Masters of Packing: Foams and Emulsions under Gravity

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In order to form a liquid foam, bubbles need to pack tightly within a continuous liquid matrix. This process is typically driven by gravity. The packing dynamics and the eventually obtained bubble organisation in equilibrium are at the heart of many important scientific questions, bridging naturally packing and space-tiling problems within the same material. For example, at sufficiently high liquid content (bottom of the foam), bubbles pack (“jam”) like soft, frictionless spheres which aim to maximise their packing density. At very low liquid content (top of the foam), on the contrary, bubbles deform into elegantly shaped polyhedra which aim to minimise the interfacial area created upon this deformation. We review here recent work on different aspects of the static and dynamic behaviour of liquid foams under gravity, taking into account in particular the influence of the bubble size distribution. Most of the introduced concepts apply equally to emulsions, i.e. liquid in liquid dispersions.

Fig. 1 Examples of polydisperse and monodisperse foams under gravity.

Literature:

Effects of Density Difference between Oils and Water on Stabilization of Powdered o/w Emulsions

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Water-in-air dispersed systems, called dry water, are formed by aerating water in the presence of very hydrophobic particles. The dry water is a material that contains a large amount of encapsulated water drops, but behave like a free-flowing powder\textsuperscript{1}. Similarly, emulsions with water as the continuous phase (oil-in-water emulsions) can be powderized by aerating the emulsions in the presence of very hydrophobic particles. It has been found that oil droplet velocity in water globules during aeration is a crucial factor in stabilizing the powdered emulsions\textsuperscript{2}. The powdered emulsions are increasingly stabilized by decreasing the aeration speed and oil droplet diameter of o/w emulsions, and by increasing the water phase viscosity, as predicted by the Stokes equation. Another way to control the oil droplet velocity, according to the Stokes equation, is to decrease density difference between oil and water in o/w emulsions. In this study, we have investigated how the density difference between oils and water (\(\Delta \rho\)) affect the stabilization of powdered emulsions.

By mixing two oils (\(n\)-dodecane and silicone oil with a viscosity of 100 cSt), the \(\Delta \rho\) values were controlled from 0.03 to 0.25 g cm\(^{-3}\). All the o/w emulsions prepared using oil mixtures with different \(\Delta \rho\) values showed the same oil droplet diameter. Powdered materials were formed by aerating o/w emulsions with different \(\Delta \rho\) values in the presence of very hydrophobic fumed silica (Fig. 1). Fig. 2 shows an optical micrograph of a powdered material prepared using an oil mixture with \(\Delta \rho = 0.03\) g cm\(^{-3}\), dispersed in oil (\(n\)-dodecane). The formation of oil-in-water-in-oil emulsions by dispersing the powdered materials in an oil suggests that the powdered materials are oil-in-water-in-air materials, that is, the powdered emulsions. By decreasing \(\Delta \rho\) values, the number of oil droplets in water globules in the powdered emulsions was increased and the size of the oil droplets approached to the size of the original oil droplet in the o/w emulsions. This fact indicates a decrease in the oil droplet velocity during the aeration by decreasing \(\Delta \rho\), leads to the successful preparation of the powdered emulsions.

\textbf{Literature:}


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The development of a suitable and stable texture is important in all foam-based products. The stability of the aerated products strongly depends on the interfacial properties of the stabilizer molecules around the air bubbles. Up to now, the foams that have been studied were produced mainly with surfactants and proteins. Surfactant molecules can reduce the interfacial tension of the air-water interface and enhance the foamability, however the foams break eventually within a short period of time. Recently, solid particles have been shown to enhance the stability of air bubbles in aqueous systems\(^1\), opening a new pathway towards the formulation of highly stable foams. In this work, we investigated the foamability of aqueous solutions of a well-known food surfactant, Sodium Stearoyl-2-Lactylate (SSL), and the stability of the produced foams. Those foams were stable for weeks to months depending on the surfactant concentration and preparation conditions. In addition, naturally hydrophilic Precipitated Calcium Carbonate (PCC) particles were surface activated using SSL molecules and the foaming properties of the mixtures were studied. Certain of these foams were found to be ultra-stable with a stability of over one year. The adsorption of surfactant on the surface of particles has been probed via the adsorption isotherm and by measurement of zeta potential. The data will be discussed in connection with the foaming behavior. Furthermore, inclusion of air bubbles into oil-in-water emulsions is also an important phenomenon in a range of products. We investigated the influence of the addition of functionalized PCC particles on the aeration properties of palm kernel oil-in-water emulsions. The effect of particle and surfactant concentration was probed and aerated emulsions showed excellent stability towards drainage and coalescence. The aeration time was also found to significantly affect the overrun and stiffness of the aerated emulsions.

Literature:

New Strategies for the Microencapsulation of Healing Agents


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Microcapsules can represent reservoirs of healing agents that are dispersed into materials. Matrixes such as thermoset materials undergo damages over time due to external forces such as cyclic stresses and climate conditions. This can eventually lead to the formation of cracks, thereby deteriorating and weakening the materials. Upon crack formation, the microcapsules present in the matrix should break (and not debond) and release their reactive liquid content, allowing the material to recover its strength.¹²³ The development of self-healing materials has gained considerable attention over the last decade. This is driven by the replacement of heavy materials by lightweight high performance materials. The application fields include building and construction, automotive and aerospace, industrial applications, wind energy and marine applications. Our research aims at the encapsulation of newly developed self-healing agents. Different synthetic routes for the formation of core-shell structures, well known in literature, are applied and adapted to our targeted systems. In self-healing composites, for capsules to rupture in a reliable fashion, they must have an effective embedded modulus lower than that of the surrounding polymer matrix. Typical compositions used for the shell material are poly(urea-formaldehyde) (PUF), poly(melamine-formaldehyde), polyurethane (PU) and acrylates. This study describes the complexity of having a reactive core system, such as multi-thiols or multi-isocyanates. Moreover our newly developed microcapsules hold the ability to comprise different functionalities on the shell, allowing easy post-functionalization, making the capsules more compatible with the surrounding matrices. Furthermore, a novel approach for the encapsulation of reactive ingredients, beyond the classical approaches and based on a highly efficient chemistry reaction, will be presented. This original approach allows straightforward functionalization of the shell and can be applied to a vast number of highly reactive core materials.

Fig. 1 Microcapsules filled with highly reactive self-healing agents.

Investigation of Nonionic Additives on the Structural Changes of Water Droplets Encapsulated in the AOT Reverse Micelles

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Reverse micelles are resembled to pockets of water included in bioaggregates such as membranes and mitochondrial matrix, where water is not in its bulk state, but confined to small cavities whose size and wall nature determine the way of water organisation [1]. Complexity of water structure becomes enormous when it is confined to nanometer-scale cavities. Therefore investigation of the properties of water core of the reverse micelles is urgent and topical. The additives of ionic and nonionic kosmotropes and chaotropes influence the water structure in water pockets of reverse micelles. Non-ionic kosmotropes (trehalose, glucose, etc.) are very soluble well-hydrated molecules, having no net charge and enforcing extensive hydrogen bonding. Conversely, non-ionic chaotropes (e.g. urea) increase the population of broken water decreasing the hydrogen-bonded network of water [2].

The goal of the proposed work was to study the influence of nonionic additives (kosmotrope glucose and chaotrope chloral hydrate) introduced in the water nanocages of reverse micelles on both structural changes of water pools of reverse micelles and binding of a molecular probe to AOT reverse micelles, also on chromatographic retention factor of the model compounds by using water-in-oil micellar chromatography, infrared and ultraviolet-visible spectroscopy.

The important results of the presented work may be summarized so: (i) The O-H stretching vibrational absorption spectra in the region of 3000-3800 cm\(^{-1}\) were fitted into three subpeaks with the help of a Gaussian curve fitting program. Results showed, that trapped water fraction in the presence of glucose in water pool of the reverse micelle exceeds 8 times the same fraction in the pure water. Free fraction of water is higher 7 times under the influence of chloral hydrate in comparison with system modified by additives of glucose; (ii) Results obtained via UV-vis spectroscopy showed, that binding constants of o-NA with AOT reverse micelles have higher values in the presence of chloral hydrate than glucose; (iii) At the same time, retention of solutes are less in the presence of chloral hydrate in the microemulsion chromatographic system in comparison with microemulsion mobile phases, modified with glucose. It may be suggested on the basis of discussion of the obtained results, that molecules of glucose are presumably arranged in peripheral water of AOT reverse micelles, but molecules of chloral hydrate are probably localized in the depth of water pockets.

Literature:

Using the Confinement of Nanodroplets and Polymer Nanoparticles for Templating Inorganic Crystallization

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Although most of the work conducted so far on crystallization at surfaces and interfaces has dealt with planar surfaces, particle formation on spherical geometries may open new doors for preparing materials with potential applications in different technical fields. In this context, colloidal systems provide an excellent platform for the formation of inorganic and organic–inorganic hybrid nanostructures [1]. On one hand, colloidal particles (both polymeric and inorganic) can act as a support for crystallization processes on their surface. On the other hand, the colloidal structures generated by micelles and surfactant-stabilized droplets serve as soft templates or nanoreactors for the controlled precipitation of inorganic materials.

Our work focuses on the versatility of heterophase systems like miniemulsions in the synthesis of multifunctional nanoparticles. We have shown that inorganic/polymer hybrids can be prepared by in-situ formation of metal oxide (CeO₂, Fe₂O₃, Fe₃O₄, ZnO) nanocrystals on the surface of polystyrene particles functionalized with hydrophilic groups [2]. The approach can be carried out in both aqueous and alcoholic media, which implies that it can be extended to a wide range of inorganic materials, including different chalcogenides. By combining the in-situ precipitation at the surface of particles with an additional encapsulation of previously formed inorganic nanoparticles in the polymer core, we have succeeded on preparing “second generation” of multifunctional particles containing a magnetoresponsive inorganic component (Fe₃O₄) on the core and a light-responsive functionality (CdS) on the surface [3].

The ability of miniemulsions to template inorganic synthesis, however, goes beyond the liquid–solid interfaces of polymer colloids in suspension: miniemulsion droplets stabilized with surfactants and/or block copolymers and containing inorganic precursors can also act as soft templates. Although the most common way to prepare inorganic nanoparticles by emulsion methods is to mix two emulsions containing the precursors and a reducing/precipitating agent, the precipitation can also be driven by other stimuli, such as temperature or the addition of a precipitating agent to the continuous phase. We will present our last advancements in the field, showing that interfacial crystallization can occur at the liquid–liquid under mild conditions for different transition metal oxides and hydroxides.

Literature:

Pickering Emulsions Stabilized by Nanoparticles of Bare Silica. Adsorption of Nanoparticles and Emulsion Stability

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The stabilization of Pickering emulsions comes from a strong adsorption of solid particles at the oil-water interface that builds a rigid barrier against coalescence. Either particles having a diameter above 100 nm diameter, or aggregates of nanoparticles are usually selected for the stabilization of Pickering emulsions because the adsorption energy of solid particles coming from partial wetting by water and oil, \( \Delta_{\text{ads}}F = -\pi R^2 \gamma_{\text{oil}}(1\pm \cos \theta)^2 \), is several \( kT \), which means that full adsorption of solid particles takes place.

The adsorption energy reaches the order of magnitude of thermal energy upon decreasing the size of solid particles to \( \sim 10 \) nm, and equilibrium adsorption is therefore expected. The purpose of the present work is investigating the adsorption of individual nanoparticles of 12 nm diameter at the surface of oil droplets of o/w emulsions and looking at the consequences of a weak adsorption on the emulsion stability.

Silica nanoparticles of the Ludox™ series are individual nanoparticles of 12 nm diameter in suspension in water. Most oils do not wet bare hydrophilic silica. However partial wetting conditions are fulfilled with of particular polar oils that could be dispersed as Pickering emulsions stabilized by bare fumed silica [1].

Emulsification of diisopropyladipate oil droplets using Ludox™ AS40 silica stabilizing nanoparticles was successful up to 60% oil content (Fig. 1). An unusual dependence of the oil droplet diameter with respect to silica content occurs. The linear dependence

\[
D = \frac{6M(\text{oil})}{\rho_{\text{sil}} a_{\text{SiO}_2} M(\text{SiO}_2)}
\]

expected for full adsorption of solid particles was not followed, although it is generally followed over a wide silica concentration domain [2],[3].

The adsorption isotherm of silica particles measured by ICP-AES titration of residual silica shows that adsorption equilibrium takes place over the whole silica and oil concentration ranges. A consequence is the possible de-stabilization of emulsions upon shifting the adsorption equilibrium. As example, dilution of emulsions with pure water leads to their progressive coalescence into larger droplets. Several experiments based on optical microscopy, light scattering and adsorption isotherms show this paradoxical behavior. Multilayered adsorption of silica particles is suspected on the basis of adsorption isotherms.

![Image](image_url)

Fig. 1: O/w emulsions of diisopropyladipate oil stabilized by 4% Ludox™ AS40 for increasing amounts of oil from 10% to 70%. Emulsification was successful up to 60% oil and failed at 70%.

Literature:
Particle Stabilized Foams – A Journey through Length Scales

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The combination of nanoparticles and short-chain surfactants has been shown to increase aqueous foam stability and foamability compared to the same system without nanoparticles\(^1\). The origin of the increased stability is not fully resolved, yet. Unmodified, hydrophilic nanoparticles show no attachment to the water/air interface. On addition of surfactant, the particles are rendered hydrophobic and adsorb to the interface. The location within the interface is governed by the particles’ wetting properties which can be expressed by the contact angle. Due to the interfacial attachment, foam ageing processes as coarsening and drainage are decelerated or even arrested. Within the scope of this study, nanoparticle and surfactant concentrations are kept low in order to prevent bulk coagulation which seems to be a key feature in related investigations\(^2\).

We conduct x-ray reflectivity measurements to characterize the quasi-equilibrium state of the adsorbed particle layer. Surfactant adsorption isotherms, surface tension measurements and light scattering experiments were conducted to identify the parameters which are crucial for foam stabilization. An attempt is made to relate the macroscopic foaming behavior to the observed microscopic parameters.

![Fig. 1](image)

**Fig. 1** Foam stabilization by nanoparticles – a multi-scale problem

Literature:

Numerical Simulation of Bubble Dissolution and Ostwald Ripening in Paint Films

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The application of spray paints can lead to the appearance of air bubbles which are detrimental to the quality of the coating. During the drying process of the paint film, the number of bubbles reduces with time, whereas the average bubble size increases. This process, which is known as Ostwald ripening 1, is caused by the diffusion of dissolved gas from small bubbles to both large bubbles and to the interface between the paint layer and ambient air. Due to the complexity of mass transport in a paint layer containing bubbles, the mechanisms of Ostwald ripening in paint layers are not sufficiently studied.

In this work, a computational model for the description of the dissolution process of one or several bubbles in water-based paint films has been developed using the Finite Element Method. The model takes into account the transient diffusion of dissolved gas in the liquid. Since the equilibrium concentration of dissolved gas at the liquid-gas interface is proportional to the total pressure and therefore depends on the Laplace pressure, the boundary conditions at the liquid-gas interfaces are determined by the instantaneous bubble radii.

The effects of the paint layer thickness, the bubble size and position as well as the distribution of several bubbles on dissolution time have been quantified.

Numerical simulations have shown that the dissolution times increase with increasing paint layer thickness; moreover, the dissolution times increase as initial bubble size in power three and higher, which basically prevents the dissolution of bubbles above a certain threshold size within a reasonable time frame.

