clay hybrids exhibited enhanced and instantaneous adsorption of both cationic and anionic dyes from their aqueous solutions, compared to pristine Bi_2MoO_6 nanoparticles and other clay-based composites. These dye-laden composite particles sediment, rendering their recovery trivial. Moreover, their reuse over multiple cycles can be achieved by photocatalytically degrading the adsorbed dye. [1] Furthermore, templating growth using a cationic clay-like template, such as layered double hydroxides, provided a similar composite which selectively sequestered anionic dyes from aqueous solution. [2]

Further improvements to the adsorption performance of clay- Bi_2MoO_6 hybrids could also be accomplished by encapsulating them with a thin shell of crosslinked polymers, in which crosslinker amount and polymer blend were optimized for ideal adsorption. The removal of dissolved molecular species under flow conditions was attained by depositing these polymer-particle composites on filtration membranes. The repeated reuse of these membranes was also rendered possible by photocatalytically degrading the adsorbed dye, showing that such materials have great promise in anti-fouling water filtration membranes. [3] In summary, surface modification and choice of template particles provided a means to tune the adsorptivity and selectivity of Bi_2MoO_6 composites.

Keywords: Nanoclay, Bi_2MoO_6 , Layered double hydroxides, water decontamination, adsorption, photocatalysis

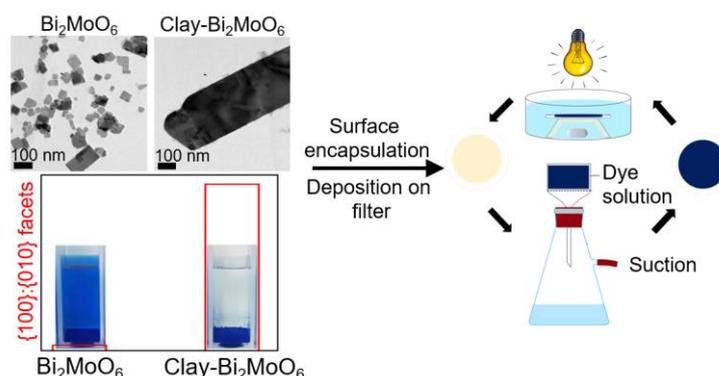


Figure 1. Highly sorbent and photocatalytic $\{100\}$ -faceted clay- Bi_2MoO_6 composite particles.

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Synthesis and application of CoFe₂O₄/TiO₂-doped activated carbon-based nanophotocatalysts

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As a result of the increasing amount of pollutants in the environment, many attempts to reduce their level are taken. Nowadays, high hopes are placed in the processes of photocatalytic oxidation, as a result of which organic pollutants are degraded to simple non-toxic compounds. The need to care for the environment also prompts the search for new procedures for the production of materials with photocatalytic properties, the production of which would not require the use of toxic chemicals. Mechanochemical processes that can initiate chemical reactions between solids come to the rescue. Additionally, they do not cause any by-products.

The aim of the presented research was to prepare activated carbon-based photocatalysts, doped with CoFe₂O₄/TiO₂ nanoparticles, causing photocomposition of organic dyes. As a precursor for obtaining activated carbons green tea leaves were used. The pyrolysis was carried out up to the temperature of 800°C (activating agent: steam; 0.5 h). CoFe₂O₄ nanoparticles were obtained applying the co-precipitation method (1.0 M CoCl₂·6H₂O; 2.0 M FeCl₃·6H₂O). The mechanochemical treatment was carried out in a planetary ball mill in 4 cycles (4 x 15 min) at 250 rpm. The three series of materials were prepared differing in the admixture content: 30%, 40% and 50% (wt. %). The obtained materials were studied for their photocatalytic properties. The UV lamp was used as a light source. The model contamination was an aqueous solution of Safranin T (C₀= 10 mg/L). The studied dye solutions were measured spectrophotometrically at a wavelength of 520 nm.

On the basis of the research it was found that the materials are characterized by large surface area with a well-developed pore structure. All obtained materials exhibit photocatalytic activity in the UV range. However, the nanophotocatalyst doped with 30% of CoFe₂O₄/TiO₂ nanoparticles shown the highest photocatalytic activity, reaching 95% degradation of Safranin T in water solution.

Keywords: activated carbon, nanophotocatalysts, UV-degradation, organic dyes

Pyrolysis atmosphere impact on the textural properties and the surface chemistry of activated carbons

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Activated carbons are obtained as a result of the pyrolysis process and the activation of carbonaceous precursor. However, the product obtained during the carbonization of the starting material is adsorption inactive and has a very poorly developed porous structure. It is well-known fact that activation is a key step in the development of the pore structure of the carbon materials. One can apply physical or/and chemical activation. In the case of physical activation, the material obtained after carbonization is activated with an oxidizing gas for extending and strengthening the surface and pores structure. The most commonly used oxidizing agents are: steam, carbon dioxide, air or mixtures of these gases.

The aim of the presented research was to investigate the influence of the atmosphere of the pyrolysis process on the development of the porous structure as well as surface chemistry of the activated carbons. Spruce cones (*Picea abies*) were used as a precursor to obtain carbon materials. The pyrolysis was carried out in an oxidizing atmosphere of carbon dioxide (100 ml/min) or in the presence of superheated steam (0.6 ml/min). The intermediate isothermal stage at 400°C (1h) was used. At the final temperature (800°C), the samples were annealed for 2 hours. The activated carbons obtained in the pyrolysis process were subjected to additional hydrothermal modification with superheated steam using microwave radiation as an energy source (60 min; 77-80 atm). Low-temperature nitrogen adsorption/desorption, thermal analysis and potentiometric titration method were used to characterize the obtained materials.

Keywords: activated carbons, pyrolysis atmosphere, textural characterization, surface chemistry

Study of the chiro-optical and electronic properties of a solid-state o-OPE at the air-water interface

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Due to their usefulness as luminous materials in optical devices and biosensors, enantiopure chiral organic compounds capable of producing circular polarized luminescence responses are of great interest. The molecules named in this work as (S,S)-1 and (R,R)-1 are flexible helical molecules with a chirally stapled ortho-oligophenylene-ethylene (o-OPE) skeleton. (S,S)-1 and (R,R)-1 are able to induce a preferential helicity in the molecules, thus obtaining enantiopure compounds with intense circular dichroism spectra and good circularly polarised luminescence[1].

This enantiomer pair was studied in detail by a combination of π -A isotherms, UV-Visible reflection spectroscopy (ΔR), Brewster Angle Microscopy (BAM), and computer simulations [2]. These studies were carried out with the aim of determining the best conditions for the design of an invisible "barcode", where the sign could be printed and evaluated in different spatial regions of a solid surfaces. Such information would only be accessible with suitable equipment.