In the case of simultaneous dissolution of several bubbles having initially the same size, the distance from the bubble centres to the ambient air and the distance between the neighbouring bubble centres significantly affect the dissolution dynamics (see Fig. 1).

The numerical results are in a good agreement with experimental data obtained by using optical microscopy to determine the temporal evolution of bubble size distribution.

The results of the present study will be applied for the development of high quality industrial coatings.

Literature:

Protein Microgels Stabilize Water-in-water Emulsions by Absorbing at the Interface.

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Water-in-water emulsions can be formed by mixing aqueous solutions of incompatible polymers. However, contrary to oil-in-water emulsions they cannot be stabilized by surfactants. Therefore in practice they are stabilized by gelling one or both water phases. We explored the potential to use protein microgels with radii varying between 50 and 300 nm to stabilize water-in-water emulsions formed by mixtures of PEO and dextran. The protein microgels were produced by heating globular proteins in the presence of a small amount of calcium ions. Native proteins had no effect on the fast microscopic phase separation of the mixtures. However, the larger proteins particles entered the interface spontaneously and this led to stabilization of the emulsions for a period of weeks. The effect of the polymer composition, i.e. the interfacial tension, and the concentration and size of the microgels on the structure and stability of the emulsions was investigated systematically. The partition of the protein particles between the two phases and the interface was quantified.

\[
\begin{array}{cccc}
C_{\text{PEO}}/C_{\text{Dex}} (%) & 7.4/2 & 5.5/5.5 & 4.3/7.7 & 1.9/12 \\
\end{array}
\]

**Fig. 1** Confocal microscopy images (160x160µm) of the dextran signal (green, top) and the protein signal (red, bottom) for PEO/dextran mixtures in the presence of 0.5wt% protein particles (\(R_h=150\text{nm}\)) for different polymer compositions on the same tie-line indicated in the figure.
On the Elasticity of Liquid Marbles

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Spraying water on a dusty surface is enough to make a few liquid marbles. Liquid marbles are liquid droplets covered completely with small particles. They exhibit hydrophobic properties even on hydrophilic surfaces. They roll off easily, bounce and deform. Their behaviour is closely related to the Cassie wetting state and the phenomenon of superhydrophobicity. Typical liquid marbles are of millimetre size but their properties are analogous to smaller capsules and droplets of Pickering emulsions.

In this work we assess the elastic properties of liquid marbles. Water marbles are covered with an uneven and complex multi-particle coating of PE particles as revealed by ESEM imaging. The liquid marbles are highly elastic and can sustain reversibly up to 20-30% deformation. The modulus of elasticity measured experimentally is of the same order of magnitude as that expected for bare liquid droplets. Upon further compression their elasticity increases considerably until, at a critical threshold, the liquid marble is destroyed. We speculate on the mechanism of these processes and specifically the role of the liquid surface and the network of particles.

![Fig. 1 The surface of a millimeter-size liquid marble seen with an ESEM.](image)

Literature:

Adsorption Layers and Foam Films from β-Lactoglobulin

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The significance of understanding the role of proteins for the production and quality of colloids in various applications initiated a number of physico-chemical approaches for investigating protein-induced stabilization of colloid systems and foams in particular. The formation and stability of a thin liquid film between two gas bubbles in foam (foam film) is a key factor, which largely determines the evolution of the foam. A successful approach for studying foams is the model of a single microscopic foam film [1]. This method allows exploring the coalescence of bubbles by means of direct measurements of the film lifetime and the surface forces in a film. It is shown for instance in Refs. [2,3] that foam film studies significantly contribute to the understanding of the behaviour of protein stabilized aqueous foams. On the other hand, the properties of the adsorption layers that constitute the foam film surfaces play a decisive role in the formation process, control the properties and stability of the foam films, thus determining the behaviour of the overall foam as a gas in liquid disperse system, e.g. [2-4].

Here we present results on foam films and corresponding adsorption layers formed from aqueous whey protein solutions. This study is in the framework of a DFG projects cluster which deals with the stability and properties of foams produced from aqueous solutions of native and modified proteins (β-Lactoglobulin and β-Casein).

Literature:


Acknowledgements:

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Droplet-Surface Interactions in the Absence and Presence of Adsorbed Polymer Layers

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Oily liquid droplets in aqueous suspension (emulsions) represent a large number of natural and industrial products and materials. Many of the applications of emulsions are dependent on the interaction of the oily droplets with solid surfaces, whether those surfaces are metals, metal oxides, skin, or hair. In spite of the critical nature of this interaction, there are few experimental techniques that can directly probe this interaction, or connect the droplet-solid interaction to the molecular characteristics of the oil/water and water/solid interface. In this work, we have used high speed video microscopy of oil droplet rise and oil droplet collisions with solid surfaces to determine the influence of adsorbed polymer layers on thin film hydrodynamics and droplet attachment.

The oil studied was dodecane, and a model hydrophobic surface (thiol-coated gold) has been used as the solid. The measurements provide direct information on thin film drainage and liquid-liquid displacement (droplet spreading) at the solid surface. The dynamic droplet collision data have been acquired in the presence and absence of polymer emulsifiers/surface modifiers (hydrophobically-modified dextrin), either pre-adsorbed on the solid surface, or pre-adsorbed at both solid and droplet surfaces. A novel microfluidic device has been used to pre-condition the droplets with polymer, prior to release into the column for collision measurements. The collision/droplet rise data has been interpreted with the aid of adsorption characterisation of the polymer layer on the solid surface (using quartz crystal microbalance) and the droplet surface (using dynamic surface tension measurements).

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Monitoring the Coalescence during Nanoparticle Preparation by Fluorescence Cross-Correlation Spectroscopy

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The use of emulsion droplets as templates is one of the most common approaches for nanoparticles preparation and is of high scientific and technological importance. However, this approach has also intrinsic drawbacks originating from the colloidal stability of the emulsions. Indeed, coalescence between droplets can lead to a large size distribution of the obtained nanoparticles. Therefore, in order to fully understand and optimize the processes of nanoparticles preparation for any specific system, it is of immense importance to monitor the nanodroplets coalescence in an unambiguous and quantitative way. Here, we show how dual-color fluorescence cross-correlation spectroscopy [1], can be efficiently applied to directly monitor the coalescence during nanoparticles preparation from emulsions. To demonstrate the generality of our approach we studied three common preparation strategies, namely the solvent evaporation process from emulsion droplets, miniemulsion polymerization, and polycondensation to inorganic silica-nanocapsules. We found that coalescence has a minor role for the two first strategies, whereas a substantial coalescence between nanodroplets takes place during the polycondensation reaction [2, 3].

Literature:

Water in Oil Emulsions either Regularly Cooled or Stored at sub Ambient Temperatures. Determination of the Amount of Ice Formed

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Due to nucleation phenomena, water dispersed within an emulsion as small droplets is expected to freeze at a temperature lower than the freezing point which is zero for pure water and less for water containing a solute depending on the composition. Two processes to get the freezing may be undertaken; either the emulsion is regularly cooled (figure 1) or stored at a fixed temperature which is defined from the knowledge of the liquid/solid diagrams phases of the dispersed solutions. A theoretical approach based on thermodynamics and kinetics considerations is described for estimating the total expected amount of ice formed that could be less than the total amount of water present in the emulsion if the total solidification is not reached. Experimental results found from calorimetric measurements (1) linked to the energy involved during the formation or melting of the ice formed are in agreement with the theoretical analysis. Applications for others materials wherein water is found has been dispersed are considered: vegetables and biomaterials essentially.

Figure 1: Photography of an emulsion showing the progressive freezing of the droplets during cooling. At – 42°C all the droplets are frozen.

Literature:


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Connecting Fundamental Phenomena and the Characteristics of Emulsions Produced by Microfluidics

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A number of food matrices are constituted of oil droplets dispersed in an aqueous phase, i.e., can be represented as oil-in-water (O/W) emulsions. To control the physical-chemical properties of the end-products, it is of upmost importance to characterize the parameters that control the formation and ageing of emulsions, notably at a mesoscopic level. Emulsions can be prepared using various equipments, for instance high pressure homogenizers or microfluidic devices; the actual choice affects the physical and chemical stability of emulsions, and needs to be considered at large scale production.

Recent work has focused on characterizing the formation of emulsion droplets in microfluidic systems, e.g., T-junctions1, flow focusing devices2, and microchannels3. In the case of small, food relevant-sized droplets, i.e., typically of a few µm, the known scaling relations describing the formation of millimetre-scale droplets no longer apply directly. In fact, the interfacial tension can then no longer be approached by values measured under equilibrium conditions.

The present work describes the use of microfluidics to predict dynamic interfacial tension values at extremely short time scales. Using a Y-shaped junction, the droplet formation mechanism was accurately described by linking shear rate, viscosity and interfacial tension to the droplet size (below 10 µm)4. For this purpose, droplets formed within a range of static interfacial tensions and shear rates were used to build a calibration curve, which was subsequently applied to estimate the dynamic interfacial tension of droplets formed in various emulsifier solutions. Droplet formation rates up to 10,000 per second could thus be assessed. In addition, microfluidics were used to study the effect of process conditions on the physical destabilisation (coalescence) of emulsions, also under enhanced gravity conditions. We notably identified a range of conditions under which droplet coalescence is favoured.

Thus, microfluidic devices are of great interest to studying the fundamental phenomena that govern the construction (droplet formation) and destruction (physical destabilisation) of emulsions. New insights regarding the effect of emulsion’s components and processing have been obtained, and will be discussed together with potential implications for optimized formulation of food emulsions, and advanced processing.

Literature:

Determining Antioxidant Distributions between Oil, Water and Interfacial Regions of Emulsions: Generalization of Pseudophase Kinetic Models

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Pseudophase kinetic models originally developed for interpreting chemical reactivity in homogeneous association colloids such as micelles, microemulsions, and vesicles also work in fluid, stirred, opaque, oil-in-water emulsions. All these surfactant-based systems have the same basic properties as media for chemical reactions—but one—droplet size. In both thermodynamically stable, single phase surfactant solutions and in kinetically stable, stirred two phase emulsions, the reactive components are in dynamic equilibrium because the diffusivities of molecules and ions are orders of magnitude faster than the rates of the thermal chemical reaction of interest. In pseudophase models both association colloids and emulsions are conceptually divided into three separate reaction regions of uniform properties (see cartoon of component distributions between reaction regions) in which the observed rate of reaction is proportional to the concentration of reactants in the totality of each region and the rate constant in each region.

The effect of surfactant on the observed rate constant for reduction of an arenediazonium ion, 16-ArN₂⁺, probe by an uncharged antioxidant, AO, e.g., TBHQ (Fig. 2), is modeled by assuming that the AO distributes between the oil, interfacial and aqueous regions of an emulsion, but the reactive group of the surfactant like 16- ArN₂⁺ is only located in the interfacial region. Values of \( k_{\text{obs}} \) are obtained by electrochemical and spectrometric methods, physical separation of the phases is not required, and the data are fit with a kinetic model that provides estimates of the partition constants, \( P^O \) and \( P^W \), for the distribution of the AO and of \( k_i \) for reaction in the interfacial region.

This talk will describe the logic and application of pseudophase models to emulsions, show that AOs, are located primarily in the interfacial region, that their distributions depend on both surfactant Concentration and oil polarity, and are applicable to cationic, anionic, and zwitterionic emulsions. We plan to establish the relationships between AO structure, emulsion composition, including oil type, pH, emulsifier type and charge, and AO distribution and develop a new scale of AO efficiency.

**Literature:**
Structural Dependency and Release Profiles of Drug Cosolubilized with Dendrimers in Q^G Lytropic Liquid Crystals

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We report on the solubilization of three generations of polypropyleneimine (PPI) dendrimers and their impact on sodium diclofenac (Na-DFC) release profiles from reverse gyroid cubic (Q^G) liquid crystals comprises on 65 wt% monoolein (GMO) and 35 wt% water. Cosolubilization of the 0.25 wt% drug along with 25 wt% of PPI of 2^{nd}, 3^{rd} and 4^{th} generations (PPI-G2, G3 and G4) and their interactions was studied using small-angle X-ray scattering (SAXS), attenuated total reflected Fourier transform infrared (ATR-FTIR) spectroscopy and differential scanning calorimetry (DSC) measurements.

A considerable decrease (~78 Å) in the lattice parameter of the mesophase was obtained upon incorporation of PPI-G2 (without the drug) and increase in PPI from G2 to G3 and G4 led to increase in the lattice parameter. All the dendrimer generations caused to phase transition from Q^G→reverse hexagonal (H_{II}) mesophase at 25 wt%. According to ATR-FTIR and DSC, the large lattice parameters values from G3 and G4 embedment was assign to their interactions with the carboxyl groups of GMO at the interface in comparison to the strong interaction of PPI-G2 with the water and not with the surfactant.

Cosolubilization of Na-DFC along with PPI-G2 in the system revealed an enlargement of the lattice parameter without any structural transition while in the G3 and G4 systems the Na-DFC did not influence the lattice parameter and did not cause phase transition.

The release of Na-DFC from the mesophases from Q^G and H_{II} systems was followed by UV-vis spectroscopy revealing a generation-dependence on the drug release. As the generation increased the release of Na-DFC decreased.
Micelle-Like Aggregates in Surfactant-Free Ternary Mixtures

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We present fully atomistic molecular dynamics simulations of ternary octanol/ethanol/water mixtures. It is commonly known that octanol is completely soluble in pure ethanol, but octanol/water mixtures show a miscibility gap, and at a critical water content phase separation takes places in the ternary system. Our study focuses on the one-phase region of the phase diagram, where a macroscopically homogeneous system is present. The molecular-scale structure in this region reveals an increasing tendency of octanol aggregation with increasing water content. At low water concentration the aggregation is characterized by the formation of small clusters, but at higher water contents micelle-like aggregates of ethanol and octanol are observed before phase separation sets in. Different approaches to the determination of the micellar interface based on structural and energetic arguments are discussed.

Our observations from molecular simulations are consistent with WAXS wide-angle x-ray scattering experimental data. Our results demonstrate the emergence of a surfactant-free microemulsion in ternary systems, which arise when two immiscible compounds are mixed by help of a third component, the hydrotrrope. The presented concept is assumed to be of general importance for such ternary mixtures.

Fig.1. Snapshot of aggregates in an octanol/ethanol/water ternary mixture. The mole fractions of ethanol and octanol are 0.2 and 0.007.
Inverse emulsions (IE) are of utmost importance in a great variety of industrial areas, such as cosmetics, pharmaceutics and oil industry. Many studies have been devoted to their preparation, stabilization and destabilization mechanisms. Despite this, no investigation has been reported in the literature on the shear-induced aggregation of IEs. Therefore, the aim of this work is i) to explore the possibility of the shear-induced gelation in IEs and ii) to identify the key parameters that regulate the observed destabilization and gelation phenomena.

The employed IE systems consist of soft, water-swollen polymer-based particles at large particle contents, dispersed in an organic solvent and stabilized by a mixture of steric surfactants. It is found that at a fixed shear rate, the shear-viscosity of the IE systems first decreases with time (shear thinning), and then, after reaching a local minimum, it increases explosively (Figure 1). Cryo-SEM experiments reveal that along the shear history, the IE systems undergo competition between coalescence and aggregation, leading eventually to fractal gelation (Figure 1).

With respect to that of non-coalescing colloidal systems, the shear-induced gelation of the IE systems results clearly from a different mechanism: coalescence slows down the gelation process by reducing the total occupied volume of the clusters. Only when the aggregation rate becomes faster than the coalescence rate, the gelation phenomenon becomes possible. Through the shear-induced gelation, we have identified the main parameters affecting the shear-stability of the IE systems, and their effects can be well interpreted by considering their role in altering the competition between coalescence and aggregation kinetics.

Literature:
**Kinetics of Drop Breakage and Drop-Drop Coalescence in Turbulent Flow**

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In the last years our group has performed several related studies\(^1\)-\(^6\) about the detailed mechanisms of emulsification in turbulent flow. One major line in these studies was to clarify experimentally and describe theoretically the role of the main factors on: (1) Drop-breakage rate constants, \(k_{BR}\) (2) Drop-drop coalescence rate constants, \(k_C\) and (3) Size distribution and number of the daughter drops, which are formed as a result of drop breakage in turbulent flow. These factors include: (i) Rate of energy dissipation in the active zone of the homogenizer, \(\varepsilon\); (ii) Interfacial tension, \(\sigma\); (iii) Viscosity of the oil phase, \(\eta_D\); (iv) Viscosity of the aqueous phase, \(\eta_C\); (v) Oil volume fraction, \(\Phi\), and (vi) Surfactant concentration. The studied emulsions were prepared using either a “narrow-gap” homogenizer or “rotor-stator” homogenizer.

The experimental data for the kinetics of drop breakage were analysed by a kinetic scheme, which took into account the generation of drops of a given size (as a result of breakage of larger drops) and their disappearance (as a result of their own breakage into smaller drops). The experimental results for \(k_{BR}\) were described well by an explicit new expression, which was presented a product of: (a) the frequency of collisions between drops and turbulent eddies of similar size, and (b) the efficiency of drop breakage, which depends on the energy required for drop deformation. We found that the breakage of a single “mother” drop leads to the formation of multiple daughter drops, and the number and size distribution of these daughter drops depend strongly on the viscosity of the dispersed phase.

The newly obtained results about the kinetics of drop-drop coalescence could be summarized as follows: (1) The coalescence rate increases with the increase of drop size, and with the decrease of surfactant concentration and viscosity of the aqueous phase. (2) The experimental results obtained with different lengths of the pipes in the emulsification equipment showed that the process of drop-drop coalescence takes place predominantly in the pipes, i.e. after the most active zone of the homogenizer where the drop breakage is realized. (3) New set of differential equations is constructed to account for the fact that the processes of drop breakage and coalescence occur in different compartments of the equipment. (4) The comparison of our experimental results with the theoretical expressions for the coalescence rate constant, which are available in the literature, show that the theoretical expression for non-deformed spherical drops (assuming Taylor regime of drop-drop approach) gives much closer predictions to the experimentally obtained data (as compared to Reynolds regime of thinning of a planar film between deformed drops). This result also supports strongly the hypothesis that the process of drop-drop coalescence takes place predominantly after the processing element of the homogenizer, in the pipes of the emulsification equipment.

**Literature:**

5. S. Tcholakova et al., *J. Colloid Interface Sci.* 2007, 310, 570-589.
Coalescence of Repelling Colloidal Droplets: A Route to Monodisperse Populations

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Coalescence is often pictured as a dangerous process when narrow size populations of colloidal objects are desired. Indeed, when the limiting step of the coalescence process is the rupture event in the film separating two droplets, large droplets coalesce together faster than with small ones, since they have more film area.

However, we have found a set of conditions under which populations of droplets evolve spontaneously toward a narrow size distribution. Our experimental system consists of swollen polymer (PMMA) nanodroplets dispersed in a solvent (acetone) + non-solvent (water) mixture, prepared through solvent-shifting (“Ouzo Effect”). These droplets carry electrical charges, located on the ionic end groups of the macromolecules. We used ultra-fast time-resolved Small Angle X-ray Scattering, at the synchrotron beam line ID02, to determine their size distribution. We find that the droplets grow through coalescence events: the average radius \( R \) increases logarithmically with elapsed time while the relative width \( \sigma_R/R \) of the distribution decreases as the inverse square root of \( R \). We interpret this evolution as resulting from coalescence events that are hindered by ionic repulsions between droplets.

We generalize this evolution through a simulation of the Smoluchowski kinetic equation, with a kernel that takes into account the interactions between droplets. For droplets that interact through long-range ionic repulsions, “large + small” droplet encounters are more successful at coalescence than “large + large” encounters. We show that the corresponding kernel leads to a particular scaling of the droplet-size distribution, known as the “second-scaling law” in the theory of critical phenomena, where \( \sigma_R/R \) decreases as \( R^{-1/2} \) and becomes independent of the initial distribution. We argue that this scaling explains the narrow size distributions of colloidal dispersions that have been synthesized through aggregation processes.

![Fig. 1](image)

Fig. 1 If coalescence is hindered by repulsions that increase with the size of the droplets, small+large encounters of droplets are favored over medium+medium encounters, which results in a decrease of the polydispersity according to the second-scaling law.

Literature:

Effect of Surface Diffusivity on the Head-on Coalescence of Viscous Drops with Insoluble Surfactants - Difference between Polymeric Systems and Oil/Water Emulsions

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Scaling arguments [1] are presented to show the effect of the surface diffusivity $D_s$ in the head-on collision and coalescence of two viscous drops in a viscous matrix compatibilized with insoluble surfactants. The scaling arguments are compared to boundary integral simulations [1]. The parameters used in the simulations are those of the experimental system studied by Yoon, Hsu and Leal [2], where the drops are Polybutadiene (PBd) in a PDMS matrix, stabilized by block –copol ymer surfactants. Overall, the scaling could predict the effect of the different important parameters on the drainage time (such as the surface Peclet number, the Marangoni number and the pushing force due to the external flow), but could not determine its experimental or simulated value.

We also test our simulations against the scaling argument of Cristini, Blawzdziewicz and Loewenberg [3]. In Ref [3], this scaling argument was invoked to show that $D_s$ is not important in emulsions stabilized by small molecule surfactants, so that these systems can be described with the assumption of non-diffusing surfactants. Here, however, following the same arguments, but without using the Stoke-Einstein expression for the surfactant surface mobility employed in Ref. [3] and by simply substituting the parameters for different emulsion systems, we show that $D_s$ can be neglected only for oil in water emulsions, not for water in oil emulsion. Moreover, when the system of interest is a polymeric system, with $D_s$ in a range appropriate of block copolymer surfactants, the effect of $D_s$ can be significant both for high and low concentration system. Thus block copolymer architecture which determines their $D_s$ is an important parameter to stabilize immiscible polymer blends, especially when we want to use block-copolymer with small steric hindrance to obtain very thin films. This is in agreement with our boundary integral simulations. This last scaling is also reported for its ability to determine the values of $D_s$ for which depending on the concentration the drainage time starts to be reduced from its limiting maximum value corresponding to immobile interface drainage.

Literature:

Hydrodynamic Cavitation: A Bottom-Up Approach to Liquid Aeration

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We report use of hydrodynamic cavitation as a novel method for continuous creation of foams comprising of micrometer sized air bubbles in aqueous systems containing surface active materials. The hydrodynamic cavitation was created using a converging-diverging nozzle. The air bubble size obtained using this technique was found to be significantly smaller than the one achieved using conventional shearing routes. In addition, the technique provided the possibility of forming non-spherical bubbles due to the high elongational stresses experienced by the bubbles as they flow through the nozzle throat. We show that surface active agents with a high surface elasticity modulus can be used to stabilize the nascent air bubbles and keep their elongated shapes for prolonged periods of time. The combination of the cavitation process with appropriate surface active agents offers an opportunity for creating bubbles smaller than 10 micrometers, which can provide unique benefit in various applications.
SWOPTM: A Microgel Stabilised, Low-HLB O/W Emulsion Concept

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SWOPTM (SWitch-Oil-Phase Technology) is an emulsion concept that combines a W/O emulsifier with a mild surfactant, giving a low-HLB O/W emulsion (HLB ~ 6-7) stabilized by a polyacrylate microgel. Such emulsions can be formulated as lotions and creams for skin care applications.

A key feature of SWOPTM emulsions is the observation that the O/W emulsions turn into W/O during application to the skin, a phase inversion that consumers can experience as a sudden change in sensorial properties.

This paper will elucidate the physico-chemical mechanism underlying these emulsions. Optical, fluorescence and Scanning Electron Microscopy show a unique colloidal structure. Oil droplets in the diameter range of (1-2)µm surround individual domains formed by the swollen polyacrylate microgel. Those domains exhibit diameters of up to 20µm.

Phase diagrams and skin conductance measurements show that SWOPTM emulsions undergo a phase inversion from O/W to W/O upon evaporation of comparably small amounts of water, i.e. at water contents of (50-55)% compared to <20% for “classical” O/W emulsions. As shown in Figure 1 (left side), the water content vs. emulsifier HLB phase diagram shows a “skewed” O/W to W/O phase boundary, illustrating the observed phase-inversion at comparably high water content.

In addition, the influence of oil polarity, NaCl content and addition of various polymers on the phase diagrams of SWOPTM emulsions will be reported.

![Fig. 1](image.png)

Fig. 1 Left: Schematic phase diagram of a SWOPTM (black solid line) and a “classical” emulsion (grey dashed line), the black dot represents a typical SWOPTM formulation. Right: Freeze-etched cryo-SEM image of a SWOPTM emulsion.
Continuous Foam Fractionation: Influence of Operating Parameters on Bubble Size Distribution and Separation Efficiency

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Continuous foam fractionation is a technique to separate surface active molecules from aqueous solutions based on their affinity to adsorb at gas-liquid interfaces. By aerating a surfactant solution with gas interfaces are generated in form of bubbles where surface-active molecules can adsorb. The emerging foam, enriched with surface active molecules, is collected at the top of the column and liquefied to get an enriched product. Foam fractionation is regarded as a gentle and economical procedure for the separation and/or concentration of highly diluted protein mixtures, including active enzymes, which makes it applicable for the early stages of downstream processing [Merz, 2011].

The bubble size distribution in the generated foam is one of the important parameters for continuous foam fractionation, because the bubble size directly determines the available surface for the adsorption of the surface-active molecules. Consequently, the bubble size distribution considerably affects the separation efficiency. Hence, the influence of the operating parameters on the bubble size distribution should be investigated.

In this study, we initially introduce an image based method for optically measuring the distribution of bubble sizes in a device for continuous foam fractionation. The approach is based on the detection and subsequent analysis of spherical bubbles in digital images fusing a template matching technique [Zabulis, 2007]. The method is implemented in MATLAB® and consists of three steps: A template-based detection step, a validation step to remove false positives, and an evaluation step for estimating the size of the selected bubbles.

Based on the developed bubble size measurement method, the influence of different operating parameters such as the gas and feed flow rate on the bubble size distribution could be investigated for the model system β-casein. Furthermore, the feasibility of two different gas spargers (a porous glass frit and a perforated plate) to generate homogeneous bubble sizes is analyzed. Due to that, it is possible to determine the provided surface for the adsorption of the surfactants and to estimate the concentration of the target molecules in the collected foam.

Literature:

Acknowledgements:
Construction of Janus Structure by Janus Emulsion

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Janus Particles (JPs), with different composition or morphology as its hemispheres, have special properties of isotropic and asymmetry. They have been used as colloidal surfactants, chemical and biological sensors, display materials of the electronic paper, and self-motile colloidal particles.[1] The Janus emulsions received an intense attention after the introduction of the microfluidics method[2] and the number of applications multiplied rapidly[3,4]. However, in spite of this remarkable progress, the method suffers from the inevitable volume limitations, preventing a general commercial application. This limitation was removed by the introduction of the bulk process[5,6] to prepare well defined Janus emulsions. In the present report, the structure of the emulsion droplets including the size distribution and the ratio of the two hemispheres were controlled by the composition of emulsion, the energy of emulsification, and the methods of phase inversion temperature (PIT) and phase inversion concentration (PIC). Based on the fundamental investigations on the Janus emulsion, the Janus materials will be synthesized by replacing the oil phases with polymerizable monomers.

Fig. 1 The microscope images of janus emulsion in the system of methacrylate/silicon oil/Tween 80(aq) with increasing molar ratio of methacrylate to silicon oil.

Literature:

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Surface and Foam Properties of SLES + CAPB + Fatty Acid Mixtures: 
Effect of pH for C12-C16 Acids

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Recently we showed that triple surfactant mixtures, comprising the anionic surfactant
SLES, zwitterionic surfactant CAPB and long-chain fatty acid (FAc), possess very high surface
modulus which can be used to modify the dynamic properties of foams.1 In the current study2 we
investigate the effects of several factors on the surface and foam properties, for such triple
surfactant mixtures. The factors studied are: (1) chain length of fatty acid; (2) fatty acid
concentration; (3) pH; (4) presence of glycerol in the aqueous solution. We observed that
increasing FAc concentration above threshold value, leads to significant decrease of surface
tension, increase of surface modulus, decrease of mean bubble size in sheared foams, and strong
increase of the inside-foam friction and foam-wall friction. The main role of FAc is to induce a
surface phase transition, leading to formation of surface condensed phase in the mixed
adsorption layer. For all systems studied, the increase of pH above a certain transitional value
leads to a sharp increase of surface tension and decrease of surface dilatational modulus, which
is accompanied with a decrease in the inside-foam and foam-wall viscous friction (see Fig.1).
The transitional pH value varies between 8 and 11, and increases with the FAc chain length. The
increase of pH causes ionization of the FAc molecules – the latter start to behave as usual
anionic surfactant without forming surface condensed phase. These results clarify the
compositional domain, in which the FAc can be used for control of surface and foam properties
in such surfactant mixtures.

![Surface modulus](image1)
![Inside foam friction](image2)

**Fig.1** (A) Surface dilatational modulus as a function of solutions pH, (B) Dimensionless viscous
stress vs. Capillary number for BS+FAc system at different pH.

**Literature:**
Efficient Control of the Rheological and Surface Properties by Using C8-C18 Fatty Acids as Cosurfactants

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Systematic experimental study is performed about the effects of chain length (varied between C8 and C18) and concentration of fatty acids (FAc), used as cosurfactants to the mixture of the anionic surfactant SLES and the zwitterionic surfactant CAPB. The following properties are studied: bulk viscosity of the concentrated solutions (10 wt % surfactants), and dynamic and equilibrium surface tensions, surface modulus, and foam rheological properties for the diluted foaming solutions (0.5 wt % surfactants). The obtained results show that C8-C10 FAc induce formation of worm-like micelles in the concentrated surfactant solutions, which leads to transformation of these solutions into visco-elastic fluids with very high apparent viscosity, see Fig. 1. The same FAc shorten the characteristic adsorption time of the diluted solutions by more than 10 times. In contrast, C14-C18 FAc have small effect on the viscosity of the concentrated solutions, but increase the surface modulus above 350 mN/m which leads to higher friction inside sheared foams and to much smaller bubbles in the formed foams. The intermediate chain C12 FAc combines some of the properties seen with C10 FAc and other properties seen with C14 FAc. These results clearly demonstrate how appropriate cosurfactants can be used for efficient control of the rheological properties of concentrated surfactant solutions and some of the foam attributes.

![Figure 1](image)

**Figure 1.** Apparent shear viscosity as a function of fatty acid concentration, in 10 wt % BS solution for C8Ac (blue squares), C10Ac (red circles), C12Ac (green triangles), and C14Ac (pink diamonds).