Keywords: thin films; Langmuir; air-water interface; BAM

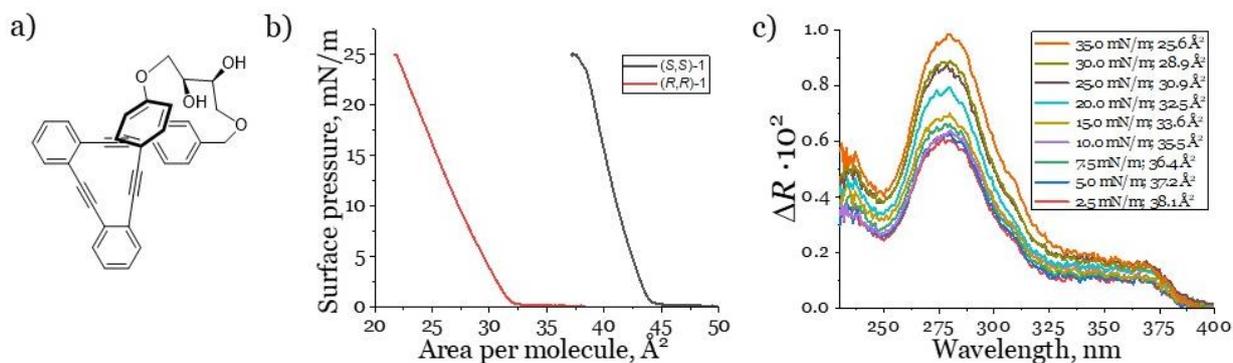


Figure 1. a) chemical formula b) π -A isotherm of (S,S)-1 and (R,R)-1 c) UV-vis reflection spectroscopy at the air/water interface of (R,R)-1

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Influence of Ionic Strength and Anion Type on the Properties of Chitosan-Carboxymethylcellulose Nanofilm

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Polyelectrolyte multilayer films based on natural polymers, such as polysaccharides, polyaminoacids and proteins, are interesting due to their intrinsic properties such as biocompatibility and non-toxicity to humans. Combined with antibacterial and antifungal properties, such nanofilms could be used as protective agents in medicine and food packaging industry [1]. It is known that antibacterial activity of the nanofilms arises from its morphology and thickness [2], which in turn depends on the conditions of the solution in which they are prepared as well as the type of the surface they are formed on [3]. In order for the nanofilms to be successfully used as food packaging materials their growth and preparation method has to be predictable and somewhat affordable.

Compared to polyaminoacids and proteins, polysaccharides such as chitosan (CHI) and carboxymethylcellulose (CMC) are not expensive because they are derived from an abundant source. In our study, CHI-CMC multilayers were prepared by layer-by-layer (LbL) technique on silicon wafers (Si-SiO₂) and titanium plates (Ti-TiO₂) as solid surfaces. For both surfaces the growth regime of the CHI-CMC film has been studied by ellipsometry. After dissolution of the polyelectrolytes the pH has been adjusted to desired value and different sodium salts have been added to examine the thickness dependence on both ionic strength and anion type.

The surface morphology, more precisely roughness of the final layer and porosity of the film, has been determined by atomic force microscopy (AFM) in tapping mode. The thickness of the films obtained by ellipsometry has been confirmed with AFM measurements by comparing the height of the film relative to the solid surface. It was shown that both anion type and ionic strength influence the growth of CHI-CMC multilayers. The obtained results could be helpful for designing polyelectrolyte multilayers with tuned properties, especially suited for applications in the field of biomedicine.

Keywords: polyelectrolyte multilayers, ellipsometry, atomic force microscopy, chitosan, carboxymethylcellulose

Acknowledgements: This research was supported by the Croatian Science Foundation under the bilateral Slovenian-Croatian APPLPEMS project (IPS-2020-01-6126).

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Hybrid soft micro-actuators with tunable response to the magnetic field

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Hybrid materials that can respond to multiple stimuli are promising materials with the potential to be employed as carrier materials in biological systems [1]. The thermo-responsive nature of Poly(N-isopropylacrylamide) PNIPAm hydrogels makes those excellent candidates to fabricate such systems. By adding magnetic nanofillers and pre-programming their alignment during the synthesis, thermo- and magneto-responsive systems can be designed.

Different microgel shapes with embedded maghemites were synthesized using Particle Replication in Non-wetting Template (PRINT). Their thermo- and magneto- responsivities were determined through swelling experiments and under the application of rotating magnetic fields of different strengths. These systems were characterized by a maximum rotation speed ω_c marking their transition from a synchronous to an asynchronous rotation, which is strongly varying with the temperature (Figure 1a).

When the hydrogels were additionally coated with a metal layer, the restricted swelling of the soft layer enabled the formation of more complex shapes [2-3]. The conformations and polarizability to the applied magnetic field can then be controlled by temperature change (Figure 1 b). These properties were further utilized to create diverse actuations combining the response to temperature, magnetic field, and light.

Additionally, active micro-swimmers were designed and their swimming as a response to photoactuation was directed by an external magnetic field [4].

Keywords: smart polymers. soft, thermo-response, magnetization, PRINT

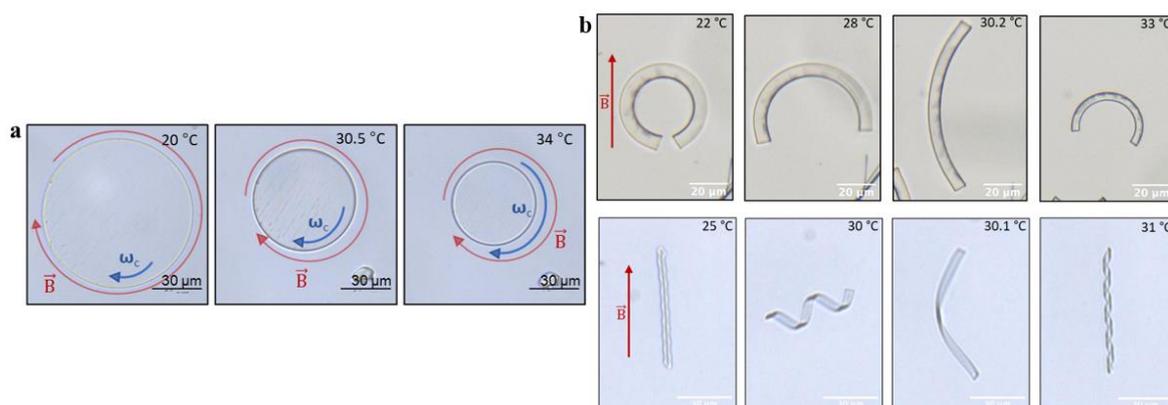


Figure 1. Thermo-responsive and magnetic microgels. a) Hybrid disks with tunable response under a rotating magnetic field. b) Arc and helix bilayer structures that change their shape and polarizability as a function of the temperature.

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New porous material design via emulsion freezing

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The formation of solid foam-like porous structures obtained when applying freeze-thaw cycles to nanoparticle suspension drops was previously reported [1].

Here pore organization of silica microstructure obtained via the freezing of emulsions is studied [2]. First, silica microparticles are synthesized by an emulsion freezing method. Aqueous mixtures of silica nanoparticles are used as a dispersed phase in water-in-oil emulsions. Freeze-thaw cycles are applied to the emulsion to generate flocculated microstructures that have spherical shapes as shown in figure 1. Physico-chemical techniques such as mercury porosimetry and nitrogen sorption are used to study the microstructure in term of pore size distribution, surface area and pore organization.

The characterization of these micrometer sized spherical aggregates reveals meso and macro intraparticle porosity. The particle shape is due to the emulsification of the nanosuspension whereas the observed hierarchical porosity and its evolution with particle size is probably related to the evolution of freezing mechanism with the size of aqueous suspension droplets. This material with hierarchical porous structure could be used in catalysis or sensing applications.

Keywords: emulsion freezing, silica nanoparticle, double-scale structure

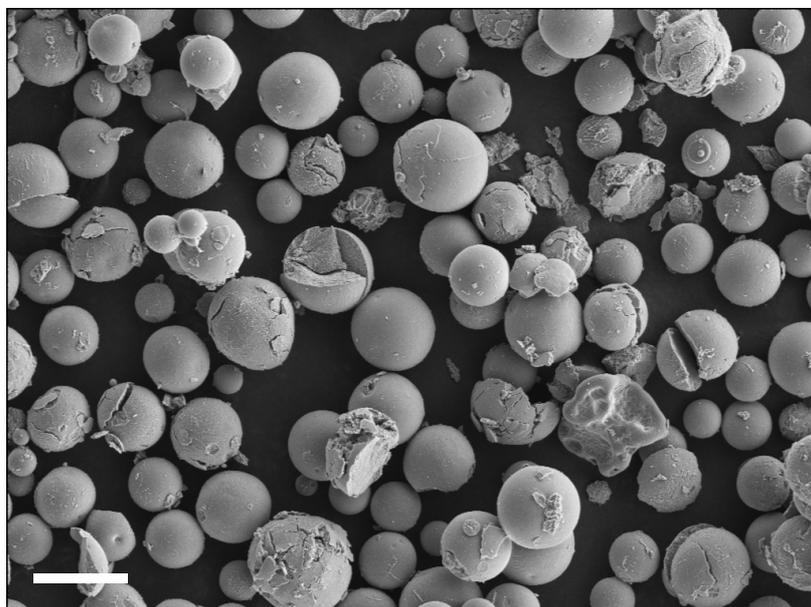


Figure 1. Scanning electron microscopy pictures of silica microstructure obtained from freeze-dried emulsion. Scale bar is 40 μm

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Kaolin-based composites structural, morphological, thermal, and adsorption characteristics

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Kaolin is a hydrated aluminum silicate with a crystalline structure [1]. Activated carbon is carbon produced from a carbonaceous source such as bamboo, coconut husk, willow peat, or wood [2]. Both, kaolin, as well as activated carbon, are used as adsorbent systems for the removal of dyes (or other organic pollutants) from wastewater because of their porous characteristics [3].