**Acknowledgements:** The authors are grateful to Dr. Konstantin Golemanov from Sofia University for the useful discussions. This study is supported by the Unilever R&D Center in Trumbull, USA. The study is under the umbrella of the FP7 European project “Beyond Everest” and the COST action MP1106 “Smart and green interfaces”.
Crystallization-in-emulsion Process: In Situ Video Monitoring of the Evolution of Droplet and Particle Size Distributions

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Crystallization of an emulsified melt is a common process taking place in the manufacture of several fat emulsions for food and cosmetic applications [1]. Several fundamental phenomena are still open issues such as the mechanism of nucleation in confined media, the competition between nucleation and growth with respect to supercooling conditions, the role of the interfacial species (surfactants) on crystallization events. The aim of this study was to get more insight into the mechanisms occurring upon cooling molten droplets dispersed in stirred vessel.

A molten organic model material (ethylene glycol distearate) was emulsified in water in the presence of an emulsifier (tricosaethylene glycol dodecyl ether) leading to an o/w emulsion. The stirring conditions and amount of emulsifier allowed the control of the droplet size distribution [2]. The emulsion was progressively converted into a suspension of solid particles upon cooling. The hydrophilic emulsifier avoided the inversion of the emulsion in the whole temperature range. An optical probe EZ Probe D25 L220\textsuperscript{®} was designed for \textit{in situ} monitoring of the transition from droplets to particles under stirring into the vessel [3]. Since crystallization in a droplet took less than one tenth of a second, the visualized items appeared either totally liquid or wholly crystallized. Droplet and particle diameters were measured on captured frames (Fig. 1).

![Fig 1: Frames captured at 50°C - droplet diameter (solid arrow); particle diameter (dotted arrow)](image1)

![Fig 2: DSD and PSD evolution with the temperature](image2)

![Fig 3: SEM images of final particles](image3)

Fig 2 displays an example of the evolution of the droplet size distribution (DSD) and particle size distribution (PSD) during a cooling profile of 1°C.h\textsuperscript{-1}. The DSD slowly shifted to smaller sizes and the distribution width progressively became narrower. In the same time the PSD progressively moved to smaller sizes and the distribution became broader. Indeed the induction time of primary nucleation depends on the droplet size: the larger droplets first nucleated with a reduced induction time at low supercooling, and a higher supercooling was necessary to crystallize the smaller ones. There was also a close match between the initial DSD (at 55°C) and the final PSD (at 30°C) when almost all the droplets had been solidified (Fig. 2). A qualitative examination of the particles under SEM showed rounded dense particles which size corresponded to the initial droplets (Fig. 3) showing that each droplet was converted into one solid particle.

Literature:

In Situ Monitoring of the Droplet Size Distribution of O/W Emulsion During the Emulsification Process
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The aim of the study was to investigate the evolution of the droplet size distribution in situ inside the stirred emulsification vessel. An in situ video probe has been designed in order to record images of the droplet in line during the emulsification process. The expected outcome is a better understanding of the emulsion droplets fragmentation and re-coalescence as a function of time, and to disclose the influence of the main parameters that control the emulsification such as the type of stirrer, the stirring speed and the emulsifier concentration.

The size distribution of droplets oil (molten ethylene glycol di-stearate at 70°C) stabilized by the (tricosaethylene glycol dodecyl ether) surfactant was measured using an optical probe EZ Probe D25 L220 designed for in situ monitoring inside stirred vessels [1] (Fig. 1). Mechanical stirring was ensured by either a four blades propeller or Rushton propeller. Recorded frames were treated off line after the recording in order to extract the droplet size distributions (DSD). The Hough circular transform appeared a suitable method for the automatic treatment of pictures since it allows considering several thousands of droplets for building a statistically relevant DSD (Fig. 2). The droplet sizes could be measured in the range 10 μm - 100 μm; the relative accuracy on the droplet number average diameter was 10 %. The DSD was finally obtained as a function of time, showing the different transient stages before a stationary regime was reached where the fragmentation and re-coalescence rates are the same (Fig. 3). The measured sizes were in agreement with the characteristic size of the smallest eddies of the turbulent flow calculated according to Kolmogoroff.

The specific power input of stirring was the main parameter acting on the reduction of the mean droplet diameter and of the width of the DSD owing to its action on the droplet break up mechanism. The surfactant concentration was a parameter of secondary relevance on the DSD probably due to the reduction of the coalescence rate and to a faster stabilization of the o/w interface. The use of a flat blade propeller instead of a Rushton turbine was preferred for the production of a narrower DSD. Finally the time required to reach the stationary regime was found higher by a factor of 3 to 4 than predicted in the literature.

Fig 1: Scheme of the EZ Probe D25 L220
Fig 2: Picture of an emulsion analyzed using the Hough circular transform
Fig 3: Droplet size distribution as a function of emulsification time

Demulsification Behavior of O/W Emulsions Using a Photoresponsive Cationic Surfactant

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Stimuli-responsive surfactantshaveinterfacial properties that can be controlledby external stimuli such as pH, temperature, electricity, and light. In particular, the use of light as the external stimuli is very attractive because of its low cost, low energy consumption, and ease of use. Photoinduced demulsification of O/W emulsions, using a photoresponsive gemini surfactant, have been successfully accomplished. The phenomenon results from coalescence of the emulsion droplets with photoisomerization of the surfactant molecules at the O/W interface because of UV light irradiation. In this study, a photoresponsive cationic surfactant, (AZTMA, Figure 1) containing an azobenzene group, was applied to a binary mixture of n-octane and water, and the influence of UV light irradiation on the resultant stable emulsions was examined.

When mixtures of the trans-AZTMA aqueous solution and n-octane were homogenized for 5 min at 10,000 rpm, stable emulsions were obtained in a region of specific weight fractions. The emulsions were stable for over a week and found, by dilution method, to be of the oil-in-water (O/W)-type. UV light irradiation of the stable O/W emulsions promoted cis isomerization of trans-AZTMA; however, no phase separation of the emulsions was observed.

Next, the influence of UV light irradiation on stable emulsions consisting of n-octane and aqueous AZTMA/SDS solutions was investigated. Aqueous trans-AZTMA/SDS solutions and n-octane were homogenized to the same condition to obtain the corresponding emulsions. UV light irradiation of the stable O/W emulsions led to the coalescence of oil droplets in the emulsions, i.e., demulsification, and then the oil and water phases were separated (Figure 2). These results suggest that cis isomerization of the trans-AZTMA molecules with UV light irradiation brought about the exposure of the n-octane/water interface in the emulsions. Consequently, the stability of the obtained emulsions was drastically decreased by UV light irradiation in this novel system.

Figure 1: Chemical structure of AZTMA.

Figure 2: n-octane/(trans-AZTMA/SDS)aqueous solution system: a) stable emulsion before UV irradiation; b) phase separation after UV irradiation.
Double Stimuli Responsive O/W Emulsions Act as Magnetic Fluid and Heat-induced Gelator

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Magnetic fluids are colloidal liquids made of ferromagnetic nanoparticles (NPs), which become strongly magnetized in a magnetic field, and the fluids are of considerable interest because of their potential novel applications in several technological fields of nanoscience. To make high performance magnetic fluids, control of the magnetic NPs dispersibility is a vital issue. In this work, we synthesized highly dispersive magnetite nanoparticles (Fe\textsubscript{3}O\textsubscript{4} NPs) using a long-chain amidoamine derivative (Fig.1: C18AA), and demonstrated that the aqueous dispersion has a magnetic fluid property. Further, we showed that the combination of Fe\textsubscript{3}O\textsubscript{4} NPs and C18AA enable to prepare double stimuli responsive O/W emulsions which act as heat induced gelator and magnetic fluid.\textsuperscript{[1]}

Synthesis of Fe\textsubscript{3}O\textsubscript{4} NPs is as follows. 1 M aqueous solution of FeCl\textsubscript{2} was added into C18AA aqueous solution, and the mixture was stood for 24 h at room temperature without stirring. Double stimuli responsive O/W emulsions were prepared by adding Fe\textsubscript{3}O\textsubscript{4} NPs obtained at [C18AA]=200 mM into O/W emulsions consisting of C18AA, toluene and aqueous LiCl. The resultant Fe\textsubscript{3}O\textsubscript{4} NPs were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and zeta potential analyzer.

Fe\textsubscript{3}O\textsubscript{4} NPs obtained at [C18AA]=200 mM were dispersed in water for a long time and the dispersion showed magnetic fluid property (Fig.2a), whereas Fe\textsubscript{3}O\textsubscript{4} NPs prepared at a low concentration of C18AA rapidly precipitated, because the former and latter diameters were \textsim 10 nm (Fig.2b) and \textsim 60 nm, respectively. Obviously, this result indicated that the size control of Fe\textsubscript{3}O\textsubscript{4} NPs is essential for preparing magnetic fluid. Further, the presence of C18AA brought about a shift of zero-point of charge (ZPC) of Fe\textsubscript{3}O\textsubscript{4} NPs from pH7 to pH11, as shown in Fig.3, which is probably caused by the adsorption of C18AA onto Fe\textsubscript{3}O\textsubscript{4} NPs. Consequently, the dispersion of Fe\textsubscript{3}O\textsubscript{4} NPs capped with C18AA had a high resistance against pH.

Interestingly, we can easily prepare magnetic fluids of Fe\textsubscript{3}O\textsubscript{4} NPs dispersed in toluene, instead of water. Apparently, this fact leads to the result that Fe\textsubscript{3}O\textsubscript{4} NPs can be easily dispersed in O/W emulsions of C18AA/toluene/aqueous LiCl. The O/W emulsions containing Fe\textsubscript{3}O\textsubscript{4} NPs were acted as both magnetic fluid and heat-induced gelator. This enable us to give an opportunity to hold the shape of the dispersion by heating, after we made a desirable shape by magnetic field.

Generation of Crystalline Polyurethane Foams Using Lab-on-a-Chip Techniques

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We show here how polyurethane (PU) foams with well-controlled polymer and structural properties can be generated using millifluidic Lab-on-a-Chip techniques. In this approach, the foam is created by injecting a gas and the liquid solutions at constant flow rate into a purpose-designed channel network of millimetric dimensions. This network is designed such that physical bubble blowing and homogeneous mixing of the chemicals form an integrated, continuous process. Chemistry and foam stability are adapted in a way which ensures that an initially liquid foam with equal-volume bubbles leaves the Lab-on-a-Chip. Within this foam, the bubbles have enough time to self-order into crystalline foam structures under gravity or confinement before solidifying in-situ. This approach provides explicit and simultaneous control over the chemistry, the foam density, the bubble size and the pore connectivity of the final foam via the flow rates of the different reactants. This currently unequalled control over the properties of the final PU foam is hoped to provide new experimental insight into their structure/property relationships and to open up new avenues for PU foam applications.

Fig. 1 Left: Example of a Lab-on-a-Chip used to generate equal-volume bubbles and to perform the flow-chemistry for on-chip generation of PU foams. Right: Examples of obtained fully polymerized PU foams.

Literature:
Double Emulsion for Encapsulating B12 Vitamin

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Water-in-oil-in-water double emulsions are dispersions of an inverse emulsion in an aqueous continuous phase. These emulsions are interesting systems to encapsulate hydrophilic substances in the inner aqueous phase. Double emulsions enable a good protection of encapsulated agents against external environment, and a controlled release thereof. Despite their interest, they are still not widespread in industrial applications because of the difficulty to formulate stable systems. Indeed they require the presence of two antagonistic types of stabilizers: a more lipophilic surfactant to stabilize the inverse emulsion, and a more hydrophilic one to disperse the oil droplets in the aqueous phase.

Herein, we propose to study double emulsions stabilized by a polysaccharide or a protein. We determine the influence of both formulation and process parameters on the encapsulation rate just after emulsification as well as during storage. We build up a “stability map” evidencing the formulation regions where the capsules are stable or not. For non-stable systems, we identify the destabilization mechanisms and determine the kinetics of release combining several techniques (confocal microscopy, tensiometry, rheology, and UV-visible spectrometry).

Fig. 1 Example of a water-in-oil-in water emulsion. The scale bar corresponds to 10µm
Characteristics of Spontaneously Formed Biocompatible Nanoemulsions Stabilized by Ionic Dicephalic-type Surfactants

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In the recent years much effort has been made in the nanomedicine research to develop new effective and biocompatible nanocarriers for hydrophobic molecules having a colloidal phase as a key prerequisite for their effectiveness. Among these systems an important role is played by nanoemulsions which constitute transparent or translucent isotropic dispersions comprising water and/or oil nano-domains and coexisting in high kinetic equilibrium due to the presence of a surfactant layer at the oil/water interface. Those formulations can be fabricated using either high-energy or low-energy methods, but the latter offer advantages in terms of low cost, higher energy efficiency, and simplicity of implementation. Therefore, it can be seen that the influence of an appropriate surfactant on the long-term stability of designed nanosystems is very important [1-2].

The present work has been carried out to explore the potential to form spontaneously stable and nearly monodisperse oil-in-water (o/w) nanoemulsions of two recently synthesized ionic dicephalic-type surfactants, i.e., positively charged N,N-bis[3,3′-(trimethylammonio)propyl] dodecanamide dimethylsulphate, C₁₂(TAPAMS)₂ and anionic, disodium N-dodecyl iminodiacetate, C₁₂(COONa)₂ [2-3]. Initially, we examined by titration method the ternary phase diagrams of surfactant-oil-water (SOW) systems containing different ratios of C₁₂(TAPAMS)₂ or C₁₂(COONa)₂ as the surfactant (S), oleic acid or isopropyl myristate as the oil phase (O) and the water phase (W). Then, the obtained nanoemulsions were characterized by visual and microscopic observations (Cryo-TEM), the particle size and distribution (DLS) as well as ζ-potential measurements (Doppler electrophoresis), showing that the nanoemulsions’ droplets have a nearly monodisperse size distribution (D₄ <100nm, PDI<0.2) and spherical morphology, as well as a long-term stability. Oil composition, surfactant type, and surfactant-to-oil ratio were all found to influence the droplet size, charge and stability of the systems produced. Our results give new insights of the o/w nanoemulsions containing dicephalic-type surfactants and may serve as guidelines for design and preparation of new nanoemulsion-based delivery systems for practical applications such as personal and household care products, drug delivery, particle synthesis, detergency and nanoparticle phase-transfer.

Literature:


Acknowledgements:

The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Technology (research related to C₁₂(TAPAMS)₂) and by the Wrocław Research Center EIT+ under the project ‘Biotechnologies and advanced medical technologies’-BioMed (POIG 01.01.02-02-003/08-00) financed from the European Regional Development Fund Operational Programme Innovative Economy, 1.1.2 (research related to C₁₂(COONa)₂).
Stabilization of Multiple Emulsions Using Hydrocolloids and Evaluation of Their Encapsulation Efficiency by Rheometry

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Over the last years, the interest of research and industry in food grade multiple emulsions has constantly been growing. This is mainly due to the fact that multiple emulsions offer interesting possibilities to encapsulate sensitive bioactive substances or can be used to reduce the fat content of food products. One of the crucial points in formulating and producing such emulsions is to ensure the stability of the emulsion’s microstructure during shelf-life. Release of innermost droplets goes hand in hand with a loss of emulsion functionality. Bioactive substances could be exposed to harsh environmental conditions and fat reduced emulsions might lose their creamy mouthfeel. In order to avoid this, one current research focus is the development of new encapsulation systems for active substances in food and pharmaceutical emulsions. In this context, particularly natural or even organically produced materials are of interest. Citrus pectin is a suitable substance to form and stabilize multiple oil-in-water-in-oil (O/W/O) emulsions. This hydrocolloid exhibits surface active behavior to a satisfying extent and increases the viscosity of aqueous solutions. In emulsions, this can enhance stability by suppressing droplet movement and also coalescence which in turn leaves the microstructure of an emulsion unchanged. In order to evaluate the stability of the microstructure of multiple emulsions integrally, the encapsulation efficiency is mostly used. This term describes how much of a given substance or inner dispersed phase is still encapsulated after a certain amount of time or energy intake into the system during emulsification. However, measuring this quantity is still a challenge. Although there are several measurement methods available for water-in-oil-in-water emulsions, most of these cannot be applied to O/W/O emulsions. Rheometry is a promising tool to quantify the encapsulation efficiency of multiple O/W/O emulsions. A loss of encapsulated oil phase reduces the volume of encapsulating water phase and dilutes the continuous phase which leads to changes in the viscosity of the overall emulsion. In this presentation, we want to outline how hydrocolloids can be used to form and stabilize O/W/O emulsions. It will be demonstrated how the application of hydrocolloids can reduce the amount of conventional synthetic emulsifier employed. Rheological measurements regarding the encapsulation efficiency will be introduced and limits of this measurement technique will be discussed. Furthermore, measurements will underline the extraordinary encapsulation efficiency of the investigated formulations.

Literature:

Acknowledgements:
This research was conducted in the frame of the project “Allipids – A range of preventive food on the basis of healthy lipids” (FKZ 0315682). The authors would like to thank the German Federal Ministry of Research and Education (BMBF) and Projektträger Jülich for financial support of the project.
Foamability, Foam Stability and Foam Structure of Various Types of Milk

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Milk foams are colloidal systems formed by air bubbles, water, and surface active proteins. Not only the recent emerging growth in the consumption of cappuccino-style beverages revived the scientific interest in the foaming properties of milk. In the past, various studies have investigated milk-foam properties (Ref.1,2,3, and references therein) and interesting characteristics were reported. For example, whereas, the foamability of UHT skim milk and pasteurized skim milk was found to increase continuously with rising temperature from 5 to 80 °C, the foamability of pasteurized homogenized whole milk exhibits a strong anomaly around 25 °C (Ref. 1). In this work, the foamability and foam stability of different types of milk as determined by a fully automized foam-height measurement will be presented and compared to previous studies. The effect of temperature on foamability and the different kinetics in the foam-decay phase are investigated. As in previous studies, foam is generated by purging air through the liquid. In addition to this, foam is generated by stirring whereby different stirrer geometries are compared. Moreover, the foam-structure characterised by the bubble-size distribution and the total number of bubbles within a well-defined area was determined. In contrast to previous studies on the foam structure of milk, in this work the optical set-up of the foam-structure measuring device is based on the principle of total-light reflection guaranteeing sharp images of highest contrast (Fig.1). This, in combination with a digital image analysis has the great advantage that the foam structure is continuously monitored during the foaming and the foam-decay phase (Fig.1 right panel). As a result, a simultaneous and continuous observation of the total-foam volume and the foam structure during the foam-decay phase is possible. This provides valuable information about decay kinetics depending on temperature and / or type of milk.

Fig. 1: Foam structure of UHT whole milk: Image (left) and bubble size distribution at 600 seconds after foaming (center). Time dependence of total bubble count and mean-bubble area (right)

Literature:
Incorporation of air/gas bubbles into (semi-)solid food products is well known. Examples of aerated food products include e.g. bread, cheese, ice cream, mousses, chocolate, protein shakes, whipped cream and cereals. While aeration of water-continuous compositions is quite well understood, aeration of oil-continuous systems received much less attention. Here we discuss fundamental aspects of aeration of w/o emulsions containing elevated (0.2-1.0 wt%) levels of emulsifiers compared to regular usage levels in margarines and spreads. We concentrated our research on w/o-promoting emulsifiers with low HLB values, such as monoacylglycerides (MAG) and polyglycerol esters of fatty acids (PGE). Experimental design included preparation of 40 wt% and 60 wt% w/o emulsions based on a triacylglyceride oil blend and aerated with nitrogen (0-35 vol% of gas phase in final compositions).

Rheology of aerated w/o emulsions was investigated at various temperatures in the interval between 5 and 35°C. Also, inversion of w/o emulsions under simulated oral conditions was quantified. Based on the experimental evidence we conclude that excessive amounts of emulsifiers with low/medium (3-7) HLB values have a profound effect on rheology, but to less extent on emulsion inversion and formation/stability of foam phase. Oral behavior of aerated emulsions was assessed by a small sensory panel (N=5), and results of this trial are summarized in Table 1. While compositions prepared with PGE, cis-unsaturated and saturated MAG exhibit negative sensory qualities (e.g., graininess and lack of consistency), aerated w/o emulsions made with elevated amounts of trans-unsaturated MAG have clearly superior sensory behavior. We attribute our observations to the partitioning of MAG and PGE in aerated w/o emulsions between oil-water and oil-gas interfaces. Excessive amounts of emulsifiers introduced to w/o emulsions prior to aeration lead to the increase of the relative amount of the emulsifier in the fat blend. As a result, properties of aerated emulsions will be influenced by both crystallization behavior of fat blends in the presence of emulsifiers and molecular properties of emulsifiers at gas-oil interfaces.

We conclude that trans-unsaturated MAG have outstanding effect on physical and sensory properties of aerated w/o emulsions compared to fully saturated and cis-unsaturated MAG, as well as PGE. The nature of the observed effect is not fully understood and can be linked to the peculiarities of fat crystallization in the presence of trans-unsaturated MAG, as well as with properties of the latter at gas-oil interfaces. Understanding of the mechanism of this phenomenon will be addressed in our future studies and should enable structural design of aerated spreads with desired consumer properties through the tailored use of selected emulsifiers.

Table 1: Sensory behavior of 60 wt% w/o emulsions aerated to 35 vol% of gas phase, formulated with an elevated dosage (1.0 wt%) of low/medium HLB emulsifiers.

<table>
<thead>
<tr>
<th>Emulsifier</th>
<th>Sensory behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>fully saturated MAG</td>
<td>too hard, grainy, sandy (poor)</td>
</tr>
<tr>
<td>trans-unsaturated MAG</td>
<td>soft, creamy (good)</td>
</tr>
<tr>
<td>cis-unsaturated MAG</td>
<td>very soft, bitter, watery (poor)</td>
</tr>
<tr>
<td>PGE</td>
<td>sticky, waxy (poor)</td>
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</tbody>
</table>
Stabilization of W/O Emulsions by Hybrid Amphiphilic Polymers: Exploration of Emulsion Stability and Its Mechanism

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We have developed a hybrid amphiphilic polymer (AIM-FN) consisting of a silicone backbone modified with hydrocarbon chains and hydrolyzed silk peptides. AIM-FN is molecularly soluble neither in water nor in most of organic solvents, but is attractive with these solvents due to its amphiphilic nature. This property enables the polymer to form “an independent third phase” being located at a silicone oil/water interface (Fig 1), and hence, the emulsions are stabilized effectively based on a fundamentally distinguishable mechanism from the approach by conventional surfactants\textsuperscript{1}.

The size of the emulsion droplets prepared with AIM-FN is ca. 2 to 4 \( \mu \text{m} \), independently on the composition in the stable water-in-oil (W/O) emulsion region\textsuperscript{2}. This W/O emulsion has long kinetic stability: coalescence hardly takes place, although creaming and flocculation are operative. Thus, the water droplets in the emulsion can be redispersed by a weak energy input.

Unlike conventional surfactants, AIM-FN does not lower the interfacial tension between water and silicone oil (decamethylcyclopentasiloxane, D5) at room temperature (Fig.2). The behavior seems like “pickering emulsion”, in which an interfacial active agent does not need to compensate the interfacial free energy to make the dispersed phase stable. We will bring a key outlook in terms of novel stabilization mechanism using the sustainable material.

**Literature:**


**Acknowledgements:**

We thank Seiwa Kasei for providing the hybrid amphiphilic material for us. A part of this work was supported by Japan Aerospace Exploration Agency (JAXA).
Impact of the Surface Rheology on the Kinetics of Ostwald Ripening of Foams Stabilized with Saponins

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Saponins are a class of natural surfactants found in more than 500 plant species, which are known to have very good foaming properties. They consist of flat hydrophobic head group (triterpenoid or steroid) with hydrophilic oligosaccharide chains. In previous articles [1] we studied the surface rheological behavior of saponin adsorption layers, subjected to steady or oscillatory shear deformation, which we have recently extended to include surface dilatation as well. Generally triterpenoids exhibited high modulus both in dilatation (E) and in shear (G) deformation, while steroids had moderate modulus in dilatation, and negligible modulus in shear. In this work we study the kinetics of Ostwald ripening (OR) [2] of foams stabilized by various saponins, with well-characterized surface rheological properties as motioned above. Our experimental results indicate that triterpenoid saponins where able significantly to inhibit the rate of OR, while the steroidal type of saponins have much less pronounced inhibitory effect, which seems to be in line with the findings from surface rheology experiments and in support of some of the OR models proposed in the literature. However when all the surface rheological data are combined and correlated with foam stability, it become clear that that for similar values of given surface rheological parameter (e.g. example surface dilatational or shear viscosity/elasticity) one can have foams with markedly different OR stability and vice versa, foams with same OR stability can be made with systems having markedly different surface rheological parameter. Thus it became clear that no clear correlation can be established between the rate of OR and the surface modulus in particular mode of deformation (shear or dilatational). The impact of other surface properties and phenomena on the rate of OR will be discussed, alongside with analysis of several literature proposed mechanism to control OR in liquid foams.

Literature:

Instability of Stretched and Twisted Soap Films in a Cylinder

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If a single rectangular soap film is confined between parallel walls it can be stretched indefinitely. However, if the rectangular film is confined in a cylinder, oriented parallel to the axis, we find that this cylindrical constraint induces a surface-tension-driven instability in sufficiently long films. Once this instability is triggered, at some critical aspect ratio, the film rapidly deforms (Figure 1) and collapses. If the film is twisted, taking the shape of a helicoid, then this critical aspect ratio is reduced.

We describe soap film experiments and Surface Evolver simulations that were carried out to determine the critical aspect ratio of both stretched and twisted films. A theoretical analysis confirms the values for the critical aspect ratio found in experiment and simulation for the stretched film, and this threshold decreases with increasing twist of the film.

This instability places an upper limit on the aspect ratio of any structure where a soap film, or any flexible membrane without bending and torsional stiffness, is confined in a cylinder.

Fig. 1 The shape of a single stretched film just after the instability is triggered, in simulation (left) and experiment (right).
Protein Concentration and Protein Exposed Hydrophobicity as Dominant Parameters Determining Flocculation of Protein-stabilized Oil-in-Water Emulsions

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The DLVO theory is often considered applicable for the description of flocculation of protein-stabilized oil-in-water emulsions. To test this, emulsions made with different globular proteins (β-lactoglobulin, ovalbumin, patatin and two variants of ovalbumin) were compared under different conditions (pH and electrolyte concentration). As expected, flocculation was observed under conditions in which the zeta potential is decreased (around the iso-electric point and at high ionic strength). However, the extent of flocculation at higher ionic strength (>50 mM NaCl) decreased with increasing protein exposed hydrophobicity. A higher exposed hydrophobicity resulted in a higher zeta potential of the emulsion droplets, and consequently in increased stability against flocculation. Furthermore, the addition of excess protein strongly increased the stability against salt induced flocculation, which is not described by the DLVO theory. In the protein poor regime, emulsions showed flocculation at high ionic strength (>100 mM NaCl), whereas the emulsions were stable against flocculation if excess protein was present (figure 1). This research shows that the exposed hydrophobicity of the proteins, and the presence of excess protein affect the flocculation behavior.

Fig. 1 Graphical overview of the effect of ionic strength, protein hydrophobicity and protein concentration on the flocculation behavior of protein-stabilized emulsions.
Study of Polyelectrolyte and Oppositely Charged Surfactant Mixture for Stabilization of Emulsion

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Emulsion is a very complex but at the same time most interesting object for studies in modern colloid chemistry. Although much work is devoted to this topic, the stabilization of emulsions remains an actual problem. The emulsifying ability of low molecular weight surfactants is sufficiently studied. However, the use of complexes formed by surfactants and oppositely charged polymers is of interest due to their high adsorbability at interfaces, a key property for the formation and stability of emulsions.

In the presented work complexes of the water-soluble polymer Polysterensulphonate (PSS) and cationic surfactant dodecyltrimethylammonium bromide (DOTAB) were prepared and their stabilizing effect on oil-water emulsions investigated. The PSS-DOTAB complexes were prepared by mixing the solutions of the individual compounds at concentration ratio 0,1; 0,2; 0,3; 0,4; 0,5. Solutions of the complexes were used 24 h after mixing. The interfacial tension at the tetradecane-water interface was measured by Drop profile analysis tensiometry (PAT-1, SINTERFACE), and DLS and zeta-potential measurements were performed at 25°C using Nano-ZS90 system (Malvern Instruments). Emulsions were prepared at room temperature by ultrasound at a mixing time of 2 minute. The obtained emulsions were poured into 14 ml calibration tubes and then their emulsifying efficiency was studied by observation of emulsion stability every 30 minute. The principle of observation was based on the determination of the volume of the separated oil phase. The size distribution of emulsion droplets was measured directly after emulsion formation by using a Zetasizer (Malvern), and repeated over 10 days.

It was established that there is an optimum ratio for the surfactant-anion-active polymer mixture at which the emulsion stability reaches a maximum. As it was proposed very recently in [1] this optimum ratio, probably, correspond to the stoichiometric composition of surfactant-polymer complexes. Any further increase in the surfactants concentration above this optimum leads to a decrease in the emulsion stability.

![Fig 1. Mean drop size of the dispersed phase of an oil-water emulsion, in dependence on concentration of the stabilizing system DOTAB/PSS](image)

The mean drop size shows that within optimum concentration ratios the emulsion stability is growing. The results after 3 days show that there was no coalescence in the emulsion, i.e. a negligible change of the mean droplet size was observed.

Literature:
Role of Polymer-Surfactant Interactions in Foams

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Solutions of surfactant-polymer mixtures often exhibit different foaming properties, compared to the solutions of the individual components, due to the strong tendency for formation of polymer-surfactant complexes in the bulk and on the surface of the mixed solutions. In this study we combine foam tests with model experiments to evaluate and explain the effect of several polymer-surfactant mixtures on the foaminess and foam stability of the respective solutions. Anionic, cationic, and non-ionic surfactants (SDS, C_{12}TAB and C_{12}EO_{23}) were studied to clarify the role of surfactant charge. Highly hydrophilic cationic and non-ionic polymers (polyvinylamine and polyvinylformamide respectively) were chosen to eliminate the effect of direct hydrophobic interactions between the surfactant tails and the hydrophobic regions on the polymer chains. Our experiments showed clearly that the presence of opposite charges is not a necessary condition for boosting the foaminess and foam stability in the surfactant-polymer mixtures studied. We showed that the foamability of the cationic polymer polyvinylamine (PVAm) and anionic surfactant dodecyl sulphate (SDS) is strongly reduced, whereas the stability of the formed foams is strongly enhanced, as compared to the solutions of SDS alone [1]. The effect of the surfactant head group is studied [2] by comparing SDS with another anionic surfactant (sodium dodecyl oxyethylene sulphate, SDP1S) which contains an additional ethoxy fragment in the charged head group. For changing the electrostatic polymer-surfactant interactions, we varied pH between 6 and 10, thus crossing the polymer pKa ≈ 8.6. The foam tests showed that the foamability of all mixed solutions is strongly reduced in the entire range of pH values studied. Surprisingly, we found that the stability of SDP1S foams is also strongly reduced by PVAm, at lower pH, when the polymer charge density is high ( contrary to SDS and to the common understanding). These results clearly demonstrate that the effect of cationic polymers on the foaming properties of anionic surfactants could depend significantly on the specific head group of the surfactant. Moreover, we showed that excessively strong polymer-surfactant interactions could be a serious problem in the formation and stabilization of foams from mixed polymer-surfactant solutions.