In this work, the kaolin-carbon composites were obtained by mechanochemical activation using a knife-milling. The influence of the differentiated composition of kaolin-based composites on their structural, morphological, porous, thermal, or acid-base properties was examined. Moreover, the studies of the adsorption of the selected dyes on the proposed adsorbents were carried out. The SEM images of kaolin, activated carbon, and kaolin-carbon composites are presented in Figure 1.

Keywords: kaolin, activated carbon, composite, dye adsorption

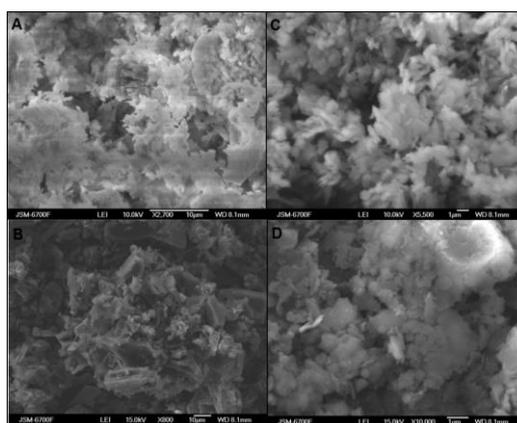


Figure 1. SEM images of kaolin (A), activated carbon (B), kaolin-carbon composite with 5% carbon (C), kaolin-carbon-composite with 30% carbon (D).

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Physicochemical and adsorption properties of polymer microspheres as materials for the removal of organic compounds

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Water contamination caused by industrial processes is a common global problem. Organic pollutants (benzene derivatives, dyes, pharmaceuticals) are hazardous substances that do not decompose easily in water. For this reason, novel adsorbents for water or wastewater purification from organic compounds are the subject of search [1-3].

Polymers are characterized by numerous beneficial properties encompassing tensile strength, modulus, toughness, or viscoelasticity, however, these materials have some limitations in their usage because of the inferior mechanical or thermal properties in comparison to metals or ceramics. To improve polymer features the combination of them in the form of a multi-phase system could be an appropriate solution. Porosity is one of the major factors affecting the adsorption properties of adsorbents. The difference in the composition of adsorbents may cause distinctions in their porous system [4].

In this work, the two-phase polymer microspheres with different compositions were received in the emulsion-suspension polymerization reaction. The structural, porous, morphological, thermal, and adsorption properties of inorganic-organic materials were examined using several instrumental techniques: scanning electron microscopy (SEM), Fourier transform infrared/attenuated total reflection spectroscopy (FT-IR/ATR), nitrogen low-temperature adsorption-desorption, and thermal analysis. Also, the kinetic and equilibrium adsorption studies revealed the potential applicability of these adsorbents in the removal of aromatic organic compounds from water or wastewater.

Keywords: inorganic-organic materials, polymers, microspheres, adsorption, water treatment

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The synthesis and adsorption studies of biphasic calcium phosphate material originated from avian eggshells

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Due to the extended demand for ecological, environmentally friendly and low-cost industrial materials, the investigations are focused on the recycled reagents usage. The wastes composed mainly of calcium carbonate- eggshells are the excellent material being a calcium source during the synthesis of calcium phosphates [1].

Hydroxyapatite (HA), a well-known calcium phosphate material present in the human hard tissue was extensively applied as an orthopaedical and dental replacement, drug delivery system, fertilizing agent as well as an adsorbent for the ground water treatment. Over 30 years of intensive studies proved its bioavailability, biocompatibility and biodegradability. However, for elaboration of new, beneficial characteristics biphasic composites were suggested instead of pure HA[1,2].

The objective of the presented studies is to obtain a biphasic calcium phosphate material composed of HA and β - tricalcium phosphate (β -TCP) using eggshells of different avian species with and without the inner eggshell membrane (ESM) to analyse, compare and select the best synthesis path in relation to the environmental applications of the obtained products. The SEM, XRD and FTIR analyses were performed to determine the composition and morphology of each product and it was proved that the most beneficial structure was obtained for the material originated from hens eggshells with ESM.

Next, the selected materials were analysed in order to test their ability to remove heavy metals (Ni(II), Cd(II), Cu(II) and Pb(II)) from the aqueous solutions. The static sorption method in the pH range from 3 to 7 was investigated. The mechanism of the process was studied based on the Langmuir and Freundlich adsorption models.

Keywords: BCP, hydroxyapatite, adsorption, heavy metal pollution, wastewater treatment

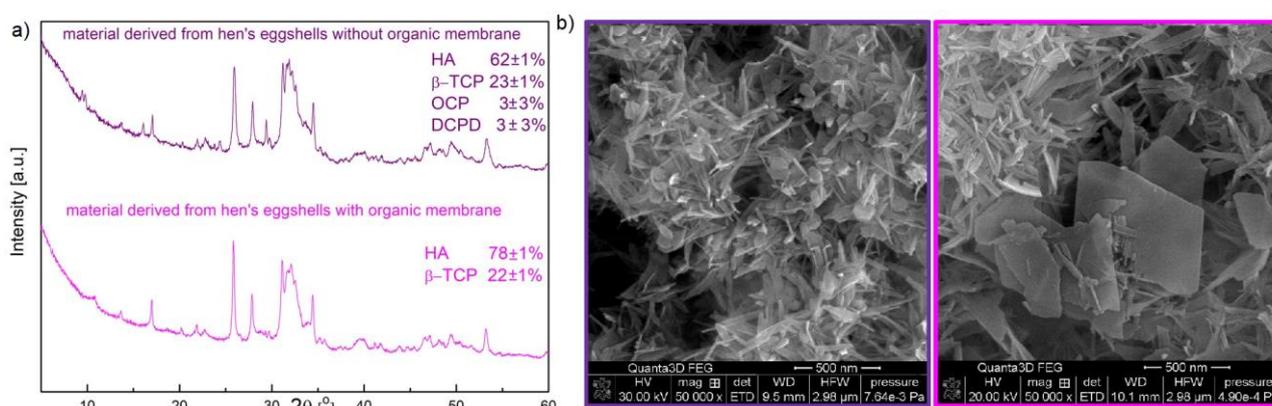


Figure 1. XRD patterns (a) and SEM pictures (b) of the material obtained using hen eggshells with and without ESM.

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Chloride SCISEs based on a nanocomposite of polyaniline nanofibers and multiwalled carbon nanotubes (PANINFs-Cl:MWCNTs)

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Among the potentiometric sensors, ion-selective electrodes without an internal electrolyte solution (electrodes with solid contact, SCISEs), are gaining more and more popularity. These types of electrodes are characterized by very good analytical parameters, often even better than their classic predecessors. Their main advantage is simple structure, low production cost, mechanical resistance and the possibility of miniaturization and operation in any position. A special material (so-called solid contact) responsible for ensuring the appropriate stability and reversibility of the electrode potential is placed between the material of the inner electrode and the ion-selective membrane layer. Various materials are used as solid contacts, for example conductive polymers[1], nanoparticles[2], nanofibers[3], carbon-based nanomaterials and nanocomposites synthesized for this purpose[4,5].

The work describes the use of a nanocomposite consisting of polyaniline nanofibers doped with chloride ions with multiwalled carbon nanotubes as a solid contact in the construction of chloride ion-selective electrodes. Nanocomposites with various weight ratios of PANINFs-Cl:MWCNTs were obtained and used as an intermediate layer. The properties of nanocomposites and the intermediate layers obtained from them were investigated, and then electrodes differing in the type of solid contact were constructed. In addition to electrodes with nanocomposites, unmodified electrodes with only basic membrane or with additional layer of only nanofibers and carbon nanotubes were also constructed. A series of potentiometric measurements as well as electrochemical impedance spectroscopy and chronopotentiometry measurements were performed in order to compare the obtained sensors and their sensitivity to variable measurement conditions was examined. On the basis of the obtained results, it was found that the modification of the electrodes has a positive effect on their work, in particular on extending the linearity range, lowering the detection limits and improving their potential stability. In the last stage, electrodes were also used to determine the chloride content in water samples.

Keywords: nanocomposite, nanofibers, nanotubes, electrodes, solid contact, chlorides

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Synthesis of Micron-sized Silica-Coated PMMA Latex Particles

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Near-monodisperse poly(methyl methacrylate) (PMMA) latex particles of 6, 10 or 15 μm diameter are coated with a silica overlayer. Two deposition protocols are evaluated using either tetraethyl orthosilicate (TEOS) or sodium silicate as the soluble silica precursor. To promote surface deposition of the silica onto the latex surface, various additives were examined in order to minimize secondary nucleation. Thermogravimetric analysis was used to determine the silica yield and scanning electron microscopy (see **Figure 1**) was used to estimate the mean silica shell thickness. Optimized conditions enabled relatively thin, uniform silica shells to be deposited with high efficiency and minimal secondary nucleation. Laser diffraction was used to compare the degree of dispersion of the final silica-coated latex particles with that of the original PMMA latex. Surface compositions were assessed using aqueous electrophoresis and X-ray photoelectron spectroscopy (XPS). This new protocol enables well-defined silica-coated latex particles to be prepared at relatively high solids and is expected to become a model system for understanding certain industrial formulations.

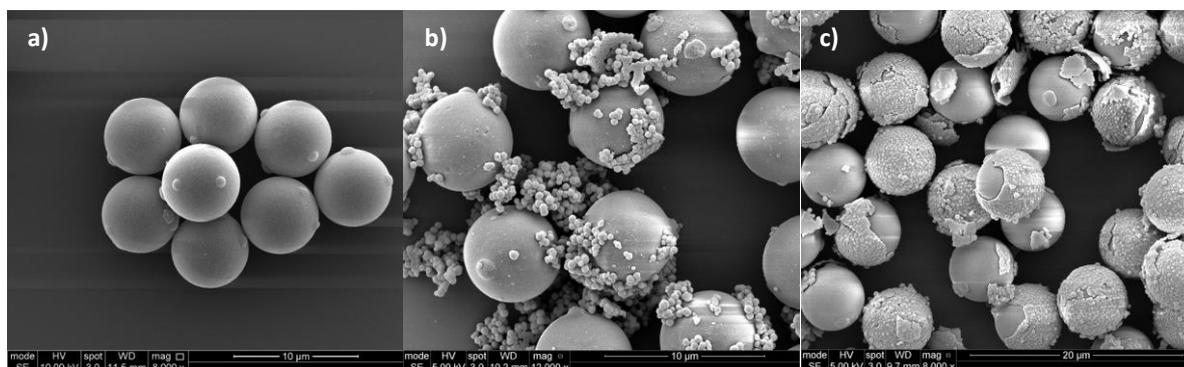


Figure 1. Scanning electron microscopy images recorded for (a) 6 μm PMMA latex particles, (b) silica deposition on PMMA latex particles in the absence of a surface additive and (c) silica-coated PMMA latex particles prepared under optimized conditions. In this case, the mean silica shell thickness is estimated to be ~ 170 nm.

Keywords: silica shells, sacrificial templates, PMMA

Testing water samples for the content of nitrate ions using ion-selective electrodes with solid contact

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Research on ion-selective electrodes with solid contact (SCISEs) is currently very popular among scientists dealing with potentiometric methods. In order to obtain sensors with the best analytical parameters, it is necessary to use new materials for their construction. The improvement of their properties is most often influenced by the modification of the membrane composition (in particular, the change of the active substance for better selectivity and sensitivity of the electrode) and the addition of a substance acting as a solid contact in order to ensure the stability and reversibility of the sensor potential.

Potentiometric sensors useful for determining nitrate ions in environmental samples with the use of various materials as a solid contact - nanocomposite of multiwalled carbon nanotubes with an ionic liquid (MWCNTs-IC) [1] and polyaniline nanofibers doped with chloride and nitrate ions (PANINFs-Cl and PANINFs-NO₃) [2] were constructed. Measurements were made for electrodes differing from each other both in the place of occurrence of the solid contact (the intermediate layer between the electrode material and the ion-selective membrane and a direct addition to the membrane mixture) and the amount of material used (thickness of the intermediate layer and the content of the additive in the membrane). The obtained values of analytical parameters were compared, such as: the slope of the electrode characteristic curve, linearity range, detection limits, stability and reversibility of the potential, as well as the electrical: capacitance and resistance of the ion-selective membrane. In order to better investigate the influence of the materials used on the work of the electrodes, unmodified electrodes were also made, in which only the basic membrane mixture was spotted on the electrode surface.

On the basis of the obtained results, the best electrodes were selected and used to determine concentration of nitrate ions in water samples: river, ground and drinking water.

Keywords: nanocomposite, nanofibers, nanotubes, electrodes, solid contact, nitrates

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Conducting thin films from xylan-dispersed carbon nanotubes

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Non-covalently bound cellulose can be utilized as a dispersant (similar to surfactant molecules) of carbon nanotubes (CNT) in water. The cellulose polymer molecules form complexes with the CNTs, whose accurate nature is still under study [1]. Processability of CNTs via dispersion in water has obvious advantages with respect to environmental concerns, and enhances the prospects for scaled-up production of CNT based devices.

As the role of the cellulose is solely that of a dispersant, then usually the cellulose is to be considered a nuisance for the end purpose. For electronic applications, dispersions of CNT materials (often single wall carbon nanotubes (SWNT)) are processed into different types of conductors, which range from truly 2D networks to essentially 3D films and fibers. A prime example is the fabrication of conductive transparent thin films.

An effective method for dispersing CNTs non-covalently functionalized with hemicellulose (Xylan) has previously been reported by two of the authors in a patent [2]. We have prepared CNT based thin films, via dispersion in water of the nanotubes with xylan. The CNT/xylan complexes can be stably imaged with ultra-high vacuum scanning tunnelling microscopy (STM) at 4.9K. The STM images exhibit a non-uniform structure at their surface, which in some cases is found to have a certain (~60nm-scale) periodicity. This structure may be assigned to the presence of xylan which spirals up along the CNT (Fig. 1). Measurements of low temperature conductivity, Kelvin Probe Force Microscopy, and high frequency (THz) conductivity elucidated the intra-tube and inter-tube charge transport processes in this material [3]. The measurements show excellent conductive properties of the as prepared thin films, with bulk conductivity up to 2000 S/cm. The transport results demonstrate that the hemicellulose does not seriously interfere with the inter-tube conductance.

Keywords: Carbon nanotubes, hemicellulose, electronic transport

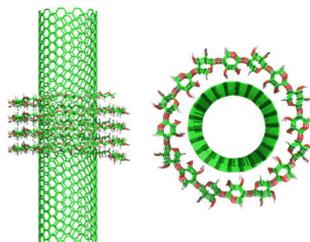


Figure 1. Schematic picture of xylene molecules wrapped around a single wall carbon nanotube [courtesy of Ph.D Jouko Virtanen].