Literature:

Carboxylate Based Surfactant for Ion Flotation: Salt and pH Effects

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The process called ion flotation allows to concentrate metal ions or other charged entities from aqueous solution by developing interfaces. This is achieved using a surfactant molecule which complexes ion and entrains it in a foam. Afterwards the drainage of the foam leads to concentrate the metal ions and the surfactant. The skimming of the foam enables ultimately to extract metal ions from the native solution. Ion flotation covers two main application fields: recovery of valuable material and water decontamination. Compared to solvent extraction, used for example in the nuclear fuel recycling, ion flotation shows the main advantage of using gas instead of an organic solvent.

In the present contribution a commercial carboxylic surfactant (AKYPO® RO 90 VG) is investigated in terms of ion flotation. This surfactant is composed of an alkyl chain, ethoxy groups keeping efficient the foaming property, even after complexation, and a terminal carboxylic acid function which acts as a complexing part when it is under its charged carboxylate form.

The efficiency of this process in term of decontamination factor, enrichment ratio and effluent volume is a subtle interplay between the solution chemistry and the physical of the foam. The main part of the study focuses on the influence on pH and the nature of metal ion such as neodymium (Nd³⁺), europium (Eu³⁺), copper (Cu²⁺), calcium (Ca²⁺), strontium (Sr²⁺), and lithium (Li⁺), both on the solution speciation of metals and surfactant than on the hydrodynamics and wetness of the foam. The complexation between the surfactant and neodymium ion in the bulk was studied by pH titration and the complexation constants were estimated by modelisation of the titration curves. The foam structure was characterized by conductometry and small angle neutron scattering.

Literature:

Imaging Ellipsometry at the Liquid/Liquid Interface

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Imaging and metrology of thin films at the liquid/liquid interface is of increasing interest for a number of applications like emulsion, crude oil technology, biophysics. Imaging ellipsometry can be used to characterize the behavior of molecules, polymers, nanoparticles or cells at the liquid/liquid interface. Benjamins et al. (2002) presented a light guides based setup using ellipsometry to study the liquid–liquid interfaces. Based on developments at Twente University the setup was adapted to Brewster angle microscopy and Imaging ellipsometry. With this new tool, imaging ellipsometry at variable angles of incident can be performed at liquid/liquid and solid/liquid interfaces.

A number of different amphiphilic molecules were characterized at different interfaces. Examples are DMPE at the water/oil interface (Fig. 1a), cetylpyridinium chloride at the toluene/water interface (Fig1b,c).

![Fig. 1. Imaging ellipsometry (c) at the liquid liquid interface: ellipsometric contrast micrographs of DMPE (a), cetylpyridinium chloride (b,d) and angle of incident spectra at the toluene/water interface.](image)

Based on molecular and particular systems, methods to increase the image quality, effects of four zone nulling and optical modeling will be discussed.

**Literature:**


**Acknowledgements:**

We thank the working group of Prof. Mugele (Twente University) for their good collaboration.
Aqueous Foam Generation: What Determines the Foam Properties

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Foams are widely used in a large number of technical processes, such as flotation. They are also present in various forms in our daily lives as soft solids or fluids in food and beverage products or in insulating materials as solids. For many practical applications it is very important to control the foam formation parameters, the most important of which are the bubble size and the liquid fraction. However, dependence of these parameters on conditions of foam generation is still unclear despite of the large amount of experimental and theoretical work.

In the present study foam is generated by a number of methods: by blowing gas through nozzles, sieve plates and porous plates at fixed flow rates and by turbulent mixing into a T-junction module at fixed pressures. The radii and the liquid fraction of the foam are measured for different foaming solutions (varying the surfactant type and concentration). The properties of the foam formed depend strongly on the experimental conditions and the method of fabrication. But in all cases a strong and universal correlation between the bubble size and the liquid fraction is observed. This dependence can be fully accounted for by describing the entry of the bubbles into the foam. The impossibility of controlling the bubble size and the liquid fraction independently in any given method of generation is demonstrated.

Our work sheds some light on the complex process of foam generation and highlights the difficulty of controlled foam production, opening up many further questions.
Physical Factors Influencing Beer Overfoaming

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Gushing is a negative phenomenon characterized by spontaneous overfoaming of beer after opening a bottle or can which is not caused by high temperatures or shaking. Despite long-term research it is still not possible to predict. The aim of this work was to find a gushing-active matrix on which it would be possible to observe the influence of physical factors (pH, pressure, surface tension). The solution of bovine serum albumin of concentration 0.5 g/l was determined as the most convenient matrix. In this solution micelles of albumin are formed which act like nucleation sites for the formation of gushing foam. This solution was used to estimate the influence of pH, surface tension and the suppressing effect of increased pressure over the solution on gushing. All measurements were carried out in for this purpose specially constructed apparatus consisting of a pressure column, a high-speed camera and a pressure probe. The results are the relationships between the physical factors and beer overfoaming.

Acknowledgements:

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Molecular Dynamics Study of the Structure and Stability of Toluene Layers in Water

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The mechanical properties of thin toluene film and rupture caused by applied external electric field have been studied using molecular dynamic simulation approach. The critical value of external field and thin film capacitance were obtained. The mechanism of thin film rupture driven by the applied local pressure is proposed and comparison with thin film experiment is provided.

We have performed 5ns large-scale molecular dynamics simulations of model of the toluene layer with GROMACS package. The simulations were performed in the NVT ensemble at temperature T=298 K. The simulation parameters were generally maintained at the default values offered in GROMOS force field. The water model is SPC (simple point charge). The size of the simulation box: 25x25x25 nm. Molecular dynamics simulations were run with applied electric fields ranging from 0 to 120 mV/nm.

Film Rupture Mechanism Revealed from Simulations

/Side view/
Preparation of κ-carrageenan Porous Particles via Multiple O/W/O Emulsion Templating for the Delivery of Food Actives

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The encapsulation of bioactive compounds to produce healthy and high quality food products is an area of emerging interest. Hence, the design of novel encapsulating structures meeting the increasing demands is a scientific and technological challenge [1]. In this context, the use of multiple emulsions offers, among others, the following advantages: they can entrap agents with a low compatibility with the encapsulating system and release them in a programmed fashion [2]. In addition, multiple emulsions can be used as templates for the production of porous particles [3]. However, the complexity of multiple emulsions implies the interplay of numerous, often competing, interactions among the different components which make their formulation a complex task. Nevertheless, it has been shown that the stability of the primary emulsion play a critical role in achieving a kinetically stable multiple emulsion [4]. The purpose of this work was to prepare and optimize edible κ-carrageenan porous particles suitable for the encapsulation and release of lipophilic bioactive compounds using multiple oil-in-water-in-oil (O1/W/O2) emulsions as templates. Multiple emulsions were generated by a two-step process, namely, a primary O1/W emulsion was firstly prepared and further dispersed into the external oil phase O2. A Box-Behnken experimental design [5] was used to optimize the primary O1/W emulsion formulation. The studied factors were: the percentage of water, the oil to surfactant ratio, the κ-carrageenan concentration and the concentration of the gel-inducing agent (KCl). The evaluated responses were the emulsion stability, droplet size, melting temperature and elastic modulus. It was found that the optimal formulation was strongly associated with the κ-carrageenan concentration. Such primary emulsion formulation resulted in the formation of stable multiple O1/W/O2 emulsions. Subsequently, κ-carrageenan porous particles were prepared via a temperature-induced gelation of the intermediate phase. Stable particles with spherical shape, a mean particle size of 11.5 µm and containing multiple inner oil droplets were obtained. Retinyl palmitate was successfully encapsulated in the inner oil phase with a 86% of efficiency. Moreover, particles were found to be thermo-sensitive, undergoing disruption and releasing the inner oil droplets above 35ºC. Such thermal sensitivity could be a promising and attractive mechanism to release the encapsulated retinyl palmitate. Therefore, these particles could be useful to produce multivitamin supplements, functional and fortified food products.

Literature:
We study the effect of two cationic polymers, with trade names Jaguar C13s and Merquat 100, on the rheological properties of foams stabilized with mixture of anionic and zwitterionic surfactants (SLES and CAPB) and series of five co-surfactants leading to high or low surface dilatational moduli of the foaming solutions. The experiments revealed that the addition of Jaguar to the foaming solutions leads to: (1) Significant increase of the foam yield stress for all systems studied; (2) Presence of consecutive maximum and minimum in the rheological curve stress vs. shear rate, for foams stabilized by co-surfactants with high surface modulus, see Fig. 1. These systems cannot be described by Herschel-Bulkley rheological model anymore; (3) Presence of significant foam-wall yield stress. These effects are explained with the formation of polymer bridges between the neighboring bubbles in slowly sheared foams (for inside foam friction), and between the bubbles and the confining solid wall (for foam-wall friction). In contrast, the addition of Merquat does not affect noticeably any of the foam rheological properties studied. Optical observations of foam films formed from these systems showed a very good correlation between the polymer bridging of the foam film surfaces and the strong polymer effect on foam rheological properties. The obtained results demonstrate that the bubble-bubble attraction can be used for efficient control of the foam yield stress and foam-wall yield stress, without affecting significantly the viscous friction in sheared foams [1].

Figure 1. (A) Total stress, as a function of shear rate for foams stabilized by SLES+CAPB+MAc+Jaguar solutions with different concentrations of Jaguar. (B) Schematic presentation of the foam film between two neighboring bubbles at low shear rates - the film surfaces are bridged by cationic polymer chains. (C) At high shear rates, the film thickness is larger than the size of the adsorbed polymer molecules and the polymer bridges are broken.

Literature:
1. N. Politova¹, S. Tcholakova¹, K. Golemov¹, N.D. Denkov¹, M. Vethamuthu², K.P. Ananthapadmanabhan², “Effect of Cationic Polymers on Foam Rheological Properties”, Langmuir 2012, 28, 1115–1126.
Properties of Water/Sodium Dodecyl Sulfate/n-propanol/allylbenzene Micellar Systems

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Water/n-propanol/sodium dodecyl sulfate/allylbenzene micellar systems were formulated. The ratio (w/w) of n-propanol/surfactant equals 2/1. The extent of the micellar region as function of temperature was determined. The micellar systems were characterized by the volumetric parameters, density, excess volume, ultrasonic velocity and isentropic compressibility. The micellar densities increase with the increase in the water volume fraction. Excess volumes of the sodium dodecyl sulfate decrease for water volume fraction below 0.3, stabilize for water volume fractions between 0.2 and 0.5 then increase for water volume fraction above 0.5. Excess volumes of the studied micellar systems increase with temperature. Ultrasonic velocities increase with the increase in water volume fraction up to 0.8 then decrease. Ultrasonic velocities increase with temperature for water volume fractions below 0.8 and increase for water volume fractions above 0.8. Isentropic compressibilities decrease with the water volume fraction up to 0.8 then increase. Isentropic compressibilities increase with temperature for water volume fractions below 0.8 and decrease for water volume fractions above 0.8. Structural transitions from water-in-oil to bicontinuous to oil-in-water occur along the micellar phase. The particle hydrodynamic diameter of the oil-in-water micellar systems was found to decrease with temperature. In the diluted region nanoemulsions systems were observed.
Formation and Stability of Foams Prepared by Concentrated Silica Suspensions and Amphoteric Surfactant

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Particle-stabilized foams have attracted considerable research interest, due to their unique properties and potential technological applications. The remarkable stability of these foams (months and years) and the opportunity of using them for production of novel materials have brought a number of researches in the field of “Pickering” stabilization. The major aim of our study is to define the factors controlling the foaming and stabilization processes in the presence of silica particles with high concentration (15-25 wt. % in the foamed suspension) and the amphoteric surfactant cocoamidopropylbetaine (CAPB).

Systematic experiments were made to characterize the foamability of the suspensions with respect to: (a) Concentration of particles, $C_p$; and (b) Concentration of surfactant, $C_s$. In addition, the adsorption of surfactant on particle surface, the behavior of foam films, and the rheological properties of the foamed suspensions were studied to analyse the relation between these properties, on one hand, and the suspension foamability and foam stability, on the other hand. The most important experimental results could be summarized as follows: (1) Three regions with respect to suspension foamability are observed: Region 1 - good foaming, Region 2 - reduced foaming and Region 3 - no foaming. Two sub-regions are seen in Region 1, with respect to foam stability to water drainage: 1S - stable foams and 1U - unstable foams. (2) Some minor component(s) present in CAPB adsorb on the silica surface and modify the interactions between the silica particles. Nevertheless, the silica particles remain predominantly hydrophilic and stabilize the foams to water drainage by blocking the nodes and plateau borders in the foam. No particles are trapped in the foam films and the latter are stabilized by surfactant molecules. (3) Foams stability to water drainage is governed by the suspensions yield stress and bubble size.

Fig. 1 Photo of dried foam, formed from CAPB-silica dispersions at pH=8.5.
Dynamics and Structure of the Lipase *Candida Antarctica B* in Bicontinuous Microemulsions

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One of the major challenges in biotechnology arises from the fact that interesting substrates for the pharmaceutical industry are insoluble in water whereas enzymes that are supposed to convert them are mainly soluble in water and often require an interface to be active. Recently, bicontinuous microemulsions have been identified as promising reaction media to overcome this enzyme-substrate incompatibility [1]. Bicontinuous microemulsions consist of interpenetrating nanometre-sized domains of water and oil being separated by a connected surfactant monolayer [2] providing a large interfacial area for the enzyme to adsorb and convert the substrate. In contrast to especially droplet microemulsions, enzyme and substrate are confined to the same structural motif. Anticipating similar diffusion we expect a positive influence on the kinetics of the reaction as well. In this contribution we present results on how the conformation of the lipase *Candida Antarctica B* changes if it is incorporated into a bicontinuous microemulsion. In addition, we also investigated to which extent the presence of the lipase changes the properties, *i.e.* the phase behavior and the structure, of the bicontinuous microemulsion. We combined several experimental techniques to obtain a comprehensive picture of the system H2O/4wt% NaCl/Cal B – n-octane – nonionic surfactant C10E5 [3]. The respective phase diagrams of the microemulsion together with UV/Vis, fluorescence and circular dichroism spectroscopy lead to the conclusion that the surfactant monolayer takes up around 80wt.% of the initial amount of lipase whereas the rest is located in the water domains of the microemulsion. Treating the lipase as an interfacially active biopolymer we studied the structure of the microemulsion using PFG-NMR and tensiometry. A comparison between lipase-free and lipase-containing microemulsions completes the picture.