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Mixed dimensionality: Highly robust and multifunctional carbon-based composites

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The effect of loading a polymer matrix with more than one filler was investigated for nanocarbon-based fillers of different dimensionalities, namely, 1D carbon nanotubes (CNTs) and 2D graphene nanoplatelets (GNPs). Since both fillers have superior intrinsic mechanical, electrical and thermal properties, their use in tandem enhanced the properties of the resulting composites. The robustness, i.e., the range of nanofiller concentrations at which a substantial enhancement is achieved (considered as a weakness in single filler systems), was dramatically increased in the hybrid system as well as the thermal and electrical conductivities due to the formation of a CNT-GNP 3D structure. These measurements were in keeping with the Kreiger-Dougherty and the effective medium models, respectively. The overall performance of the hybrid composite was compared to single filler systems (using an index of performance) demonstrating the superiority of the hybrid composite in multifunctionality and robustness.

Keywords: nanocarbons, hybrid composites, mechanical properties, 3D structure, multifunctionality.

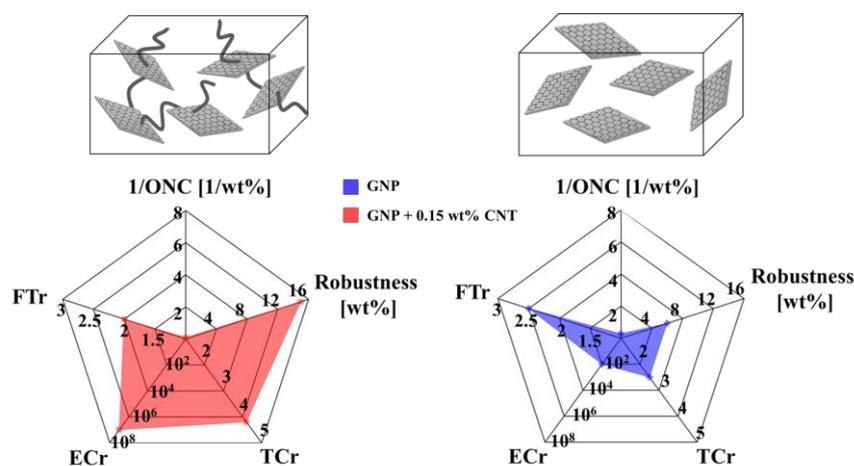


Figure 1. Overall properties of GNP (blue), and GNP + 0.15 wt% CNT (red) at the ONC, presented in a radar graph.

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Plasmonic Stimulation of Gold Nanorods for the Control of Living Materials

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Composites of living cells in polymer gel matrices are called “Living Materials” [1]. They are useful for the controlled release of drugs that are secreted by the cells while protecting them and their environment. Here, we establish optical control of the drug production in a Living Material that contains engineered thermoresponsive bacteria. A core of gel-bacteria composite is enclosed inside a gold nanorod composite (GNC) shell. Incident near-infrared light is absorbed by the GNC shell, which generates heat that diffuses to the core and activates the thermoresponsive bacteria, inducing the production of proteins such as Green Fluorescence Proteins (GFP) (see illustration below).

The nanorod composite hydrogel was characterized to assess possible particle aggregation and its overall photothermal properties. A shell was formed around a hydrogel core that contained *Escherichia coli*. Illumination with laser light at 808 nm heated the core-shell structure from initial 20°C to 40°C. Combined IR-Tomography and a thermocouple in the core layer provided spatially and temporally resolved temperature distribution. The GFP production was quantified as a function of light stimulation via *ex situ* fluorescence microscopy and the fluorescence intensity was analyzed in dependence of plasmonic stimulation duration.

Our results contribute to stimuli-responsive Living Therapeutic Materials, that can be used in biomedical applications and supplement existing schemes for drug delivery (oral, injection, nasal, ocular). The concept profits from the wide range of engineered bacteria that can provide different drugs. The optical stimulus discussed here can be combined with other stimuli.

Keywords: Engineered Living Materials, nanocomposite hydrogels, plasmonic heating

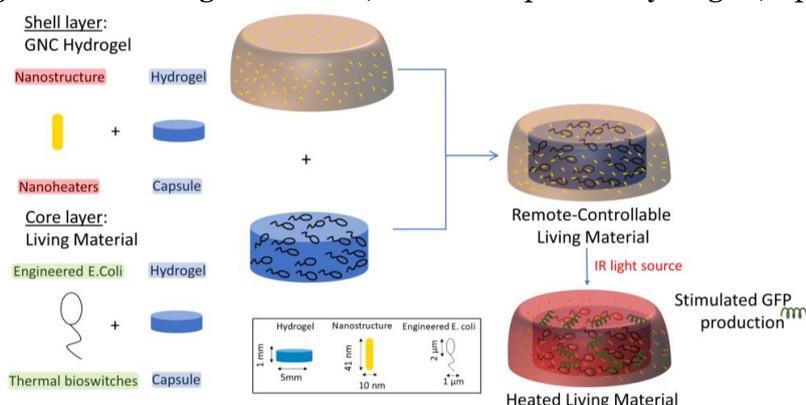


Figure 1. Schematic depiction of the core-shell construct. The core-layer includes the bacteria which is externally stimulated to produce GFP.

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Nanocomposite pastes based on metallic nanoparticles for fabrication of conductive coatings

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In recent years, silver has been the most frequently used material for the production of protective coatings for power contacts. The disadvantage of silver is its high friction coefficient and significant plasticity, therefore such silver-based coatings can be easily damaged and deformed. These phenomena lead to the destruction of power contacts, which results in an increase in their resistance and operating temperature. It significantly reduces the “life” of power contacts. Recently, nickel nanoparticles (NPs) have been considered as a replacement for Ag NPs due to their lower price, better mechanical properties, and high electrical conductivity. However, nickel NPs are unstable under ambient conditions due to oxidation. As a suitable option to overcome the high cost of Ag and to prevent the spontaneous oxidation of nickel, bimetallic Ni-Ag NPs with the core-shell structure can be utilized [1, 2].

In our studies, as a result of the transmetalation reaction, where the surface of the obtained Ni NPs acted as the reducing agent of silver ions, spherical Ni-Ag nanoparticles at average diameters of 220 nm were synthesized and utilized for the preparation of conductive coatings. In addition, the effect of the doping of the Ni NPs based pastes with noble metal NPs and the sintering temperature on the conductivity of deposited coatings were investigated. The obtained results show that the addition of noble metal NPs enhances the conductive properties of coatings compared to layers containing only nickel-silver nanoparticles. The conductivity of the sintered coatings increases with increasing sintering temperature. From the economic point of view, the coating with the most promising conductivity (44% of bulk nickel) was obtained after the sintering at 200 °C, while the coating with the highest conductivity values (61%) were obtained after the sintering process at 300 °C.

We believe that such conductive pastes composed mainly of low-cost non-noble metals NPs with high electrical conductivity can have great potential applications in the power industry and will contribute to developing an efficient and low-cost manufacturing route for the preparation of coatings for the protection of power contacts.

Keywords: nickel-silver core-shell nanoparticles, conductive coatings, power contacts

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Improving the Self-healing Properties of Polyurethanes by Incorporation of Reduced Graphene Oxide

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In recent years, self-healing coatings have been the subject of increasing research interest due to their ability to self-repair local damages caused by external forces. Polymeric materials comprise one of the most promising materials to use towards this direction [1]. On the other hand, incorporation of nanoadditives within a polymeric matrix is a common strategy to improve their mechanical, thermal and self-healing properties [2]. In the current work, reduced graphene oxide (rGO) was incorporated within a waterborne polyurethane dispersion based on polycarbonate polyol to develop nanocomposites in different compositions and investigate its effect on the self-healing properties. The polyurethane dispersions were prepared according to the prepolymer method, using isophorone diisocyanate (IPDI), polycarbonate polyol, dimethyl propionic acid (DMPA), ethylene diamine (EDA) and triethylamine (TEA), as neutralizing agent. Graphene oxide (GO) synthesized via a modified Hummers method was subsequently reduced using hydroiodic acid (HI) as a reducing agent to prepare the rGO [3]. The self-healing ability of the polyurethanes was found enhanced in the nanocomposites and the healing rate was found much higher compared to that of the pure polymer, as confirmed by microscopic and thermal analysis techniques, mainly due to better heat dissipation. The superior heat conductivity of rGO allowed for the optimization of the self-healing ability with the incorporation of just a small amount of the additive, whereas its presence of rGO enhanced the mechanical properties of the nanocomposites after healing, as well.

Keywords: self-healing coatings, polyurethanes, reduced graphene oxide

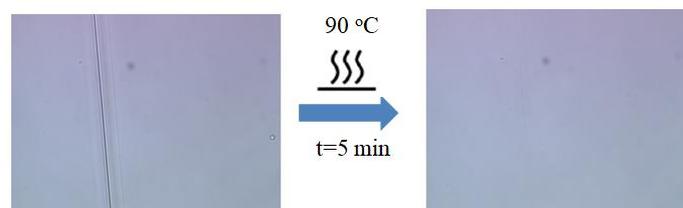


Figure 1. Schematic healing process of a crack in the nanocomposite film upon heat treatment.

Acknowledgements: This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH-CREATE-INNOVATE (SEFNANOPUD, MIS: 5067612).

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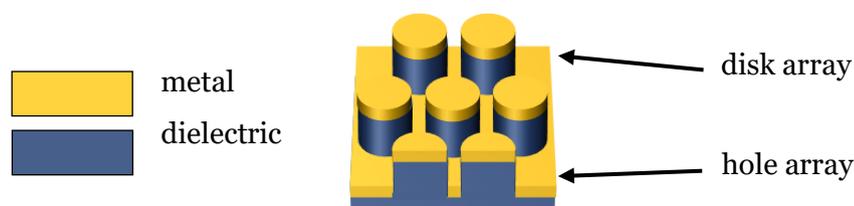
Quasi-Babinet complementary plasmonic templates: Optical properties and applications

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Plasmonic meta-surfaces have important applications in life science, optics, and catalysis. However, their industrial usage is limited by the challenges of high throughput nanofabrication. A promising solution is the transfer of a pattern into a substrate using block copolymers, nanostructured stamps or moulds to create binary, three dimensional templates, which can then be decorated with plasmonically active metals. Here, we report on the optical properties of vertically coupled plasmonic arrays which consist of a nanopillar support, that is covered with metal disks on top of the pillars and a quasi-Babinet complementary hole array film at the base of the pillars from the visible to the mid-infrared spectrum. Strong vertical plasmonic coupling occurs for small separation distances of the plasmonic slabs. We present how vertically couple plasmonic arrays can be fabricated with nanosphere lithography and can be used as a platform for surface enhanced infrared spectroscopy. Further, we give a perspective on how these structures can be used for spectro-electrochemistry and bio-photonics.



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Altering the Interfacial Interactions in Polymer / Graphene Oxide Nanocomposites

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Polymer nanocomposites have been in focus of interest of the research community due to their improved properties compared to the respective ones of the pure polymers. In the current work, nanohybrids which consist of hyperbranched polymers of different generation and graphene oxides (GO) with different degree of oxidation at different concentrations were developed to cover the whole regime from pure polymer to pure graphene oxide; the aim was to investigate the effect of the varying polymer / surface interactions on the nanocomposite structure and properties. Initially, the GO samples were synthesized either by altering the oxidation time or the amount of oxidizing agent to achieve different degrees of oxidation. Weakly to fully oxidized graphene oxides were synthesized by changing the mass of the oxidizing agent while the oxidation time did not seem to significantly affect the results. Subsequently, nanohybrids were synthesized using hyperbranched polyester polyols of three different generations and the aforementioned GOs. Differences were observed in the structure of the nanocomposites with X-ray Diffraction indicating the existence of either a phase-separated structure or an intercalated structure depending on the degree of oxidation of GO. The thermal properties are also influenced by the observed structure of the nanohybrids whereas there is a significant effect of the presence of GO on the thermal stability of the polymer and of the presence of the polymer on the reduction temperature of GO.

Keywords: graphene oxide; oxidation degree; hyperbranched polymers; intercalated structure.

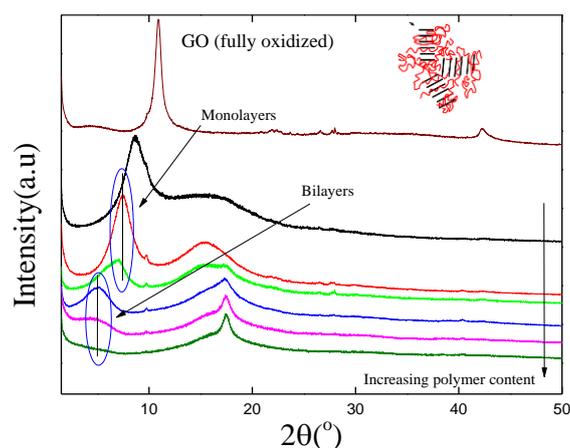


Figure 1. X-ray diffraction measurements illustrating the intercalated structure in polymer/GO nanocomposites

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The interior amorphous architecture of proteinaceous adhesive marine mussel plaques

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To attach to rocks, piers, or other mussels, marine mussels —such as *Mytilus galloprovincialis*— utilize their byssal collagen-rich threads that terminate and insert in a proteinaceous adhesive plaque. We have previously reported [1] on its porous internal architecture, which bears similarity to structural foams. However, as opposed to most foam structures, this operates under tension.

We are interested in understanding the effect of porosity on plaque mechanics, create experimental models of doubly porous materials, and explore whether there is a link between mussel genera and the forces they are subjected to in their respective habitats. Towards this end, our ongoing image analysis from SEM, TEM and optical microscopy images of plaque cross-sections show that the fraction of large pores (~1 μm) versus the dense meshwork regions (~100 nm) varies among genera. In some cases, there is even no porosity observed. Our current efforts focus on quantifying the 3d porosity from 2d sections via image analysis and stereology methods [2], while direct tomography approaches are attempted that may provide a direct view of the large pores.

Keywords: mussels, biomaterials, adhesion, interface, porosity, TEM

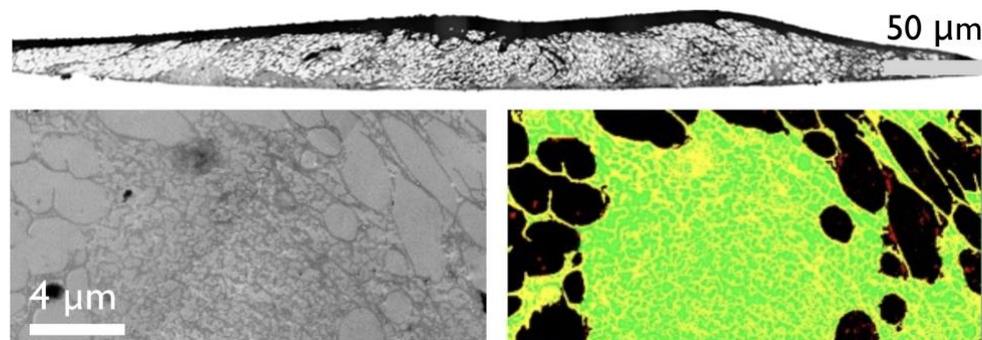


Figure 1. Vertical sections of *Mytilus galloprovincialis* adhesive plaques revealing the porous internal structure. (Top) Optical microscopy image. (Bottom) TEM image, and its segmentation identifying large pores, small pores and proteinaceous dividing walls.