Literature:

Effect of Adsorbed Film Composition on Foam Film Thickness in Cationic - Nonionic Surfactant System

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Foam film is a thin aqueous one stabilized by two surfactant adsorbed films facing with each other and its stability depends on interfacial forces determined by the property of the adsorbed film such as surface density, surface potential and so on. Although, it is well known that the mixing of surfactants dramatically changes the property of the adsorbed film, there are only a few studies performed to clarify the effect of surfactant mixing on the foam film stability. Therefore, in this study, we have measured the surface tension \( \gamma \) and foam film thickness \( h_w \) of the hexadecyltrimethylammonium bromide (HTAB) - pentaethylene glycol monododecyl ether (C_{12}E_5) system as a function of the total molality of surfactants \( \hat{m} \) and the C_{12}E_5 composition in the mixture \( \hat{X}_2 \). All the experiments were done at 298.15 K under atmospheric pressure and in the presence of NaCl of 10 mmol kg\(^{-1}\) for the films to be stabilized. The \( \gamma \) and \( h_w \) were measured respectively by the pendant drop method and microinterferometry.

The thickness was shown in Figure 1. In the pure HTAB and C_{12}E_5 systems, \( h_w \) did not change remarkably against \( \hat{m} \). The difference in \( h_w \) value of these systems can be explained by strong double-layer repulsion in the HTAB system. In the case of \( \hat{X}_2 = 0.5005 \), however, a rapid increase of \( h_w \) is observed around 0.15 mmol kg\(^{-1}\). This is due to that the adsorbed film was enriched with C_{12}E_5 at a lower \( \hat{m} \) but with HTAB at a higher.

The thermodynamic analysis of surface tension data provides the composition of surfactants at the water/air surface, \( \hat{X}_2^H \) and then the phase diagram of absorption is constructed. We will examine the relation between \( \hat{X}_2^H \) and \( h_w \) and the change in interfacial forces in the foam film of mixed surfactant system.

Figure 1. Foam film thickness vs. total molality plots of pure HTAB (■), \( \hat{X}_2 = 0.5005 \) (●) and pure C_{12}E_5 (○) aqueous solutions.
Simulation of a Droplet in Gravity and non-isothermal Conditions

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This work presents numerical studies of a water droplet evolving in a paraffin oil continuous phase. This droplet is submitted to gravity and to non-isothermal boundary conditions. The simulation of such a simplified multiphase system is important in both academic and industrial context. This is particularly the case for emulsions, wetting problems and evaporation [1]. But, to achieve the simulation of such complex systems, there are still important algorithmic problems to be solved in particular due to the free moving interfaces and capillarity. Here, a Volume of Fluid (VOF) technique has been implemented with high order temporal and spatial schemes to preserve the sharpness of the interface of the considered droplet. Capillary contributions are fully accounted for using a continuum surface force (CSF) approach [2]. The droplet has one 1 mm radius and is confined in a square two dimensional finite simulation domain (SD) of 1 cm side. Although simplified, this model has the important advantage to allow the study of initially non symmetric configurations and therefore the influence of boundary walls.

The drainage dynamics of the droplet shows the existence of three different regimes with characteristic times that depend on the initial condition [3] and on temperature. The hydrodynamics in the complete SD (figure (a)) and in the frame of the droplet is investigated. When considering an initial condition with a vertical temperature gradient and a symmetric configuration for the droplet position, simulations show an evolution of the temperature field consistent with the literature (figure (b)). But, this situation is strongly changed when the initial droplet becomes closer to one of the side walls of the SD [4].

The role of the droplet initial position and temperature field is described with good numerical stability. But there are still important problems remaining in the simulation of free interface systems. Spurious currents induced by the description of capillarity can in particular come into play. These latter become negligible in this study, once the droplet drainage velocity becomes large enough.

Literature

Interactions of blast-waves with foam barriers have been studied mostly for two limiting cases: in the near field of the blast source or in the far field [1]. In the far field, the leading shock wave is weak, and while the foam remains generally intact, the penetrating shock wave loses energy by scattering numerous interfaces and through viscous dissipation of the liquid flowing through the Plateau borders and films [2]. Close to the explosive charge, the processes are far more complicated. The peak overpressures are so high that the foam is shattered into extremely fine droplets immediately behind the leading shock wave. Internally generated blast waves of high intensity are expected to trigger numerous additional mechanisms for energy dissipation, such as high temperature effects at the fireball-foam boundary, heat transfer, bubble shattering, evaporation, rearrangement and pulsation.

In the current work, we implement an exploding wire technique to generate small-scale spherical blast waves. Owing to a high electric current pulse the wire undergoes an extremely fast Joule heating, which causes a rapid expansion of a hot vaporized metal column, accompanied by the creation of a strong blast wave [3]. It was shown by using a similitude analysis that the results obtained from the small-scale experiments can be applied to full-scale problems. Therefore the exploding wire system offers an inexpensive, safe, easy to operate and effective tool for studying blast-wave–foam interaction related phenomena in real explosion scenarios. We consider the transient features of draining aqueous foams and use coal ash particulates to decrease the rate of changing the liquid distribution. Besides serving as effective stabilizers, the particulates also enhance the capacity of particulate foams in blast mitigation [2,4]. We study the mitigation of blast wave as a function of the initial impact intensity, the barrier geometry, the foam structure, the density and the thickness of the barrier, and concentration of the particulates.

Literature:


Oil in water emulsions were obtained by using limonene as the disperse phase and Pluronic PE 9400 as the emulsifier. Recent results obtained by our research group have demonstrated that concentrated limonene-in-water emulsions, \( \phi = 50\% \), stabilized by Pluronic PE9400, are destabilized by both, Ostwald ripening and creaming. The former is more pronounced in concentrated emulsions (\( \phi =50\%) \) and both destabilization processes increase with surfactant concentration in the range 3%-5% (w/w) where monomodal submicron emulsions are obtained (d3,2 \( \sim 0.8 \mu m \), Uniformity \( \sim 0.35 \)).

It is well-known that Ostwald ripening can be delayed by adding a second water insoluble compound to the oil phase [1,2]. This study is focused on the development of a stable concentrated (\( \phi = 50\% \)) limonene-in-water emulsion formulation by studying the properties as Ostwald ripening inhibitors of different additives (tetradecane, silicone oil and rosin gum). The droplet size growth in the presence of each of these chemicals was monitored by means of laser diffraction (Mastersizer X, Malvern) and creaming destabilization was studied by multiple light scattering technique (Turbiscan Lab-expert, Formulaction).

The influence of additive concentration was also studied. It is shown that a low concentration of tetradecane and silicone oil (ca. 2% (w/w)) drastically reduced the Ostwald ripening rate. Nevertheless, a much higher concentration of rosin gum was needed to prevent droplet growth (>15%(w/w)).

Although emulsions containing tetradecane and silicone oil maintained the same droplet size, they became destabilized by creaming. However, the addition of rosin gum at concentrations higher than 15% (w/w) resulted in stable limonene emulsions avoiding creaming separation. This may be due to the combination of two cooperative effects. Rosin gum acts as a weighting agent increasing the density of the disperse phase and on top of that the droplet size turns out to be lower (d3,2 \( \sim 0.5 \mu m \), Uniformity~ 0.35 ), which will also prevent creaming from occurring.

**Literature:**


**Acknowledgements:**

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Pickering Emulsions Stabilized by Nanoparticles of Bare Silica. 
Adsorption of Nanoparticles and Emulsion Stability

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The stabilization of Pickering emulsions comes from a strong adsorption of solid particles at the oil-water interface that builds a rigid barrier against coalescence. Either particles having a diameter above 100 nm diameter, or aggregates of nanoparticles are usually selected for the stabilization of Pickering emulsions because the adsorption energy of solid particles coming from partial wetting by water and oil, \( \Delta_{\text{ads}} = \pi R^2 \gamma_{\text{ow}} (1 \pm \cos \theta)^2 \), is several \( kT \), which means that full adsorption of solid particles takes place.

The adsorption energy reaches the order of magnitude of thermal energy upon decreasing the size of solid particles to \( \sim 10 \text{ nm} \), and equilibrium adsorption is therefore expected. The purpose of the present work is investigating the adsorption of individual nanoparticles of 12 nm diameter at the surface of oil droplets of o/w emulsions and looking at the consequences of a weak adsorption on the emulsion stability.

Silica nanoparticles of the Ludox™ series are individual nanoparticles of 12 nm diameter in suspension in water. Most oils do not wet bare hydrophilic silica. However partial wetting conditions are fulfilled with of particular polar oils that could be dispersed as Pickering emulsions stabilized by bare fumed silica [1].

Emulsification of diisopropyladipate oil droplets using Ludox™ AS40 silica stabilizing nanoparticles was successful up to 60% oil content (Fig. 1). An unusual dependence of the oil droplet diameter with respect to silica content occurs. The linear dependence \( d = \frac{6}{\rho_{\text{oil}} a_{\text{SiO}_2} M(\text{SiO}_2)} \) expected for full adsorption of solid particles was not followed, although it is generally followed over a wide silica concentration domain [2],[3].

The adsorption isotherm of silica particles measured by ICP-AES titration of residual silica shows that adsorption equilibrium takes place over the whole silica and oil concentration ranges. A consequence is the possible de-stabilization of emulsions upon shifting the adsorption equilibrium. As example, dilution of emulsions with pure water leads to their progressive coalescence into larger droplets. Several experiments based on optical microscopy, light scattering and adsorption isotherms show this paradoxical behavior. Multilayered adsorption of silica particles is suspected on the basis of adsorption isotherms.

Fig. 1: O/w emulsions of diisopropyladipate oil stabilized by 4% Ludox™ AS40 for increasing amounts of oil from 10% to 70%. Emulsification was successful up to 60% oil and failed at 70%.

Literature:
Stabilization of O/W Emulsion with Nanoclay

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In this study, we investigate whether nanoclay particles can give a stabilization effect on an oil-in-water(O/W) emulsion. From the microscopic and macroscopic point of view, emulsion morphology is observed depending on the composition of oil phase, quantity of nanoclay and wetting property of nanoclay. Based on the microscopic observations, emulsion morphology is stabilized with the addition of nanoclay of the balanced wetting property and the size of droplet is reduced with nanoclay(Fig. 1(a)), while, if nanoclay does not, droplets is coalescing each other(Fig. 1(b)). Nanoclay seems to give an effect to prevent a coalescence between droplets when nanoclay has the balanced wetting behavior. When nanoclay shows the balanced wetting behavior, it is localized at the interface and forms interfacial layer (ref 1,2). The formation of interfacial layer seems to give a stabilization effect. When we increases the amount of nanoclay, it gives the further improved stabilization. However, from macroscopic observations, the addition of nanoclay does not stabilize the emulsion as expected from microscopic observations. Two different nanoclay shows different location depending on the wetting behavior of nanoclay. Different with expectation from microscopic observations, emulsion with nanoclay results in phase separation. Nanoclay of the unbalanced wetting behavior rather enhances the separation of oil and water out of emulsion.

![Fig. 1 Morphology of 20 O/W emulsion with nanoclay: a. nanoclay of hydrophilic surface property b. nanoclay of hydrophobic surface property](image_url)

Literature:


Acknowledgements:

This study was supported by Mid-career Researcher Program through NRF grant funded by the Korea government (MEST) (No. 20110016890)
Separation and Concentration of Hydrogen Peroxide Using Microfluidics

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Hydrogen peroxide (H₂O₂) is widely used in industry for bleaching purposes and water treatment. So far the production is made through the Riedl-Pfleiderer (or antraquinone) process, which faces problems with byproducts of antraquinone that are not biodegradable. Another issue which needs to be addressed is that the manufacture of concentrated hydrogen peroxide cannot be made on-site; therefore it requires transporting H₂O₂ to the place where it will be used, which is neither cost-effective nor eco-friendly. In that context, the production of H₂O₂ by direct synthesis using microfluidic technology has become an active research topics 1 as it solves both of the above mentioned issues. One of the crucial steps in this microfluidic process is to obtain after reaction concentrated H₂O₂ by separation from the other liquids present in the synthetic process. In this research, we therefore define and outline the conditions for efficient microdistillation and concentration of hydrogen peroxide.

Literature:


Fig. 1 Illustration of H₂O₂ production

Acknowledgements: We acknowledge the Brussels Region for financial support and Solvay company for sponsoring this research.
Effect on Nonionic Surfactants on the Emulsification and Stability of Emulsions

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We study the relation between emulsion stability and surfactant structure and concentration. The emulsion stability is determined by both kinetic (as rate and time of stirring, rate of coalescence) and thermodynamic factors related to the processes of adsorption, partitioning and micellization. The thermodynamic parameters determine the emulsion composition in terms of surfactant distribution between water, oil, micelles and the interface (fig. 1). The calculation of the emulsion composition requires knowledge of:

(i) adsorption parameters (surfactant adsorption constant and molecular area α),
(ii) partition coefficient,
(iii) critical micelle concentration,
(iv) disjoining pressure as a function of surfactant hydrophobic tail length and hydrophilic head structure.

The knowledge of the emulsion composition allows the analysis of criteria for stability (resp. instability). Emulsion experiments suggest that the following criteria are significant:

(i) Condition for a critical surface coverage, αΓcr, above which emulsion is stable. The degree of coverage is limited by the depletion effect;
(ii) Conditions related to the dynamics of emulsification (e.g., Bancroft instability due to the location of the surfactant);
(iii) Condition for stratification stabilization due to presence of ordered layers of micelles.

The analysis of the suggested stability parameters as a function of surfactant structure shows that there are optimal lengths of the alkyl and the polyethyleneglycol chains, at which the surfactant’s performance is maximized.

Fig. 1

Acknowledgements: the study is supported by BASF and Project BG 051PO001-3.3.06-0038.
Effect of Phase Transition in the Adsorbed Film on Foam Film Thickness

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A thin foam film held in a porous glass ring is utilized for understanding the stability of foams. The foam film stabilized by the electrical double-layer repulsion is called Common Black Film (CBF) and the one stabilized by the steric repulsion is Newton Black Film (NBF). Thus the CBF – NBF transitions have been well investigated by increasing salt or surfactant concentrations. Recently we found that some alkyltrimethylammonium halides show a first-order transition of the adsorbed film in the presence of alkanes of similar chain length to the surfactant\(^1\), which motivated us to study the influence of surface phase on the foam film thickness. For this purpose, we applied hexadecyltrimethylammonium chloride (HTAC) – tetradecane (C\(_{14}\)) mixed adsorbed film in the presence of a small amount of NaCl.

We first measured the ellipticity and surface tension to examine the state of adsorbed film and then the foam film thickness \(h\) by the microinterferometry around the phase transition temperature. Figure 1 shows the results of the thickness as a function of temperature \(T\) at fixed HTAC and NaCl concentrations. It was demonstrated that \(h\) changes discontinuously at the temperature close to the surface phase transition, indicating that the phase transition promotes the binding of chloride ions to the adsorbed films and shields the double-layer repulsion. Our previous study demonstrated that, since the surface density of surfactant is changed only slightly, this phase transition occurs mainly by the penetration of alkane molecules in the adsorbed film.

Figure 1 shows that \(h\) still remains in the thickness range of CBF even after the thickness transition. It should be noted that the salt concentration of 50 ~ 100 mmol kg\(^{-1}\) is required to reduce the foam film thickness to about 15 nm. Therefore, it can be said that the counter ion binding driven by the surface phase transition effectively shields the surface potential compared to the salt addition. In literature, the CBF – NBF transition occurs at salt concentrations at several hundreds mmol kg\(^{-1}\). Thus, we are examining whether the CBF – NBF and NBF – NBF transitions are induced by the surface phase transition in the presence of oil at a lower salt concentration.