Acknowledgements: E.F. would like to acknowledge funding from the Otis Williams postdoctoral fellowship in bioengineering at UCSB. We thank Sevasti Papadogiorgaki for help with TEM, and Luis Manuel Cruz Orive for useful discussions.

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Unusual Rheological Response in PEO / SiO₂ nanocomposites

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Polymer nanocomposites, comprised of a polymer matrix and inorganic additives, possess improved and often innovative physicochemical properties compared to conventionally filled systems. In this work we report on the rheological behavior of series of poly(ethylene oxide) / silica, PEO/SiO₂, nanocomposites through oscillatory shear rheology measurements. The nanohybrids were synthesized by dispersing spherical SiO₂ nanoparticles of two different radii (NP₇ and NP₆₇) within high molecular weight PEO (PEO₁₀₀, M.W.=100,000 g/mol, PEO₃₀₀, M.W.=300,000 g/mol) and at different compositions to investigate the effect of the additive on the material rheological properties. Dynamic time and strain sweep tests verify the material thermal stability and linear viscoelastic behavior whereas dynamic frequency sweeps probe its dynamic response. In these nanohybrids, PEO crystallinity was found to depend on the degree of spatial confinement that the nanoparticles impose as well as their adsorption capacity. The effect of nanoparticle size and concentration as well as of the polymer molecular weight on the behavior is examined to correlate the morphological changes to the materials rheological response in an attempt to better understand the structure-properties relationship. A liquid- to solid-like transition is observed and the corresponding composition shows a strong dependence on the size of the nanoadditives. Additionally, there is a non-monotonous dependence of the viscosity on the composition that depends on the polymer molecular weight.

Keywords: polymer nanocomposites, rheology, liquid-/solid-like behavior, complex viscosity

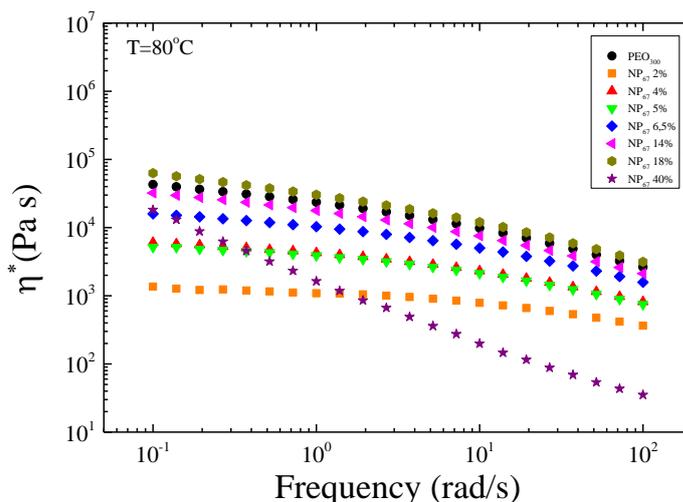


Figure 1. Frequency dependence of the complex viscosity for PEO₃₀₀ / NP₆₇ nanocomposites with different NP content.

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Antimicrobial effect on photoreactive nanocomposite thin films

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One type of self-cleaning surfaces is the photocatalytic coating which can chemically degrade organic materials when exposed to light [1-3]. During the photocatalytic process the irradiated photocatalyst particles produce highly reactive oxygen species and due to these formed reactive radicals the photocatalyst particles can degrade many organic compounds.

The main goal of our present work was to synthesized durable photoreactive coatings that exert antimicrobial and antiviral effects upon illumination.

The photocatalyst particles (like TiO₂, ZnO, Ag-TiO₂, Cu-TiO₂) were shown photocatalytic properties under LED-light irradiation and the use of poly(ethyl acrylate-co-methyl methacrylate [p(EA-co-MMA)] polymer binder increase the mechanical durability of the photoreactive composites. The structure and morphology of the synthesised photocatalyst/polymer coatings were examined by SEM measurements. According to our experiments the structure of the thin films becomes more and more structured and roughened with the increasing of nanoparticles in the nanocomposite content. The photocatalytic activity of the prepared hybrid thin films were verified via ethanol photodegradation tests by gas chromatography (Shimadzu GC-14B) under LED light illumination (λ_{\max} = 405 nm) at S/G interface. The antimicrobial property of the photoreactive coatings were also examined and the prepared coatings were exposed to bacterial suspension of *Escherichia coli* (Gram negative), *Staphylococcus aureus* (Gram positive) and *Pseudomonas aeruginosa* (Gram negative). The results showed that surfaceroughness influenced wetting properties of the hybrid layers and they have an important role on the bacterial adhesion and inactivation.

The virucidal effect were also examined of the illuminated photoreactive coatings using an airborne-transmitted herpesvirus. As a result, we obtained a drastic decrease in infection capability of the virus on the photoreactive surface compared to the control surface.

Keywords: self-cleaning coatings, photocatalyst particles, antimicrobial and antiviral property

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The synthesis of zinc-doped multiphasic calcium phosphates

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Due to the multitude of applications introducing antibacterial properties onto the calcium phosphates (CaPs) surfaces is desirable. Substitution of calcium by other metal cations in the crystal lattice seems to be a perfect way to improve their antimicrobial activity. Moreover, such modification can have positive impact on the mechanical properties of the product. Many reports shown the possibilities of introducing such cations as gallium, silver, strontium, titanium or zinc[1].

Zinc is commonly known to be an antibacterial agent used in the surface of dental implants, as well as additive in daily oral care products. Nanoparticles of zinc oxide present not only antimicrobial properties. It was proved that Zn plays an important role in many biological processes as an enzyme and hormonal activity, DNA synthesis as well as biomineralization process. Numerous the scientific reports indicate the supportive influence of Zn in the bone regeneration process. Moreover, Zn exhibits non-cytotoxic behaviour in a proper concentration and is considered to be safe for human health[2].

In the presented studies, the procedure of biphasic calcium phosphate synthesis was modified with adding 5, 10 and 15 molar% of zinc ions for introduction of antibacterial behaviour. To determine the composition of the obtained products as well as to investigate the Ca²⁺ substitution with Zn²⁺ all samples were examined with the SEM, XRD and XPS techniques. Moreover, the ICP OES measurements were adopted for the studies of Ca, Zn and P release from the products in PBS solution due to biomedical and environmental purposes.

Keywords: CaPs, antibacterial properties, zinc-doped calcium phosphates

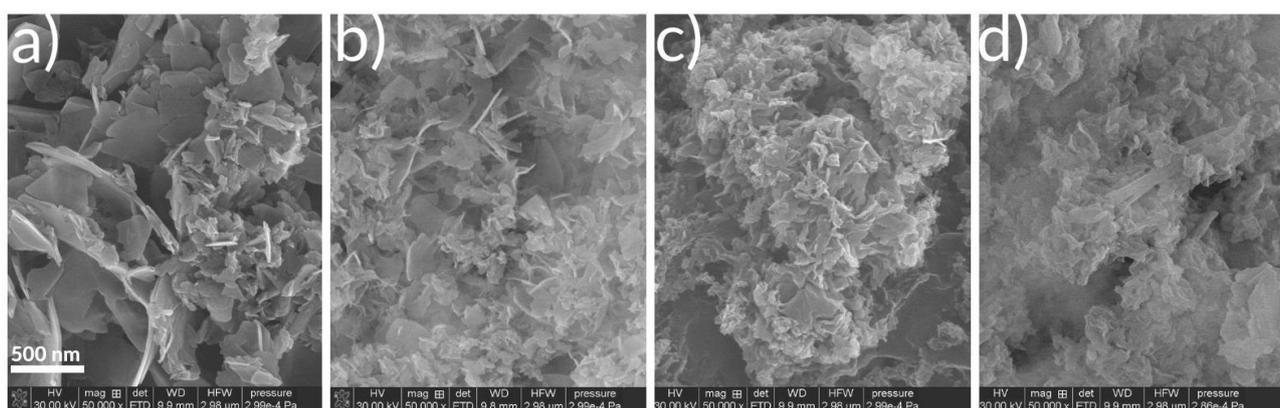


Figure 1. SEM pictures of products without (a) and with 5(b), 10(c) and 15(d) molar % of Zn (50 000x magnification).

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Nanostructured composite materials as electrocatalysts for electrochemical energy-conversion devices

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Electrochemical energy conversion (EEC) is an emerging field of energy technology, which applies the electrochemistry for storing energy and supplying electricity. Fuel cells, electrolyzers or photoelectrolyzers, batteries, and supercapacitors are some representative EEC devices, which display a key role for the advance of electric vehicles, grid storage and other uses that will be explored. The development of low-cost high-performance electrocatalysts is essential in the overall performance of these devices [1].

More concretely, highly active electrocatalyst materials for the oxygen reduction reaction (ORR) are of increasing interest due to their extensive applicability in a wide variety of renewable energy technologies, such as cathodic electrode for rechargeable metal-air batteries and hydrogen fuel cells. These electrocatalysts are also useful for other cathodic reactions, such as hydrogen evolution reaction (HER) in water splitting and nitrogen reduction reaction (NRR) [2]. Similarly, oxygen evolution reaction (OER) is a limiting anodic reaction in the process of generating molecular oxygen through water splitting. Developing improved catalysts for the OER is the key to the advancement of a number of renewable energy technologies, involving solar fuels production and metal-air batteries [3].

Our research group is joining different strategies for generating efficient and sustainable electrocatalysts materials, based on engineered plasmonic nanoparticles,[4] heteroatom-doped carbon materials (HDCMs),[3] and non-sacrificial metal-organic frameworks (MOFs) synthesis technologies. An overview of our more interesting results to date will be presented, providing insights into the design of highly active electrocatalysts for these reactions involved in water electrolysis and the fuel cell.

Keywords: Fuel cell, oxygen reduction reaction (ORR), water splitting, hydrogen evolution reaction (HER), oxygen evolution reaction (OER).

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Noble metal nanoclusters with structure-tunable fluorescent properties: synthesis, characterization and biomedical utilizations

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Metallic nanoclusters (MeNCs) have become one of the most important nanostructured materials that have been extensively investigated in several research fields. They exhibit molecule-like characteristics as their size approaches the Fermi-wavelength of electrons. Due to the discrete energy levels, MeNCs possess different electric, optical and chemical properties from those of larger metal nanoparticles. Their characteristic feature is the strong photoluminescence. Due to the facile synthesis, good quantum yields, tunable fluorescence emission, large Stokes shift and high photostability they are excellent nano-objects in biomedical applications as well. Therefore, there is a continuous demand to prepare new MeNCs having biocompatible features via development of mainly cost-effective “green” synthetic approaches using small biomolecules, peptides and commonly used proteins.

In actual presentation, we demonstrate several “green” preparation protocols for fabrication of Au NCs using proteins (bovine serum albumin (BSA); lysozyme (LYZ), gamma-globulin (γ G)), nucleotide (adenosine monophosphate (AMP) and amino acids (histidine (His); tryptophan (Trp), cysteine (Cys) *etc.* which result in different nanostructures having tunable blue, green, yellow and orange emissions [1-3]. The main goal of this work was to investigate the spontaneous interactions of AuCl_4^- and the studied biomolecules as well to optimize the gold/biomolecule ratios and pH on the formation of gold nanosized objects by several physico-chemical techniques. Based on the experimental results we provided important information on the structure and optical features. Moreover, we plan to present the application possibilities of these fluorescent Au NCs for selective detection of different transition metal ions and small molecules. Furthermore, the potential utilizations of these fluorescent nanostructures in bioimaging/biolabeling will be presented.

Keywords: gold nanoclusters, tunable fluorescence, biosensor, bioimaging

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Colloid assembly of (GnP@MoS₂)/MWNT nanocomposites and their electrocatalytic activity for energy-related oxygen reactions

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1D and 2D nanomaterials, like, respectively, carbon nanotubes and graphene (and its analogues), may be used as building blocks to assemble new structures with enhanced properties. The hard surfaces can be non-covalently functionalized upon adsorption of amphiphiles, providing versatility in interactions, hierarchical organization and, potentially, the desired properties [1]. Among other uses, these composites can be employed and benchmarked as electrocatalysts for the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), relevant to water splitting and fuel cells [1]. In this work, we developed new nanocomposites using a combination of multiwalled carbon nanotubes (MWNTs) with graphene nanoplatelets (GnPs) and the transition metal dichalcogenide MoS₂, and evaluated their electrocatalytic performance (Fig. 1). First, the building blocks were exfoliated and functionalized by surfactants and polymer/surfactant mixtures of opposite charge in aqueous media, using an optimized and strictly controlled methodology [2,3]. This step was followed by the assembly of the ternary composites via electrostatic interactions in solution [4,5]. Significant structural differences between the nanocomposites were observed by SEM. The electrocatalytic studies evidenced the influence of 1D/2D ratio on the ORR performance, and an increased activity of the composites compared to the building blocks. The most optimized electrocatalyst showed good performance also towards the OER. This cost-effective, robust and versatile methodology can be explored for further optimization of electrocatalysts and other types of functional nanocomposites.

Keywords: 1D/2D nanocomposites • Functionalization • Surfactants • OER/ORR electrocatalysis

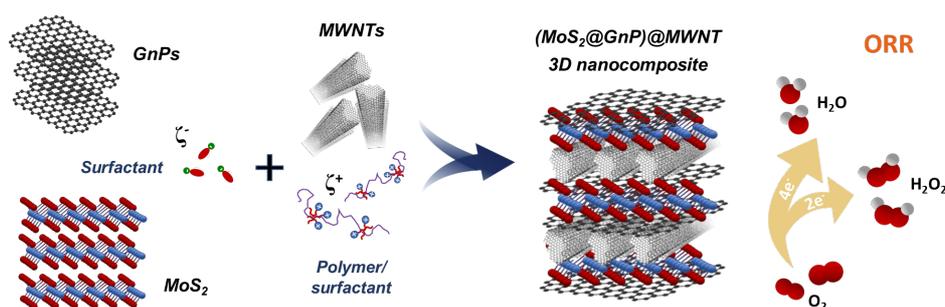


Fig. 1. Bottom up construction of the amphiphile-mediated ternary nanocomposites for ORR/OER.

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Enhanced condensation by rapid droplet coalescence of binary liquids on PDMS brushes

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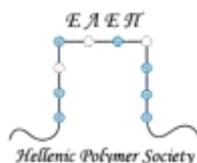
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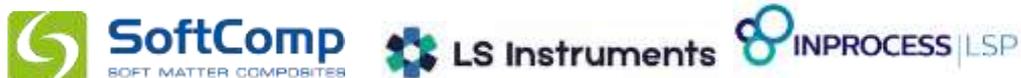
When the vapor condenses as discrete droplets on a non-wettable surface, the droplet coalescence velocity plays a critical role in the condensation dynamics and heat transfer performance. Under a high condensation rate, the slow droplet coalescence may lead to liquid film formation, even on an omniphobic surface. Here we report that the binary liquids of water and ethanol can accelerate the condensing droplet coalescence on PDMS brushes by more than 200% compared to pure ethanol. Due to the optimized thermophysical properties, the binary liquids effectively stabilized the dropwise wetting state during condensation, while increasing the heat transfer coefficient by more than one order of magnitude than the filmwise condensation of pure ethanol. Our work not only reveals the effect of droplet coalescence velocity on condensation heat transfer, but also helps to improve thermal efficiency in a wide range of applications such as power generation, thermal management, and waste heat recovery.

Keywords: droplet coalescence, wetting transition, condensation, omniphobic surface.

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