Literature:

Rapid “Droplling” Devices for the Generation of Monodisperse Emulsions with Well-controlled Interfacial Properties

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Milli/microfluidics is now recognized as a very versatile tool to produce monodisperse droplets which may be polymerized in-situ to generate monodisperse particles. The availability of such systems provides researchers with an unprecedented control over the study of complex physical problems, such as jamming in emulsions, foams or suspensions. For such investigations, large quantities of droplets/particles are required. Classical fluidic geometries such as flow-focusing or T-junction devices yield only small amounts of droplets, making them impractical for high-throughput applications. To produce a lot of objects in a short amount of time, techniques based on parallelized object production have been developed, including terrace emulsification or microfluidic arrays. Studies of these geometries focused on micrometric flows, whilst here we describe the development of these techniques at millimetric scales with low-cost materials. We developed devices to investigate different parameters controlling the formation of droplets, paying particular attention to the static and dynamic properties of the liquid/liquid interfaces covered in interfacially active agents of different kinds. The presence of these agents confers non-negligible visco-elastic properties to the interfaces, which influence the rapid dynamics of the drop generation. It also modifies significantly the interaction of the generated drops, prohibiting, for example, their coalescence.

![Fig. 1 Optical micrograph of generating fine droplets](image_url)

**Fig. 1** Optical micrograph of generating fine droplets

**Literature:**

Hyaluronan-based Porous Foams as Drug Delivery Systems

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Hyaluronan (HA) is a biopolymer widely distributed into the human body. Their physicochemical properties and biocompatibility make it a suitable candidate for biomedical and pharmaceutical use.¹ The incorporation of a preformed polymer in the continuous phase of highly concentrated emulsions (HIPREs) allows the preparation of porous materials with very high pore volume.² In the present work, O/W highly concentrated emulsions were used as template for the preparation of macroporous materials based on chemically crosslinked hyaluronan. The hyaluronan-based porous foams were prepared from HIPREs formulated using biocompatible components: an ethoxylated castor oil surfactant, and a medium chain triglyceride oil. Surfactant and oil were removed from the porous material by solvent extraction with ethanol and water for 12 hours, and finally, the porous foams were freeze-dried (Fig.1). The porosity of the obtained materials was dependent on the surfactant concentration in the HIPREs. Ketoprofen, a model anti-inflammatory drug, was incorporated to the hyaluronan-based porous materials to study their suitability as controlled drug delivery systems. Drug release from hyaluronan-based porous materials, HIPREs and hydrogels³ to a receptor solution was studied for comparative purposes. The results obtained showed that controlled drug release can be obtained as a function of formulation parameters.

Fig. 1 SEM image of the porous material based on hyaluronan obtained from highly concentrated emulsions.

Literature:

Acknowledgements:
The authors acknowledge financial support to the Spanish Ministerio de Economía y Competitividad, DGI (CTQ 2011-29336-C03/PPQ)
pH-responsive Colloidosomes and Their Use for Controlling Release

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Colloidosome microcapsules have been developed which offer options for the encapsulation and release of active ingredients.

We use latex particles, stabilised with a responsive polymer, as building blocks for colloidosome microcapsule membranes and demonstrate their use as a pH-responsive delivery system.

Oil-in-water emulsions are prepared and stabilised with latex particles produced by emulsion polymerisation. The core-facing polymer on the surface of the latex particles is chemically cross-linked from the oil phase to produce a robust capsule shell.

The pH-responsive polymer on the surface of the constituent particles within the microcapsule membrane can be induced to expand and contract as a function of protonation/deprotonation, thus altering the pore size of the membrane.

We show that fluorescently-labelled dextran molecules can be successfully used to demonstrate successful uptake, retention and release from the core.
Interfacial Properties of Mixed Carbon Nanoparticles – Surfactant Suspensions and Application on Carbon Based Foams

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In recent years, an increasing interest has been paid to the study of the effect of solid particles in association with surfactants on the properties and structure of fluid interfaces. This is motivated by the effects that particles segregation may have, under certain conditions, such as the creation of mixed layers stabilizing the interfaces and opposing to the droplet/bubble coalescence.

The work here presented focuses on the interfacial properties of aqueous suspensions containing carbon nanoparticles and different type surfactant species, which can modify the degree of hydrophobicity/philicity of particles favoring their transfer from the suspension bulk to the interfacial layer.

Aim of this work is a deeper understanding of particle/surfactant and particle/fluid interface interactions and their effect on those macroscopic interfacial properties of the mixed systems which are expected to be related to the stabilization of foams and theirs structure.

To this purpose a systematic characterization of dispersions composed by Carbon nanoparticles associated with different ionic surfactants, decane sulfonate (C10), cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS), and polymer, poly(vinyl) alcohol (PVA), have been carried out measuring the dynamic and equilibrium surface tension and surface rheology by using a drop Profile Analysis Tensiometer (PAT). These results have been, moreover, crossed with the characterization of the bulk suspensions by Dynamic Light Scattering (DLS techniques, to check the effects of surfactant on the particle aggregation. The stability of the foams obtained with the same compositions has been also investigated and correlated to the interfacial properties.

The results here obtained contribute to the understanding of the relation between the interfacial properties of nanoparticles (NP) mixed systems and the stability and 3D structure of liquid and solid (green body) foams obtained by carbonaceous NPs. Thus they can be used in the field of tailoring and production of porous materials because provide new insight into the role of the composition of the initial dispersion, used as precursor.

Literature:
Solidified Microemulsions

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Microemulsions are well-known nanostructured liquids, made with water, oil and surfactants. These thermodynamically stable mixtures allow to prepare easily nanostructured liquids with high surface to volume ratio, controlled connectivity and characteristic sizes. Quenching these nanostructures into the solid state is a fundamental challenge and would open breakthrough perspectives in many fields like synthesis, catalysis, optics and energy storage.

Here, we address the competition between quenching and crystallization in solidified microemulsions. A nonpolar phase which is solid at room temperature was used to prepare microemulsions above its melting point and then the mixture is cooled down to go towards solidified microemulsions. Ideally, the as prepared material must be a clear solid with the same nanostructure as the starting mixture and containing a large amount of liquid [1]. This type of materials has been to date poorly studied. We are particularly interested in studying the liquid-solid transition as it determines whether the initial structure of the microemulsion may be quenched.

Fig. 1: Phase diagram of the ternary mixture (Myristic Acid/CTAB/H2O), T = 60°C

As a first system, we have focused on an oil phase with a melting point at 55°C (myristic acid) and strong attractive interactions between oil and surfactant (CTAB). The phase diagram in the liquid state (T > 55°C) was studied (Fig. 1). Clear and isotropic mixtures have been identified in the oil-rich part of the diagram. In the liquid state, the mixture has a microemulsion-like structure with unexpected thermotropism. This nanostructure is lost in the solid state because of crystallization of the oil phase, even upon fast cooling.

An original approach to characterize the nanostructure destabilization during crystallization is to replace the crystallizing oil phase by an apolar phase with variable crystallization kinetics. In this talk, I will also present a new system where the crystallization problem is avoided. This study opens a wide range of fundamental studies on how we can keep the microemulsion nanostructure in the solid phase.

Literature:

Foamability and Foam Stability at Low Surfactant Concentrations

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Surfactants are essential ingredients in laundry, household and personal care products, and in various technological applications. Our work is focused on understanding the basic processes which control the foam formation and stability at low surfactant concentrations, around and below the critical micellization concentration (CMC). The major aims of our study are: (1) To investigate the main factors which control the volume of the produced foam and its stability; and (2) To reveal the mechanisms of foam stabilization/destabilization at low surfactant concentrations. Systematic experiments were performed with anionic and nonionic surfactants. Several experimental methods were combined to obtain complementary information about the studied phenomena: foam tests, dynamic surface tension measurements, equilibrium surface tension measurements, foam film observations in Scheludko-Exerowa cell, and foam film tests with a new experimental method for studying dynamic foam films. The main experimental results could be summarized as follows: (1) In most systems we observed a clear correlation between the stability of the dynamic foam films, generated by the new method and the foamability of the respective surfactant solutions; (2) Correlation between the dynamic surface tension and the foamability was observed only at sufficiently high surfactant concentrations, when the same main surfactant is used and different co-surfactants are added to change the adsorption rate; (3) The observed trends could not be explained by considering only the disjoining pressure or only the kinetics of adsorption of the surfactant molecules. A theoretical model is under development to incorporate all important processes, governing the stability of dynamic foam films.
Activity of the Lipase *Candida Antarctica* B in Bicontinuous Microemulsions

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Enzymes as catalysts provide excellent specificity and selectivity towards their substrates, allowing for saving energy due to mild reaction conditions and open up new pathways in synthetic organic chemistry. A major challenge in the industrial application of biocatalysis is the accessibility of a hydrophobic substrate for an enzyme preferring a hydrophilic environment. In the last decade, non-conventional reaction media have been proposed to overcome enzyme-substrate incompatibilities, these include heterogeneous two phase systems, immobilised enzymes in organic media, ionic liquids, and microemulsions [1]. Each of these reaction media features different properties suitable for different applications. In this work, we present a bicontinuous microemulsion to be used as reaction media for the enzyme-catalysed hydrolysis of hydrophobic substrates. Bicontinuous microemulsions offer a suitable microenvironment for water soluble or interfacially active enzymes combined with application-relevant substrate concentrations. Interpenetrating water and oil channels separated by a continuous surfactant monolayer allow confining enzyme and substrate to the same nanostructured motif. The high interface to volume ratio enhances the contact between enzyme and substrate, and provides a fast mass transfer [2].

High solubilisation capacity allows for high substrate concentrations. We chose the lipase *Candida Antarctica* B (Cal B) to investigate the activity of an enzyme introduced in this reaction media. Cal B is interfacially active and thus is able to adsorb to the surfactant monolayer present in the microemulsion where a hydrophobic substrate being solubilized in the oil channel can be converted. The structure and the properties of the surfactant film is therefore a crucial parameter determining the activity of the enzyme. To compare the influence of the composition of the interfacial surfactant monolayer on the activity of Cal B, microemulsions based on the nonionic surfactant C10E5 were compared with microemulsions containing as well a sugar surfactant C10E5/β-C10G1 (1:1 mixing ratio). As a model reaction, the hydrolysis of *p*-nitrophenylpalmitate to *p*-nitrophenol and palmitic acid was used and the formation of *p*-nitrophenol was followed photometrically. The reactions were carried out in microemulsions consisting of buffer/NaCl - *n*-octane/substrate - nonionic surfactant(s). Different enzyme and substrate concentrations were measured to obtain the second order rate constants *k*₂. Results showed that in the presence of the sugar surfactant β-C10G1 a significantly higher enzymatic activity could be observed. The influence of the substrate, the products and the enzyme on the phase behaviour of the microemulsions was measured beforehand, to ensure that the microstructure would be bicontinuous throughout the reaction.

Literature:

Step-by-step Investigation of Droplet Breakup and Release of Water by Coalescence in W/O/W Multiple Emulsions

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Multiple water-in-oil-in-water (W/O/W) emulsions are complex multiphase systems that consist of a water-in-oil emulsion dispersed in a second continuous water phase. There is a great interest in the production of multiple W/O/W emulsions for different applications ranging from separation / extraction, encapsulation of sensitive molecules for food, cosmetic and pharmaceutical products to fat reduction in food. However, the production of these structures is still a challenge and the processes are not fully understood.

One possibility to produce W/O/W double emulsions is by means of a two-step process. Therefore, first a so called inner water-in-oil emulsion is produced. In the second step this emulsion is taken as the dispersed phase of the double emulsion. The second step contains two main challenges. The droplets which have to be broken up show non-Newtonian flow behavior especially for high dispersed phase concentration of the inner emulsion. Moreover, instabilities like coalescence of the inner water droplets with each other or with the outer water phase may occur. Especially coalescence between inner and outer water phase is crucial as it leads to the release of inner water droplets and thus to a loss of functionality.

In order to investigate double emulsion droplet breakup and the release of water by coalescence we first conducted single droplet experiments in a 4-roll mill. This approach enabled the visual observation of the phenomena. We observed that droplet deformation and breakup are independent of the dispersed phase content of the inner emulsion for viscosity ratios smaller than one. The immobilization of the interface by the surfactant used is responsible for this behavior. Concerning coalescence of inner droplets with the outer water phase we found that this process is strongly dependent on the surfactants used. If coalescence occurred, it was independent of deformation of the droplets. This observation is in contrast to former visual observations by Stroeve et al. [1].

In order to quantify these visually observed phenomena we conducted emulsification experiments in a colloid mill. We characterized the droplet size distributions of the final double emulsions as well as the encapsulation efficiency (percentage of water still encapsulated in the inner droplets). We found a direct correlation between double emulsion droplet sizes and encapsulation efficiency. This dependency is strongly influenced by the dispersed phase content of the inner emulsion and by the droplet sizes of the inner droplets. We want to show and discuss a first geometrical approach to model this coalescence behavior.

Literature:

Acknowledgements:

We want to thank Prof. Gary Leal, University of California Santa Barbara for enabling the experiments in the 4-roll mill.

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Self Assembly in a Magnetic Room Temperature Ionic Liquid (MRTIL)

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Magnetic room-temperature ionic liquids (MRTIL) are a specific class of RTIL where an ion confers a paramagnetic behavior to the liquid. The first occurrence of this new class of liquid media was discovered in 2004 [1, 2] based on the organic cation 1-butyl-3-methylimidazolium (bmim+) and the anion tetrachloroferrate (FeCl4−). Thanks to the high spin FeCl4−, a small magnet is enough to modify the meniscus of the fluid, and stronger macroscopic effects are visible when the surface tension is reduced.

MRTIL can be used as a solvent for self assembly of surfactant systems which leads to structures like micelles, liquid crystals, macro- and microemulsions [3] that possess magnetic properties. In our experiments we studied such microemulsions that were formulated with the help of cationic surfactants of different alkyl chain length and decanol as a cosurfactant. The phase behavior was determined and the corresponding structures were determined by comprehensive SANS experiments. The analysis showed a generally similar behavior as in normal microemulsions but compared to aqueous systems the surfactants show much weaker amphiphilicity. New insights into the nature of self assembly by studying these water-free, aprotic systems are to be derived from these investigations.

Fig. 1 Pictures of a paramagnetic microemulsion with a modified miniscus by exposing to a magnet and schematic draws of the structure [3].

Literature:
How Long Does a Soap Film Last During Generation?

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Soap films are well-known for being unstable entities, with lifetimes ranging from less than a second to several hours. However, the mechanism leading to the rupture of a vertical thin film during its generation from a surfactant solution is still poorly understood.

We have built an experiment, in which we measure the life time of a film during its generation. We showed that the faster the film is pulled, the longer the film and the shorter its lifetime. It turns out that to understand this feature, it is necessary to determine first the entire shape of the liquid film [1].

We founded that the film is made of two parts: the bottom part is of uniform and stationary thickness, well described by the Frankel’s law [2]; whereas in the top part, the film thins until a black film appears near the frame upper boundary. We showed that the lifetime is controled by the drainage of the upper zone due to film deformation.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{film.png}
  \caption{(a) Photography of a film during vertical entrainment and just before spontaneous rupture. It is made of a bottom part of uniform and stationary thickness and a thinning part where a black film appears. (b) Photography of the film bursting during its generation.}
\end{figure}

Literature: