Supercooled Water Drops on Superhydrophobic Surfaces: Wettability, Interaction with Substrate, Freezing

Ludmila Boinovich¹*, Alexandre Emelyanenko¹

¹ – A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky prospect 31, 119071 Moscow, Russia
* - boinovich@mail.ru

Increasing demands for ice resistant functional materials and coatings prescribes the intensive development of new anti-icing technologies. Besides in recent decades, efforts have been made to attain a more detailed understanding of the physicochemical phenomena governing the icing processes. One of the most promising approaches to the creation of ice resistant surfaces involves the fabrication of superhydrophobic coatings on the surfaces of materials to be protected. The physico-chemical behavior of water drops on superhydrophobic surfaces at negative temperatures plays the crucial role for the anti-icing efficiency of such coatings. In this talk we will discuss the behavior of supercooled water drops on different superhydrophobic surfaces in saturated water vapor atmosphere.

The wettability of superhydrophobic surfaces at negative temperatures, interaction of water with superhydrophobic surface and kinetics of water drop freezing will be analyzed on the basis of water drop shape analysis. The influence of surface wettability and surface forces on the energetic barrier for heterogeneous nucleation and freezing delay will be considered.
Adhesive Forces between Particles

Hans-Jürgen Butt1*

1 – Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany
* - butt@mpip-mainz.mpg.de

Adhesive force between small particles are essential for the flow of granular matter, coating and cleaning. After discussing some general aspects of adhesion between particles, capillary forces are described. The adhesion between hydrophilic particles in air is often dominated by capillary forces. The reason for capillary forces under ambient conditions is that water condenses into the gaps between neighboring particles. Such a water meniscus causes an attractive force, called capillary force. Several aspects of capillary forces are discussed: (1) Surface roughness influences the humidity dependence of capillary attraction. This can lead to various shapes of the adhesion force-versus-humidity curve. (2) Capillary forces can be used in colloid probe experiments to measure certain properties of thin liquid films. (3) Capillary forces play a significant role in bioadhesion. Motivated by the adhesion of tree frogs capillary forces between very soft surfaces are analyzed. For soft spherical particles the usually proportional increase of the adhesive capillary force with particles radius, \( F_{adh} \sim R \), changes to a \( R^2 \) dependence. (4) Strong electric fields such as in STM or electric modes of AFM can cause capillary condensation and lead to a capillary attraction. Finally some technical advances in measuring adhesive forces are described.

Literature:

Is CMC of Surfactant Mixtures an Ill-defined Parameter?

Grace Cookey *, Julian Eastoe and Wuge H Briscoe

School of Chemistry, University of Bristol, United Kingdom

* - chzgc@bristol.ac.uk

Micelles were first proposed by McBain in 1913 while studying the electrical properties of sodium palmitate solutions. The surfactant concentration above which micelles form, termed critical micelle concentration (CMC), is an important parameter in surfactant chemistry, as abrupt changes in the solution and performance properties of surfactants and their mixtures occur at CMC.

To adequately evaluate the solution and performance properties of mixed surfactant solutions, the CMCs of the mixtures and component surfactants must be correctly determined. Generally, the CMCs of single surfactants are well-defined and their values do not depend on the technique used; while those of the binary mixtures obtained from different techniques are different.

We have studied several binary mixtures consisting of SDS (an anionic surfactant) and DTAB (a cationic surfactant) with non-ionic surfactants. We will compare their CMCs and those of the individual components obtained from surface tension (CMC_γ) and conductivity measurements (CMC_κ). We find that in some mixtures, CMC_κ is up to twenty times higher than CMC_γ for the same mixtures at the same bulk solution compositions. SANS measurements performed in the concentration range bounded by the CMC_γ and CMC_κ show that the micelle size does not remain constant after micellization as predicted by the current thermodynamic models. Rather, it varies with the surfactant concentration for the different compositions we have studied. We thus propose that the CMC of surfactant mixtures is not a well-defined thermodynamic parameter as previously thought.
Destabilisation of Gas Condensate-water Emulsions and Separation by Dissolved Air Flotation Using New Non-ionic Surfactants

A.M. Al-sabaghi, M.R. Noor El-din, Khaled M. Hussein and A.M. Sharaky

1 Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El-Zomor St., Nasr City, 11727, Cairo, Egypt.
2 Petrobel Company, Cairo, Egypt.
3 Institutes of African Research and Studies - Cairo University
* - mned04@yahoo.com, Tel: +2(02)22745902, Fax: +2(02)227727433.

The present paper endeavors to synthesize four types of nonionic surfactants as demulsifiers based on oleic acid monoamidite to treat gas condensate-in-water emulsion. The chemical structure of the prepared ethoxylated demulsifier was confirmed using FT-IR and ¹HNMR spectroscopes. The treatment of gas condensate -in-water emulsion was investigated by means of dissolved-air flotation jar-tests. The effect of several parameters on the flotation efficiency for separation of the emulsified oil was examined such as; the effect of pH value, the demulsifier concentrations, feed rate (L/min) and saturator working pressure (psi). Also, the surface and interfacial tensions, and thermodynamic properties of the prepared surfactants have been studied. Results show that the optimum oil removal (99.9%) was obtained by OD3 at concentration 150ppm, pH =2, feed rate=0.1 L/min and saturation pressure 10 psi.

Keywords: Dissolved air flotation; Demulsifier; Industrial wastewater; Flotation.

Figure 1: Effect of OD3 on condensate oil-water emulsion at 25 °C.

Literature:
Two-component Miscibility of Partially Fluorinated Alcohols
\((F6H_{9}OH)\) and DPPC at the Air-water Interface

Hiromichi Nakahara\(^1\), Takayoshi Yamada\(^1\), Masashi Nakaya\(^2\), Kiyoshi Kanie\(^2\), Atsushi Muramatsu\(^2\), Osamu Shibata\(^1\)*

\(^1\)Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, Huis Ten Bosch, Sasebo 859-3298, Japan
\(^2\)Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan.

* wosamu@niu.ac.jp

Miscibility between partially fluorinated amphiphiles and dipalmitoylphosphatidylcholine (DPPC), which is a major component in lung surfactants, has been investigated in the monolayer state [1-3]. In the present study, the surface pressure (\(\pi\))–molecular area (\(A\)) and surface potential (\(\Delta V\))–\(A\) isotherms were measured for two-component monolayers made of DPPC and partially fluorinated alcohols of (perfluorohexyl)nonanol (\(F6H_{9}OH\)) and (perfluorohexyl)undecanol (\(F6H_{11}OH\)) on a substrate solution of 0.15 M NaCl at 298.2 K. The Wilhelmy method and the ionizing \(^{241}\)Am electrode method were used. The resultant data for these systems were analyzed using the additivity rule. The excess Gibbs free energy of mixing for the present systems were calculated from the \(\pi–A\) isotherms. Assuming a regular surface mixture, the Joos equation, which allows description of the collapse pressure of a monolayer made of two miscible components, was used to establish the miscibility within the monolayer. An interaction parameter and an interaction energy were calculated. The phase diagrams of the two systems were classified into the positive azeotropic type. These results and thermodynamic analyses suggest that DPPC is miscible with \(F6H_{9}OH\) and \(F6H_{11}OH\) in the monolayer state. Furthermore, morphological observations with Brewster angle microscopy (BAM), fluorescence microscopy (FM), and atomic force microscopy (AFM) were carried out to support the binary miscibility. These results indicate that \(F6H_{9}OH\) fluidizes DPPC monolayers, whereas \(F6H_{11}OH\) solidifies them. This study provides a fundamental insight into the molecular function of biomembrane components and support for biomedical use of fluorinated materials.

Literature:
Interfacial Shear Rheology and Thin Liquid Film Study of Water-in-Crude Oil Emulsions

Plamen Tchoukov 1*, Fan Yang 1, David Harbottle 1, Jan Czarnecki 1, Tadeusz Dabros 2, Zhenghe Xu 1

1 Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Canada
2 CanmetENERGY, Natural Resources Canada, 1 Oil Patch Drive, Devon, Alberta, Canada

* - tchoukov@ualberta.ca

Formation of stable water-in-oil emulsions is detrimental in the petroleum industry; however, the stabilization mechanisms are not fully understood. Interfacial shear rheology at water/oil interface and drainage kinetics of water-in-oil thin films were studied. Diluted Athabasca bitumen at different solvent-to-bitumen (S/B) ratios and solvent aromaticity was used as the oil phase. Thin film properties change abruptly at a critical S/B ratio, which coincides with the onset of asphaltene precipitation. Above the critical S/B ratio films become thick and inhomogeneous, and drain slowly. At the critical dilution, water/oil interface undergoes a transition from purely viscous (below the critical S/B ratio) to viscoelastic (above the critical S/B ratio). Above the critical S/B ratio, the elastic component develops in few hours and eventually dominates interfacial rheology. A yield stress in the range of $10^{-3}$-$10^{-4}$N/m was measured. We attribute this sharp transition in the film/interfacial rheological properties to solubility-driven aggregation of asphaltenes and buildup of 3D network structures with a characteristic length well beyond the reported sizes for single asphaltene molecules, nanoaggregates or clusters of nanoaggregates. Formation of such structures results in non-Newtonian Bingham plastic properties of the film liquid. The associated yield stress prevents the film drainage before it reaches the critical thickness, where film rupture can occur (a coalescence event).
A New Method for Electro-Microinterferometric Studies of Water-in-Oil Emulsion Films: Development and Application with Natural and Synthetic Surfactants

Nikolay Panchev¹*, Khristo Khristov¹, Jan Czarnecki²

¹ – Bulgarian Academy of Sciences, Institute of Physical Chemistry
² – Department of Chemical & Materials Engineering, University of Alberta
* - patcho75@yahoo.com

Stability of water-in-oil emulsions depend to a great extent on properties of thin oil films that separate water droplets. It is now generally recognized that the thinning of these films and their resistance to rupture play a crucial role in determining the stability of emulsions. However, studies on water-in-oil emulsion films are few and information on the film stability is limited. A modified microinterferometric pressure balance technique (Sheludko-Exerowa porous plate cell) for single film studies is developed in order to apply DC electric potentials across the water-in-oil emulsion films. It allows for the first time simultaneous application of electric polarization and the use of microinterferometry. The major advantage of the technique is that a single experiment allows the independent determination of many electrical and optical film parameters such as: film thickness, film diameter, rate of film drainage, critical electric field strength of film rupture as well as disjoining pressure isotherms measurements. First experimental results were obtained for films stabilized by natural crude oil indigenous surfactants (asphaltenes, bitumen) and synthetic ones (Abil, Lecithin) in different solvents (heptane, toluene). DC potentials can be applied in two modes: as voltage ramps with given speed (mV/s) and as a constant potential. DC voltage ramps experiments allow precise measurements of the values of critical voltage of film rupture at different concentrations, film areas, film thicknesses and capillary pressures. Constant voltage application provides determination of the dependence of film lifetime at different potentials. It has been found that application of voltage ramps over equilibrium films leads to appearance of voltage threshold value where thickness starts to decrease and eventually film ruptures. This fact demonstrates the compressive action of DC potential. The thickness of film rupture decreases with increase of applied pressures. Data for film electric field strengths suggest that the thinner films are more stable. The pressure vs. thickness isotherms are measured at different DC potentials. The isotherms appear to be shifted towards lower thicknesses with increase of voltages that were applied and thus the surface forces are to be affected.

Literature:

Adhesive Behavior of Extracted Latex Polymers Towards Silicon Oxide and Cellulose

Cecilia Lidenmark1, Torbjörn Pettersson2,3*, Ola J. Karlsson4, Shannon M. Notley5, Magnus Norgren1, Håkan Edlund1

1 – Department of Applied Science and Design, Fibre Science and Communication Network, Mid Sweden University, SE-851 70 Sundsvall, Sweden
2 – Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden
3 – ForceIT, Mossvägen 14, SE-15337 Järna, Sweden
4 – Physical Chemistry, Lund University, Box 124, SE-221 00 Lund, Sweden
5 – Department of Applied Mathematics, Research School of Physical Sciences and Engineering, Australian National University, Canberra 0200 ACT, Australia
* - torbj@kth.se

The objective with this work is to compare the adhesive behavior for latex polymers of different Glass transition Temperatures ($T_g$) at different length scales and with different contact times. This is accomplished by two techniques: AFM colloidal probe force measurements and JKR-measurements. The aim is to compare the results from these two techniques and relate them to the interaction of the latex polymers towards oxidized silicon wafers and silica/cellulose probes. Theory suggests that altering the short timeframes used in the colloidal probe technique does not affect the ranking of the adhesion for the different polymers, but for the macroscopic JKR-technique it influences the measured work of adhesion. It is therefore important to let the system reach a steady state before assuming complete spreading and adhesion. AFM and JKR measurements showed the same trends where the polymer with lowest content of styrene has the lowest $T_g$ and the highest adhesion, due to the larger polymer chain mobility.

Fig. 1 Adhesion measurements with AFM colloidal probe have been compared with macroscopic JKR-measurements
Experimental and Numerical Study of Capillary Transport between Parallel Perforated Plates in Microgravity

Diana Gaulke 1*, Michael E. Dreyer1

1 – ZARM - Center of Applied Space Technology and Microgravity University of Bremen, Am Fallturm, 28359 Bremen
* - diana.gaulke@zarm.uni-bremen.de

Capillary transport of liquid is subjected to a wide range of studies. Many analyses are available for smooth or tough surfaces or the influence of structures on surfaces, but almost no literature exists about perforated surfaces. The capillary transport of liquid in such structures plays a major role in microgravity applications such as propellant management in satellites or upper stages of rockets. Here, the conflict between small capillary radii and minimal amount of structure has to be solved. The use of porous materials or perforations is a common compromise for these applications. This study aims to analyse the influence of perforations on the capillary transport capability of parallel plates under microgravity conditions.

A series of microgravity experiments was performed in the Drop Tower Bremen. Results have been used to validate numerical models implemented in the commercial software package Flow3D. A wide range of geometrical settings was investigated numerically. Figure 1 shows the experimental model and some of the resulting data.

![Experimental model and numerical results](image)

This presentation provides the introduction to the capillary transport phenomena between parallel perforated plates under microgravity. Some of the experimental and numerical results are presented to explain the influence of selected geometrical perforation parameters.

Acknowledgements:

We gratefully acknowledge the funding by the Federal Ministry of Economics and Technology (BMWi) through the German Aerospace Center (DLR) under grant number 50 RL 1320.
Film Hydrodynamic Boundary Conditions on Bubble-surface Impact

Rogerio Manica\textsuperscript{1}, Maurice H. W. Hendrix\textsuperscript{2}, Raghvendra Gupta\textsuperscript{1}, Evert Klaseboer\textsuperscript{1}, Claus-Dieter Ohl\textsuperscript{3}, Derek Y. C. Chan\textsuperscript{1,4,5*}

\textsuperscript{1} Institute of High Performance Computing, 1 Fusionopolis Way, 138632 Singapore
\textsuperscript{2} Physics of Fluids, University of Twente, Enschede 7500 AE, The Netherlands
\textsuperscript{3} Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore
\textsuperscript{4} University of Melbourne, Parkville VIC 3010 Australia
\textsuperscript{5} Swinburne University of Technology, Hawthorn VIC 3122 Australia

* - D.Chan@unimelb.edu.au

We present a detailed experimental studies \cite{Hendrix2012, Manica2013} of a rising, mm-size bubble in milli-Q water colliding with a glass plate after reaching terminal velocity. The bubble trajectory was tracked by highspeed (54,000 fps) video. We also recorded synchronized videos of the interference fringes that form when the bubble collides with the glass surface and deforms. Quantitative information about the rate of deformation and drainage of the μm-thick water film trapped between the mm-sized bubble and the surface can be extracted from the space and time evolution of interference pattern. Using measured bubble trajectory data, the dynamics of the thin water film trapped between the glass and the bubble surface can be modelled quantitatively with lubrication theory to deduce the nature of the hydrodynamic boundary condition at the air-water interface.

Fig. 1 (a) The experimental setup that measures the velocity, \( V(t) \) of the centre of mass of a rising bubble (radius \( R_0 \)) and the interference pattern of the trapped water film as it collides and bounces against a glass plate after reaching terminal velocity, \( V_T \). The Reynolds, \( Re \) and Weber, \( We \) numbers are indicated. (b) The time evolution central film thickness, \( h_c(t) \) and the thickness at the minimum at the rim, \( h_m(t) \) and (Inset) the dimple that formed during the first collision.

Literature:


Acknowledgements:

Supported by a Discovery Project Grant from the Australian Research Council.
Bubble Bouncing and Stability of Liquid Films Formed under Dynamic and Static Conditions from n-octanol Solutions

Dominik Kosior1*, Jan Zawala1, Roumen Todorov2, Dotchi Exerowa2, Kazimierz Malysa1

1 – Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Krakow, Poland
2 – Institute of Physical Chemistry, BAS, Sofia, Bulgaria
* - nckosior@cyf-kr.edu.pl

The properties of thin liquid films under dynamic and static conditions are the factors of crucial importance for formation and stability of various dispersed systems. Bubble motion, collisions and coalescence at liquid/gas are important processes in many industrial applications, i.e. foam formation, froth flotation, aeration of water tanks, waste water treatment etc. Presence of surface active substances (SAS) and their adsorption at interfaces affects significantly motion of the rising bubbles and stability of the thin liquid films. In pure liquids, the velocity of the rising bubbles depends on the viscosity and density of the continuous phase and the bubble diameter, while in solutions of SAS the bubble rising velocity is lowered as a result of formation of the motion induced dynamic architecture of adsorption layer (DAL) over the bubble surface, which retards fluidity of the interface. Simultaneously, the bubble coalescence time on liquid/gas interface in SAS solutions of different concentrations is changed not only due to lowering of the bubble impact velocity, but also as a result of (i) retardation of the film thinning velocity, and (ii) increased stability of the films formed against external distortions.

The paper presents results for influence of n-octanol on impact velocity, bouncing time, bouncing amplitude and the coalescence time of single bubbles colliding with the free solution surface. Properties (stability, rupture time and thickness) of the films formed by the colliding bubble, that is, under dynamic conditions are evaluated, compared and analysed in relation to properties of the equilibrium microscopic foam films studied under static conditions. Phenomena occurring during the bubble collisions with liquid/air interface, that is, the bouncing time and amplitude, as well as the coalescence time, were studied using a high-speed camera for two different locations (L=3 and L=250 mm) of the interface in respect to the point of the bubble formation (capillary orifice). The bubble coalescence time (t_c) and its two components, that is, the bubble bouncing time (t_{bouncing}) and lifetime (t_{film}) of the “motionless” bubble (after bouncing period) were measured. Additionally, stability and thickness of the microscopic foam films formed from n-octanol solutions of various concentrations were determined using microinterferometric method (Scheludko Exerowa cell). It was found that for low n-octanol concentration the bubble coalescence time (t_c), was slightly shortened (from 73 to 58 ms, for water and 4·10^{-6} M n-octanol concentration, respectively) due to diminishing of the bouncing amplitude. Further concentration increase, above a “threshold” value (5·10^{-6} M) prolonged significantly time of the bubble coalescence, to ca. 1200 ms, due to increased stability of the liquid film formed between “motionless” bubble and liquid/air interface. The t_{film} values were used for evaluation rupturing thicknesses of the liquid films formed under dynamic conditions. It was found that at low of n-octanol concentrations the thicknesses of the rupturing films were of an order of a few μm, that is, much larger than for the films formed under static conditions. However, at high n-octanol concentrations the values of rupture thickness were similar order for dynamic and static conditions.
Structure and Dynamics of Confined Supercritical CO$_2$

M. Heuberger $^1$$^*$, E. Schurtenberger $^{1,2}$

$^1$ - Empa, Materials Science and Technology, 9014 St. Gallen, Switzerland
$^2$ - Helveting Engineering AG, Switzerland
$^*$ - manfred.heuberger@empa.ch

Supercritical CO$_2$ is an interesting solvent of the future because it is non-flammable, chemically inert and non-toxic. It exhibits liquid-like density, gas-like diffusivity and its surface tension is very small. It is already found in a range of applications such as environmentally friendly solvent in polymer syntheses, in materials processing, for extractions, tissue engineering, or microelectronic processing.

We present the first direct measurement of surface forces across supercritical carbon dioxide. An important finding is that long-range attractive surface forces are detected not just near the critical point, but along the supercritical extension of the coexistence line, which is commonly discussed as the supercritical ridge.

Using a precisely adjustable model slit pore, our experiment can measure the change of thermodynamic potential together with changes in refractive index (mass density) in the confined CO$_2$. The model slit pore is realized between two atomically smooth mica surfaces in a specially designed high-pressure surface forces apparatus. Our data suggest that thermal fluctuations of higher density are selectively depleted, which results in observation of a time- and space-averaged density reduction in the confined film. Direct observation of this confinement effect has consequences for theoretical understanding as well as technological applications of CO$_2$ in porous materials.

In the presence of small amounts of an acrylate solute (polyethyleneglycol-dimethacrylate), we found that multiple stable menisci of solute can be created between the surfaces and stretched out several micrometers. These liquid bridges are observed as an apparent birefringence effect and are interrelated with the (super)critical Casimir effect. They might be used in the future to generate fibrillary nanostructures across micro pores or between colloids.

Literature:

Surface forces are responsible for overlapping surface layers and resulting disjoining pressure in thin liquid films. They have a bright appearance in thermodynamics and kinetics of the deliquescent transition in nucleation of a solvent vapor on soluble nanoparticles [1-3]. If a soluble particle is placed into solvent vapor, the vapor condenses with formation of an enveloping liquid film which reaches a chemical equilibrium with partly dissolved particle. There is a limiting value of the vapor relative humidity above which the particle completely dissolve in droplets. The dissolution is called the deliquescence transition, and the corresponding value of the vapor relative humidity is called the deliquescence humidity. The deliquescence humidity and the rate of the deliquescence transition depend on the initial size of the soluble particle, the solubility of the particle in the solvent and the mass transport at vapor-droplet and residue-liquid interfaces. But, depending on the solvent vapor concentration, the deliquescent transition can be barrierless or require overcoming the activation barrier. This is very important feature of the deliquescence transition and it is principally associated with the disjoining pressure isotherm in the liquid film around the particle residue in the forming droplet. To understand the thermodynamics and kinetics of heterogeneous nucleation with deliquescence of soluble nuclei one needs to study the complex behavior of the minima and saddle points of the work of droplet formation and the relevant activation barrier for deliquescence transition as a function of the chemical potential of vapor, the initial size and the solubility of condensation nucleus. This study has been undertaken previously partly only, and we summarize and extend it in this report, including the case of non-ideal solutions. Here we have proposed a thermodynamic theory for finding the deliquescence humidity and corresponding activation barrier for deliquescence transition below the deliquescence humidity and shown that there would no minimum in the work of droplet formation without the disjoining pressure of the liquid film. The theory predicts a crossover in stable and unstable variables of droplet state upon variations in vapor humidity. An advanced approach has been proposed for two-dimensional kinetic equations describing establishing equilibrium and quasi-steady distributions of binary droplets forming around soluble particles. This approach allows one to separate the variables and to solve such equations analytically. The specific times for deliquescence transition have been found.

**Literature:**


**Acknowledgements:** This work was supported by the Program of Development of St. Petersburg State University (grant 0.37.138.2011) and RFBR (grant 13-03-01049-a).
Interfacial Water Studied by Surface Forces Measurement

Kazue Kurihara¹²*, Masashi Mizukami¹², and Motohiro Kasuya²

¹ – WPI Advanced Institute for Materials Research (AIMR), Tohoku University, Sendai, Japan
² – Institute for Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai, Japan
* - kurihara@tagen.tohoku.ac.jp

Interfacial water plays important roles in physical, chemical, biological, and technological processes, e.g., self-assembly of biomolecules such as lipids and proteins in living systems, lubrication, and electrochemistry (electrolyte-electrode interfaces). The molecular level pictures of interfacial water, within several nanometers from the surface, have been gradually established for interfaces such as water/mica, water/air, and water/hydrophobic surfaces, although there has been controversy among them. For example, the distance range where the surface has an effect on the structure and properties of water has a large variation from monolayer to more than micrometer for various surfaces such as silica, polymers, and gels. Therefore, the important and interesting question remaining is the effect of chemical and physical conditions especially on the range of interfacial water. For such a purpose, surface forces measurement is the most powerful method because it can continuously study the structure and properties of a liquid between surfaces as a function of the surface separation.

Interfacial water, formed by adsorption or phase separation (prewetting transition), on a silica surface in water–cyclohexane binary liquids was investigated using a combination of colloidal probe atomic force microscopy (AFM) and sum frequency generation (SFG) vibrational spectroscopy. At 33 ± 9 ppm water, the long-range attraction extending to 19.4 ± 2.9 nm appeared, which was caused by the contact of water layers formed on silica surfaces. The attraction range increased with increasing water concentration and reached 97 ±17 nm at the saturation concentration of water in cyclohexane (C*), indicating that the thickness of the water layer formed on silica was ca. 50 nm. The interfacial energy between the water adsorption layer and bulk solution (γ = 79.3 ± 2.0 mN/m) was estimated from the pull-off force, and was significantly larger than the value for the bulk water/cyclohexane interface (γ = 50.1 mN/m). SFG spectroscopy demonstrated that the interfacial water formed an icelike structure at C*. On the other hand, the water adsorption layer induced by phase separation at water concentrations above C* was found to be less ordered and its structure at the adsorption layer/bulk interface was almost the same as that of bulk water, although its thickness was almost the same as that formed at C*. To our knowledge, this is the first report of the observation of liquid adsorption layers formed by chemical interaction up to saturation and by the wetting transition above saturation, and their differences in the structure and properties at the molecular level.

Water between silica surfaces was studied using the surface forces and resonance shear measurements. Lubrication properties of water are discussed in terms of the silanol density of the surfaces and water structure demonstrated by SFG spectroscopy.

Literature:


Acknowledgements:

This work was supported by the CREST program of the Japan Science and Technology Agency (JST).
Diffusion of Gold Nanoparticle close to solid-liquid interfaces

Werner Steffen 1*, Maryam Haghighi 1, Georg Fytas 1,2, Hans-Jürgen Butt 1

1 - Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
2 - Department of Material Science, University of Crete/F.O.R.T.H/IESL, P.O. Box 1527, 71110 Heraklion, Greece
* - steffen@mpip-mainz.mpg.de

Nanoparticle, moving in a liquid close to a solid interface, experiences an influence by this interface. Anisotropic behaviour of the translational diffusion parallel and perpendicular to the interface have been studied in the past and theories and models exist. The rotational diffusion of such particles has not been studied to great extend due to limitations in the signal for studies in the close proximity of the interface. With our recently developed light scattering techniques REDLS (resonance enhanced dynamic light scattering) [1] and WEDLS (waveguide enhanced dynamic light scattering) [2] we are able to overcome the above limitations.

We have studied the motions of gold nanorods of various sizes in water, with different stabilizers and in different salt concentrations. The results were crosschecked with standard dynamic light scattering [3] to differ between changes introduces by the interface and by varying salt concentration and stabilizer. We found a slowing down of translational and rotational diffusion far beyond what is predicted by theory. This slowing down depends on the stabilizer used and on the salt concentration.

Literature:

Automated Method for Measurement of Dynamic Contact Angles of Liquid

Mihail Z. Avramov1*, Ivan T. Ivanov1, Borian P. Radoev1

1 – University of Sofia, Faculty of Chemistry, Department of Physical Chemistry
* - mavramov@chem.uni-sofia.bg

The interest to the contact angle hysteresis in the last decades has provoked different experimental methods for its studying. Our approach is an attempt to measure the contact angle hysteresis of liquid in capillary tube. By inclination of a tube partly filled with liquid, a gravitation force, \( F = G \sin \alpha \) (\( G \) – liquid weight) arises (Fig 1a). In the case of static hysteresis, \( F \) is balanced by the three phase contacts reaction. The main difficulty of all capillary-gravitational methods is related with the mathematical description of the liquid-gas surface form. Great advantage of the proposed method is the substantial simplification of the mathematical problems. Due to the small tube diameter (~0.1mm), the menisci form can be approximated as parts of spheres and the only parameters responding to the force \( F \), remain the contact angles \( \theta_A, \theta_R \) (Fig 1a). The direct force balance shows proportionality between \( F \), and \( |\cos \theta_A - \cos \theta_R| \).

Key problem from the experimental viewpoint of the proposed method is the dioptric effect. Due to the meniscus spherical forms the optic problems can be partly eliminated by measuring the curvature of the meniscus cap, where the dioptric effects are weakest (Fig 1b). As follows from the geometry, the meniscus curvature \( H \) (i.e. the inverse sphere radius \( R \)) is proportional to the corresponding \( \cos \theta \) and the above proportionality is replaced by \( F \sim |H_A - H_R| \).

Fig. 1 a) Sketch of an inclined capillary tube partly filled with liquid. b) Scheme of meniscus profile; operative for the curvature determination is only the profile part at the meniscus cap (the solid curve).

Experiments with the constructed setup have been carried out with pure water and ionic liquids. The complete system is easy to implement using standard servo motors microscope and imaging software. Higher precision is obtained by measuring angle towards gravity with an accelerometer.

The obtained experimental results are interpreted from optical and mechanical viewpoints.

Acknowledgements:

This work have been supported by project FP7 Beyond Everest (contract No 1996 SRD department University of Sofia) and by the Metrological Laboratory of University of Sofia and BSS ltd.
The Analysis of Wettability of Highly Curved Surfaces on the Basis of Surface Forces

Alexandre Emelyanenko, Ludmila Boinovich

*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky prospect 31, 119071 Moscow, Russia*  
*ame@phyche.ac.ru*

The difference in wettability of flat and highly curved surfaces, having the same chemical nature is discussed on the basis of surface forces analysis and capillary phenomena in thin wetting films. The equations were derived for the calculations of the contact angle on concave and convex cylindrical and spherical surfaces based on the isotherms of the disjoining pressure. The results of calculations of contact angles on the curved surfaces for the systems, characterized by different isotherms of disjoining pressure with long-ranged van der Waals, electrostatic and hydrophobic forces, indicated that the stronger the surface forces and the higher the correlation lengths of the hydrophobic interaction, the more essential influence of curvature is predicted by the derived equation. Thus, when the radius of substrate curvature becomes comparable to the range of action of surface forces, an increase in the curvature for convex surfaces results in the increase in the contact angle. Therefore nanoparticles will demonstrate more enhanced hydrophobicity (oleophobicity) in comparison to nanofibers, and to flat surfaces, having the same chemical composition. In contrast, for concave surfaces the wetting improves with the curvature rise. Such behavior may lead to the wettability transition from hydrophilic (oleophilic) state of flat surface to hydrophobic (oleophobic) state of convex surface. And inversely, the chemical composition of surface layer, corresponding to hydrophobic state of flat surface, may be characterized by the contact angle less than 90° on the internal surfaces of cylindrical pore or spherical cavity at the appropriate curvatures.
Near Wall Dynamics of Colloidal Suspensions Studied by Evanescent Wave Dynamic Light Scattering

Peter R. Lang1*, Jan K. G. Dhont1, Maciej Lisicki2, Bogdan Cichocki2, Jerzy. Bławzdziewicz3, Simon Rogers4, Benoit Loppinet5

1 - Forschungszentrum Jülich, ICS-3 52425 Jülich, Germany
2 - University of Warsaw Institute of Theoretical Physics, ul. Hoz’a 69, 00-681 Warsaw, Poland
3 - Department of Mechanical Engineering, Texas Tech University, Lubbock, Texas 79409, USA
4 - University of Delaware Chemical and Biomolecular Engineering, Newark, DE19716, USA
5 - Foundation for Research and Technology, Hellas, IESL, 71110 Heraklion, Greece

* - p.lang@fz-juelich.de

The dynamics of dispersed colloidal particles close to a flat wall is strongly affected by hydrodynamic interaction with the wall. Although theoretically predicted in the early 20th century, experimental verification of this effect for Brownian particles became possible only in the late 80s. Since then a variety of experimental investigations on near wall Brownian dynamics by evanescent wave dynamic light scattering (EWDLS) has been published.

In this contribution we will present EWDLS experiments and theoretical developments for a variety of situations.

We will discuss the translational dynamics of hard sphere colloids at low and intermediate volume fraction [1-3]. On increasing the particle concentration the influence of the wall drag effect is found to diminish gradually, until it becomes negligible at volume fractions above f> 0.35. [4]

The wall effect on orientational dynamics was investigated on optically anisotropic spherical PTFE colloids. Although, the effect is less pronounced than for translational diffusion, we showed, for the first time that rotation around the axis normal to the interface is faster than around the axes parallel to the was as was theoretically predicted.

Further, we used EWDLS under flow to measure near wall shear rates, and slip lengths with an unsurpassed resolution without relying on a model for the flow profile.

Literature:

3. Lisicki, M. et al., in preparation

Acknowledgements:

Financial support by the European FP7 projects nanodirect (GA 213948) and ESMI (GA 262348) is gratefully acknowledged.
Linear Stability of Falling Films in the Presence of Soluble Surfactants

George Karapetsas¹*, Vasilis Bontozoglou¹

¹ – Department of Mechanical Engineering, University of Thessaly, Volos 38334, Greece
* - gkarapetsas@gmail.com

We model the dynamics of a liquid film flowing along an inclined planar substrate. The liquid contains a surfactant, soluble in the bulk, which adsorbs at the interface and locally decreases surface tension. Interfacial gradients in surface tension produce tangential stresses (Marangoni stresses), which attribute to the interface elastic properties. The present paper aims at expanding earlier studies in the literature to include solubility effects, in particular by taking into account the adsorption and desorption kinetics. To this end, we assume that the surfactant monomers are present in the bulk or can be adsorbed at the liquid-air and liquid-solid interfaces. The evolution of surfactant concentrations is modeled by advection-diffusion equations and the flow is modeled by the continuity and the Navier-Stokes equations of motion with appropriate boundary conditions. The model is linearized around a base solution corresponding to an undisturbed film with uniform surfactant concentration (Nusselt flow). The resulting Orr-Sommerfeld stability problem is solved numerically for arbitrary disturbances by a finite-element method. An analytic solution is obtained in the limit of disturbances of infinite wavelength. The effect of various parameters is investigated, and a maximum is predicted in the critical Reynolds number as function of amount of surfactant. The location and intensity of this maximum depends on surfactant solubility. Short-wave disturbances are found to stabilize very strongly with the addition of a soluble surfactant.

Fig. 1 Schematic of a falling film in the presence of soluble surfactants

Acknowledgements:

The authors would like to acknowledge the financial support by the General Secretariat of Research and Technology of Greece under the Action Supporting Postdoctoral Researchers (grant number: PE8/906), co-funded by the European Social Fund and National Resources.
Interaction Forces in Particle Dispersions Revealed by Aggregation and Direct Force Measurements

István Szilágyi*, Prashant Sinha, Tamás Oncsik, Gregor Trefalt, F. Javier Montes Ruiz-Cabello, Plinio Maroni, Michal Borkovec

Laboratory of Colloid and Surface Chemistry, University of Geneva, Quai Ernest-Ansermet 30, 1205 Geneva, Switzerland

* - istvan.szilagyi@unige.ch

Multivalent ions interacting with water-solid interfaces play a key role in a wide range of phenomena including condensation of nucleic acids, crystal growth, cement hardening and waste water treatment. In colloidal dispersions, aggregation rates can be measured in light scattering (LS) experiments, while the colloidal probe technique based on the atomic force microscope (AFM) is suitable to investigate interaction force profiles directly [1]. In the present work, we combine these techniques to study aggregation processes in the same aqueous dispersions contained charged colloidal particles and oppositely charged multivalent ions.

Positive amidine modified polystyrene latex particles were investigated first in the presence of anions of different valences including monovalent chloride, divalent sulfate, trivalent ferricyanide and tetravalent ferrocyanide. Surface potentials obtained from electrophoretic and AFM measurements were in good agreement and showed that anions of lower valences decrease the surface charges by screening while adsorption of ferri and ferrocyanide anions leads to charge neutralization and subsequent charge inversion. Comparison of aggregation (by LS) and direct force measurements (by AFM) revealed that the classical DLVO theory describes well colloid stability of the particles in the presence of chloride and sulfate ions. For the ferri and ferrocyanide ions, additional non-DLVO attractive forces were observed. These attractive forces can be attributed to surface charge heterogeneities induced by the adsorption of the anions, which leads to higher stability calculated from AFM measurements than the ones measured by LS. However, ion-ion correlations are equally important as they induce the charge inversion in the presence of trivalent or tetravalent ions. The critical coagulation concentrations (CCC) which separate slow and fast aggregation regimes were in good agreement with the classical Schulze-Hardy rule (Fig. 1). Similar results were observed in oppositely charged systems contained negative carboxylate latex particles and cations such as potassium(I), calcium(II), lanthanum(III) and zirconium(IV), therefore, the above trend seems to be generic.

Fig. 1. Location of CCC values obtained from LS (symbols) and AFM (lines) measurements. The thick line indicates the Schulze-Hardy rule.

Literature:
Ion Specific Structure of nano-confined Electrolytes

R.M. Espinosa Marzal1*, S. Liuzzi2, S. Chodankar2, M. Guizar-Sicairos2, M. Heuberger1,3 and J. Friso van der Veen1,2

1 – ETH Zurich, 8093 Zurich, Switzerland
2 – Paul Scherrer Institut, 5232, Villigen PSI, Switzerland
3 – EMPA, 9014 St. Gallen, Switzerland
* rosa.espinosa@mat.ethz.ch

When a liquid is nano-confined, the combination of interfacial energetics and geometrical effects often confer to the system properties that are different from those observed in bulk fluids. In particular, understanding the structure of electrolytes nano-confined between two mica surfaces could yield valuable insights in a number of fields, ranging from biology to nuclear waste management, as well as clarify some fundamental issues regarding saline hydration of charged hydrophilic surfaces (e.g. clays). We have performed studies with an extended surface force apparatus (eSFA1,2) to measure surface forces, and, synchrotron X-ray reflectivity (XRR) to elucidate the structure of the nano-confined solution. Various electrolyte solutions with monovalent and divalent cations at different concentrations have been selected for this combined study.

Our force measurements are in general agreement with previously reported results, yet the higher resolution of our eSFA reveals some new structural insights3. We discuss our data in terms of three different concentration regimes that are defined by shifts of the energetics of structures and interactions at the molecular scale. At moderate concentrations a short-range ordering of hydrated ions induced by confinement is resolved in films with thickness smaller than 3 nm. The ion hydration shell has a soft character, which gives rise to layering transitions of irregular sizes (e.g. 4±1 Å for KNO3). There is a tendency to smaller cluster sizes at higher concentrations. The water coordination number of ions at the interface, as inferred from layering transitions, is 5-10x smaller than in the surrounding bulk solution.

Model dependent fits to the X-Ray reflectivity structure factor allowed us to determine the electron density profile along the confinement direction4. The modulation of the electron density profile confirmed an ordered layering of the liquid within the gap, with the layering being most pronounced for hydrated ions closest to the confining walls. A comparison between the structures of confined chlorides with different monovalent and divalent cations (Cs+, Rb+ and Ba2+) at different concentrations reveals ion specific features, which may be linked to size of the hydrated ions, coordination number and hydration energy.

Literature:

Development of a System measuring Adhesion Forces in Powder Collectives

Stefanie Wanka¹, Michael Kappl¹*, Markus Wolkenhauer², Hans-Jürgen Butt¹

¹ – Max Planck Institute for Polymer Research, Mainz, Germany
² – Boehringer Ingelheim Pharma GmbH & Co. KG, Germany
* - kappl@mpip-mainz.mpg.de

Fine powders commonly have poor flowability and dispersibility due to interparticle adhesion that leads to formation of agglomerates. Knowing about adhesion in particle collectives is indispensable to gain a deeper fundamental understanding of particle behavior in powders. Especially in pharmaceutical industry a control of adhesion forces in powders is mandatory to improve the performance of inhalation products. Typically the size of inhalable particles is in the range of 1-5 µm [1]. Existing techniques for measurement of particle adhesion forces are experimentally demanding, time consuming and of limited applicability. This includes the two most widely used methods: the colloidal probe technique [2, 3] and the centrifuge method [4, 5]. Therefore we developed a completely new system that will allow routine measurements of adhesion in ensembles of single particles (particle collectives). The new method is based on particle detachment from a substrate caused by its inertia. The required acceleration in the order of 500 000 g is provided by a shock excitation system (Fig.1, left) based on the Hopkinson bar principle [6, 7] and measured via laser Doppler vibrometry. Particle detachment events are detected on-line by optical video microscopy (Fig.1, right). Subsequent automated data evaluation allows obtaining a statistical distribution of particle adhesion forces. Measurements were carried out with ensembles of single polystyrene and silica particles on a polystyrene coated steel surface under ambient conditions. We were able to investigate more than 150 individual particles during one single experiment and obtained adhesion values of particles in a size range of 3-15 µm. We found our measured adhesion forces in good accordance with values from colloidal probe measurements and theoretical predictions. Thus our new system can be used to study a great variety of particle-surface-systems, even for standard analysis, including strongly cohesive powders like pharmaceutical drug powders.

Fig. 1 Schematic of the Hopkinson bar method to measure adhesion forces of particles (left). Microscope images showing detachment of spherical silica particles (5 µm) with increasing acceleration of the substrate (right)

Literature:


Acknowledgements: The authors are grateful to Boehringer Ingelheim Pharma GmbH & Co. KG and SPEKTRA GmbH Dresden for the cooperation and support. They acknowledge technical support by A. Best and M. Rein.
Aggregation of Colloidal Particles in Ionic Liquids

Tamás Szabó1,2, Anthony Désert2, Sabine Pita2, István Szilágyi2, Gregor Trefalt2, Michal Borkovec2,*

1 – Department of Physical Chemistry and Materials Science, University of Szeged, Hungary
2 – Department of Inorganic and Analytical Chemistry, University of Geneva, Switzerland
* - michal.borkovec@unige.ch

Ionic liquids (ILs) are gaining increasing importance as alternative solvents in organic synthesis, electrochemistry, photocatalysis, and material science. ILs are in the liquid state at ambient conditions, but otherwise they resemble molten salts. Some reports exist that these solvents may stabilize nanoparticle dispersions. This observation is most surprising, as it is at odds with the classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO). This theory predicts that colloidal particles should aggregate rapidly at such extremely high ion concentrations due to extensive screening.

To resolve this contradiction we have carried out extensive time-resolved static and dynamic light scattering experiments of different latex particles in various ILs and their mixtures with water. Here we illustrate our principal findings by comparing 1-butyl-3-methylimidazolium cations (BMIM) and tetrafluoroborate (BF₄) or thiocyanate (SCN) anions. Fig. 1a shows the absolute aggregation rate coefficient versus the IL to water mass ratio while Fig. 1b the normalized rate coefficient to the corresponding diffusion controlled value predicted by Smoluchowski’s theory.

![Fig. 1](image)

Based on these results, we are able to identify two principal stabilization mechanisms of colloidal particles in ILs. (i) Viscous stabilization occurs due to the typically large viscosity of ILs, even though the aggregation remains diffusion controlled. (ii) Solvation stabilization occurs due to repulsive solvation forces occurring between surfaces in ILs. Fig. 1 clearly illustrates that BMIM with the BF₄⁻ anion leads only to viscous stabilization, since the normalized aggregation rate remains constant a low water content. When SCN⁻ is the anion, viscous and solvation stabilization occurs simultaneously, since the normalized rate substantially decreases in the IL at low water content. The present contribution will discuss the importance of these stabilization mechanisms for different ILs and types of particles in more detail and make preliminary conclusions concerning molecular structure-property relationships.
Frictional Properties of Confined Ionic Liquids

Filippo Federici Canova$^{1,2,*}$, Masashi Mizukami$^1$, Kazue Kurihara$^1$, Alexander L. Shluger$^2$

$^1$ – WPI-Advanced Institute for Materials Research, Tohoku University – Sendai (Japan)
$^2$ – Department of Physics and Astronomy, University College London – London (UK)

* - felix@wpi-aimr.tohoku.ac.jp

Globally, thousands of billions are spent annually on expenses attributable to friction and wear [1], and efforts to reduce and control their effects form a massive research area. In order to counter frictional processes, a lubricant in liquid form, is usually placed between the two sliding surfaces, with the idea of preventing the formation of a contact region where asperities can interlock. In recent years, ionic liquids (IL) have shown great potential as candidates for lubrication [2] because of their excellent stability in a wide range of temperatures, although, in order to be able to design an ionic liquid with better lubrication properties, atomic scale understanding of the frictional mechanisms is necessary. We focus our efforts on two IL systems, [C4MIM+]BF4- and [C4MIM+][NTf2-] confined between two silica plates: their viscous properties were previously measured with the resonance shear measurement apparatus [3]. Using classical models to represent the ILs [4], we performed molecular dynamics (MD) simulations of the nanoconfined liquid between two hydroxilated silica surfaces, in order to investigate its molecular arrangement and the dynamical processes that lead to friction. We generally observe how molecules in the boundary layers interact strongly with the surfaces and the anions arrange themselves next to the hydroxyl groups: these molecules exhibit very long residence time and effectively behave like a solid. Under shear, the anions mostly follow the surface they are attached to, although occasional slip occurs: being larger and elongated, [NTf2-] sitting normal to the surface plane feels more drag from the interaction with the mobile molecules in adjacent layers, thus giving larger lateral forces than the smaller and spherical [BF4-].

Fig. 1 Snapshot of the confined configurations for [BF4-] and [NTf2-] liquids.

Literature:

The very strong propensity of coagulation by electrolytes containing multivalent counterions is one of the oldest tenets of the stability of hydrophobic colloids. The history goes back to Schulze and Hardy, who formulated this rule qualitatively around the previous turn of the century. Quantification came with DLVO theory. According to this theory for the case of high surface potentials and purely diffuse double layers, led to the famous $z^{-6}$ law for the coagulation concentration. Later investigations showed that under conditions of coagulation the potential $\psi_d$ of the diffuse part of the double layer is mostly not so high, in fact, at given $\psi_d$ the dependence is rather as $z^{-2}$. However, as $\psi_d$ decreases with $z$, the overall observed dependence on $z$ is stronger than as $z^{-2}$. The deviation from the $z^{-2}$ dependence depends on the nature of the counterion. This trend automatically takes us to the issue of specific adsorption and creates a link to Hofmeister series, which continues to arouse interest. Acquiring reliable data remains desirable.

The experimental part of this task is to estimate as well as possible the specific contribution to the adsorption Gibbs energy so that sufficiently reliable information becomes available for theoretical interpretations. This problem is not yet obsolete because various mechanisms can operate simultaneously and it is not always obvious to discriminate between them. Recently two mechanisms for the deviations from pure diffuse theory are under discussion, viz. specific (non-electrostatic) ion adsorption and ion correlations. A prominent mechanism for specific adsorption, particularly for counterions of higher $z$, is hydrolysis which gives rise to strongly absorbable products. Both mechanisms can lead to (electrokinetic) charge-reversal, which is a frequently observed phenomenon. One way of distinguishing between these two explanations is investigating the pH influence, considering that hydrolysis is pH-dependent, in contradistinction to ion correlations. Some experiments will be shown to illustrate this option.

The conclusion is that so far no convincing direct influence of ion correlations on charge reversal has been established, but windows of experimental conditions can be established where these can be expected. It is worthwhile to continue these studies because under other conditions the action of ion correlations appears definitely established.

Literature:

Thin Liquid Films studied by Atomic Force Microscopy

Marta Krasowska 1*, Mihail N. Popescu 1, John Ralston 1

1 – Ian Wark Research Institute, University of South Australia, Adelaide, SA 5095, Australia

* - marta.krasowska@unisa.edu.au

Drainage and stability of thin liquid films play an important role in many industrial applications as well as in model processes, ranging from mineral processing and lubrication of micromechanical devices to oil drop coalescence and the stability of colloidal systems. Development of ‘Surface Force’ probing techniques, such as Thin Film Balance (TFB), Measurement and Analysis of Surface Interactions and Forces (MASIF), Surface Force Apparatus (SFA) or colloid probe Atomic Force Microscopy (AFM) allowed the studies of film drainage at nanoscale separation. Some of these techniques are restricted to model systems (e.g. atomically smooth mica surface in SFA) while others (e.g. AFM, TFB) offer wider variety of confining solid and soft surfaces to be studied.

AFM is the ideal tool for measuring both film drainage and surface forces. What is missing in a conventional AFM experiment is the possibility to measure independently the separation between interacting surfaces. For interactions between two hard objects, such as colloidal particles and flat solid surfaces, their absolute separation - which typically ranges from a few micrometres down to a few nanometres - can be determined easily by calibrating against the point of hard-wall contact. However, for soft and deformable surfaces, such contact may never occur, which makes the extraction of the absolute separation impossible. The lack of this crucial parameter in AFM experiments is a major obstacle for quantifying the surface forces in systems involving bubbles and droplets.

We have addressed the problem of the real nanoscale separation by incorporating an independent optical measurement of surface separation into the AFM instrument. This novel hybrid interferometry-AFM technique enables an independent measurement of forces and separation between interacting surfaces such as bubbles or droplets. The results will be shown and discussed.
Characterization of Liquid Films by Imaging Ellipsometry

Peter H. Thiesen

1 – Accurion GmbH, Stresemannstr. 30, 37079 Göttingen
* pt@accurion.com

Imaging ellipsometry is a versatile technique for the measurement and characterization of transparent films, liquid or non liquid. Through its imaging capabilities, both the thickness of a film and the surface expansion can be quantified. To characterize rapid changes in a speeding droplet, the ellipsometric contrast micrographs showing interference pattern can used to obtain a rapid series of measurements and can be transferred into thickness information. Oliver et al. (2008) characterized patterned trehalose glasses with ellipsometric contrast micrographs. In state of equilibrium, these measurements can than be combined with the more precise measurements obtained through the Delta- and Psi maps. Howland et al. (2007) used a similar concept to follow the Hydration-induced surface spreading of single phospholipid bilayer at the Si|SiO₂ water interface.

Fig. 1. Ellipsometric contrast micrographs of an evaporating waterdroplet - optical components in nulling conditions for the substrat (a) and thickness map of a silicon oil droplet, calculated out of delta maps at different wavelength in the VIS.

Current developments in the field of imaging ellipsometry such as the ultra_objective (Accurion GmbH, Göttingen) enable overall focused images without the need of a focus scanner. The ultra_objective enables realtime overall focused ellipsometric contrast micrographs and faster recordings of Delta-, Psi- and thickness maps. In the case of water films, the Imaging-NIR-ellipsometry has promise for distinguishing between isolated and hydrogen bonded hydroxyl groups.

Literature:


Probing Pair Distributions of Confined Fluids

Kim Nygård 1*, Roland Kjellander 1, Sten Sarman 2

1 - Department of Chemistry and Molecular Biology, University of Gothenburg, Sweden
2 - Department of Materials and Environmental Chemistry, Stockholm University, Sweden
* - kim.nygard@chem.gu.se

Pair distributions of fluids confined between two surfaces at close distance are of fundamental importance for a wide range of phenomena within colloid and interface science, including e.g. surface forces and diffusion in narrow pores. However, while the properties of bulk fluids are routinely studied microscopically by means of their pair distributions, confined fluids are very rarely analysed at such a level of sophistication. Here, we present recent work on the pair distributions of a hard-sphere fluid confined between two planar surfaces, by combining x-ray scattering experiments on colloid-filled nanofluidic channel arrays and statistical mechanics of inhomogeneous fluids. By probing confined fluids at the pair-distribution level one obtains important insights into the properties of fluids in narrow spaces, such as the mechanisms behind surface forces. Part of the results has already been published [1].

Literature:

The Unscreened Pendant of the DLVO-Repulsion

Albert P.Philipse*, Bonny W.M.Kuipers and Agienus Vrij

Van’t Hoff Laboratory for Physical and Colloid Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands
* - a.p.philipse@uu.nl

The entropic repulsion between two flat, electrical double-layers can be evaluated within the Debye-Hückel approximation for the case of weak double-layer overlap, leading to the familiar exponential decay of the repulsion due to Debye screening. It is generally assumed that for the case of strong double-layer overlap no simple formula’s exist for the plate-plate repulsion and that one has to resort to numerical solutions of the Poisson-Boltzmann equation. We show, however, that Langmuir’s disjoining pressure between two flat, charged plates can be calculated analytically in the zero-field limit for extensive double-layer overlap. The resulting repulsion has a long-range algebraic decay that stems from the thermodynamic equilibrium between homogeneously distributed inter-plate ions, and ions in the surrounding electrolyte reservoir. Together with the Van der Waals attraction the repulsion forms the zero-field pendant of the exponentially screened DLVO potential; a pendant that is always repulsive at large plate-plate distances. The experimental occurrence of algebraic repulsions can be simply predicted from surface charge density and ionic strength.

Literature:

Electric Double Layer Forces in Three Phase Contact Formation

Bart Follink 1*, Marta Krasowska1, Mihail N. Popescu 1

1 – Ian Wark Research Institute, University of South Australia, Adelaide, SA 5095, Australia
* - bart.follink@unisa.edu.au

Probability of formation of a three phase contact (TPC), between a colliding bubble and a solid substrate is determined by the stability of a thin asymmetric (wetting) liquid film formed between the bubble and the solid surface. Electrical properties of solid-liquid and liquid-gas interfaces determine the electric double layer interactions, and thus by controlling the surface charge of solid-liquid can be ‘switched’ between repulsive (when the bubble and solid interfaces bear charges of the same sign) and attractive (when the bubble and solid interfaces are oppositely charged).

The paper presents the results of studies on electrostatic interactions and wettability for the three phase contact formation (TPC) at hydrophilic and surface modified, weakly hydrophobic α-alumina single crystal (0001) surfaces. Al-OH groups determine the surface charge at the solid-liquid interface and therefore by changes in solution pH one can control electrostatic interactions. The point of zero charge of the α-alumina single crystal surface is at pH~4.5. Above pH~4.5 the α-Al₂O₃ surface is negatively charged, while below this value α-Al₂O₃ surface is positively charged. As the isoelectric point for air bubbles is at pH~3 [1], at any pH value below 4.5 the bubble and α-Al₂O₃ surfaces are oppositely charged, leading to electrostatic repulsion. On the other hand, at pH above 4.5, both interfaces are of the same charge and electrostatically attract each other.

Using a high speed camera we studied the kinetics of the TPC formation at the α-Al₂O₃ surface as a function of solution composition (ionic strength and pH) as well as surface wettability. The results of these studies are critically analysed and discussed.

Literature:

Conductivity of Aqueous Wetting Films

Stanislav Itskov¹*, Vladimir Sobolev¹, Natalia Esipova¹

¹ - A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, RAS
* - itskovs@rambler.ru

A novel method for investigation of electrical properties of thin wetting films was developed. The original method allows to indirectly determine the bulk and surface conductivity of wetting films in the range of thicknesses 10 - 100 nm by measuring the electrical resistance of an annular wetting film being in contact with the meniscus of bulk liquid. The scheme of experimental cell is shown in fig.1.

Fig.1. Experimental cell

For the determination of electrical properties of a wetting film, the experimental cell was affiliated to the electrical scheme by means of two electrodes, placed in hoses between corresponding working chambers and working vessels.

The obtained values of surface conductivity of NaCl solutions in the concentration range $10^{-3}$ ~ $10^{-4}$ M on quartz surface is between $8 \times 10^{-10}$ Cm and $1.3 \times 10^{-9}$ Cm that is lower than the previously published data.

Fig.2. Experimental data of surface conductivity of NaCl solutions on quartz surface.

Literature:


The Wetting Film Drainage and Rupture at Titania Surfaces of Different Hydrophobicity

A. Niecikowska\textsuperscript{1}, M. Krasowska\textsuperscript{2}, J. Ralston\textsuperscript{2}, K. Malysa\textsuperscript{1,*}

\textsuperscript{1} - Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Krakow, Poland
\textsuperscript{2} - Ian Wark Research Institute, University of South Australia, Australia
* - nniecik@cyf-kr.edu.pl

The drainage of the film between a colliding bubble and a solid surface followed by this film rupture is essential for the three phase contact formation. The rate of film drainage as well as the film stability is governed by the properties of the interacting interfaces, such as degree of solid surface hydrophobicity, surface charges of solid/liquid and liquid/gas interfaces, surface roughness and hydrodynamic boundary conditions.

On the basis of the dynamic air bubble collisions with hydrophobised amorphous TiO\textsubscript{2} surfaces immersed into solutions at different pH values, we demonstrate that, even in the presence of the attractive electrostatic forces, the wetting film stays stable on hydrophilic titania surface (instantaneous water spreading, no finite contact angle). For an intermediate degree of hydrophobicity the stability of the wetting film formed under dynamic condition, as well as kinetics of the three phase contact (TPC) formation are governed by the interplay of surface electrical charge and surface hydrophobicity, with significantly faster TPC formation in the presence of the attractive electrostatic forces. In the case of highly hydrophobic solids the effect of surface charge is negligible and surface roughness is the key factor determining the kinetics of the wetting film rupture and the three phase contact formation. The film ruptures via nucleation mechanism and the phenomena is shown in Fig 1. In addition, under the same conditions, the time of film drainage ($t_{\text{d}}$) and the time of the three phase contact formation ($t_{\text{TPC}}$), depend on size of the colliding bubble, with both $t_{\text{d}}$ and $t_{\text{TPC}}$ being significantly shortened with the decrease of bubble diameter.

**Fig. 1.** Sequences of interferometric images presenting the wetting film rupture at hydrophobised ($\theta_{\text{adv}}=40^\circ$) titania. The rupture starts from one single hole in the film, and leads to a complete de-wetting of the whole film area within a few milliseconds. The time interval between subsequent images is 0.33 ms. pH = 5.8.

**Acknowledgements:**

We would like to acknowledge financial support from Polish Ministry of Sciences and Higher Education (Grant 1794/B/H03/2010/39).
Information about colloid-chemical properties and aggregate stability of disperse systems can be very useful at definition of optimal preparation conditions of the nanostructured materials in modern technologies. During dispersion process of the most of industrial dry nanopowders in liquid media the polydisperse systems containing both individual nanoparticles, and small aggregate, possessing sediment stability, are received. Undoubtedly, this fact has to have influence on properties of sols and slip compositions prepared on the basis of nanopowders, their aggregate stability, and, therefore, on density and homogeneity of the materials synthesized on their basis. Therefore, at synthesis of new materials using disperse systems it is necessary both to take into account initial sol polydispersity, and to have clear ideas of a role of the surface forces determining of interaction of nanoobjects, especially at the forming of fine microstructures.

In the present work γ-Al₂O₃ hydrosol, prepared on the basis of commercial powder «Aeroxide Alu C, Degussa» (particle size 26 nm, specific surface area 100±15 m²/g) was chosen as the object of research. Coagulation kinetic of positively charged alumina sol at 4 < pH < 7 were studied on the background of NaCl solutions (10⁻⁴ M – 2 M). Zones as well as thresholds of the fast (C_f.c.) and slow (C_s.c.) coagulation were defined by method of photometry. The changing of particle size and particle size distribution at the adding of electrolyte was controlled by the method of dynamic light scattering (DLS).

High stability of alumina sol in respect to electrolyte was observed (C_f.c. > C_f.c. for typical liophobic colloids). This fact allows considering alumina sol as pseudoliophilic dispersion. It is proposed that main factors which could explain anomalous sol stability are presence of water boundary layers (BL) on the surface of oxide particles (structural component of particle interaction energy) and adsorption on a this surface of the aluminum polynuclear aquacomplexes that results in increase of surface hydration. The interaction potentials of oxide particles were calculated within the framework of the extended DLVO theory taking into account the initial polydispersity of sol and three possible types of the particle interaction: 1) nanoparticle aggregates (theirs size determined by DLS method); 2) the primary nanoparticles, and 3) the primary nanoparticles with aggregates. Parameters of structural component of particle interaction energy and effective Hamaker constant values for aggregates were estimated by means of the comparison of photometry data with calculation results.

It was established that observed kinetic of sol coagulation can be explained by two-stage non-simultaneous beginning of the coagulation of primary nanoparticles and aggregates as well as various mechanisms of their coagulation at rather high electrolyte concentrations. Coagulation of aggregates and particle aggregates with primary nanoparticles proceeds on the barrierless mechanism in the long-range potential minimum, caused by the predominance of dispersion forces of attraction on structural and ion-electrostatic repulsion forces. It is difficult to make definite conclusions about the mechanism of primary nanoparticles coagulation, because in this case there is a possibility of proceeding of the barrier coagulation with a fixation of particles in the primary minimum.

Acknowledgements: Work was supported by the Russian President program “Leading Scientific Schools of Russian Federation”, project № NSh-4464.2012.3.
The Spreading Dynamics of Liquids on Rough Surfaces

Hocine Alla¹*, Somia Freifer¹, Badra Ali Talha¹, Thibault Roques-Crames²

¹ – Laboratoire de physique des matériaux et des fluide, université des sciences et de la Technologie d’Oran, BP 1505 El M’Naouar bir el Djir 31000, Oran, Algérie.
² – Université de Lorraine, Laboratoire réactions et genie des Procédés, UPR 3349 CNRS,Nancyn F-54000, France

* - hocine.alla@partner.kit.edu

The phenomena of the spreading of liquid on a solid, particularly on rough surfaces are complex. Many industries of material processing require moving of the contact line in different substrates. A computational fluid dynamics model (CFD), based on the volume of fluid technique (VOF) is applied to simulate the time evolution of spreading drops on solid surfaces (drop base radius and contact angle). Surface tension, wall adhesion and surface roughness phenomenon are included in the computational model. The influence of different factors, such as surface roughness, drop nature, and type of surface, on the temporal evolution of the drop base radius and contact angle is systematically investigated. The numerical results reproduce perfectly the several spreading regimes which occur during the time course of the drop. The calculated results compare very well with the experimental data for a large range of drops and surfaces.

Literature:

5. K Narayan Prabhu, P Fernades, G Kumar, (2009), Mater. Design : 30 297
The work at investigating and studying of a polymeric dispersion on the acrylic basis has been carried out for many years. The main objects of investigation in this work were copolymerization of unsaturated ethers with unsaturated acids, forming of a double electric layer and preventive covers around polymeric particles and regulating of properties of disperse medium.

With the application of diverse modifying monomers - unsaturated acids [1], mono- and di-(meth)acrylates of diatomic alcohols [2], methyl-α-acrylates [3], decylmethacrylate [4] the kinetics and mechanisms of emulsive polymerization have been investigated, the dispersions on the basis of basic industrial (meth) acrylic monomers (butylacrylat, metylacrylat, metyl(meth)-acrylat) have been synthesized, their colloidal chemical properties, astringent and film making ability have been investigated.

The application of unsaturated acids, mono(meth)acrylates of diatomic alcohols as the most polar monomers, which can be re-distributed between water and monomeric phases, gave the opportunity to involve them to forming preventive layers on the surface of polymeric particles together with emulsifying agents [1,2].

The regulation of pH synthesized dispersions of carboxyl containing polymers let have a great influence on the size of solvate covers and globular structure of macromolecules in the particles of dispersed phase [1]. The substantial increase of stability of the investigated colloidal systems, which was faced in the process, became the basis of developing of technology of synthesis of frost-resistant acrylic dispersions using the technology of non-coagulate polymerization, which was realized in industrial conditions at manufacturing [5]. The reconstruction of molecules structure in polymeric particles under the influence of pH let have a big effect on their interaction with organic additives, the molecules of which contained considerable hydrophobic parts [1]. It allowed regulate the distribution of water-insoluble organic dyes in dispersions and films and their optical properties [6].

The application of monohydric alcohols for regulating properties of disperse medium let have a great influence on rheological properties of dispersions and physical and mechanical properties of films received from them without copolymers structure change [7].

The investigations allowed develop effective film-forming compositions which have been synthesized at investigating manufacturing in Russia and Ukraine. Acrylic dispersions synthesized at open joint stock company “Barva” have been successfully applied for purification of monuments surface during the restoration in Lviv [8].

**Literature:**

Fundamentals of Theory of Coagulation of Heterophilic Colloids
(Beyond DLVO)

Vladimir Smorodin\textsuperscript{1,2}\textsuperscript{*}

\textsuperscript{1} – Clarkson University, Potsdam, NY 13699-5708, USA;
\textsuperscript{2} – Moscow State University, Moscow 119899, Russia
\textsuperscript{*} - Vladimir.Smorodin@gmail.com

In colloidal chemistry, regarding interfacial/surface tensions considered as homogeneous, one
does introduce two extreme classes of colloids – lyophilic and lyophobic ones. Fundamental
principles of their interaction, coagulation and stability are developed in classical model and
theory of DLVO. However, interfaces/surfaces of all real systems are heterogeneous. A modern
progress of science and technology demands to complete the classification of colloids with third
class of heterophilic systems, i.e., systems with energetically heterogeneous interfaces/surfaces.
In our talk, we will discuss fundamentals of theory of coagulation and dynamics of such systems,
beyond the DLVO model. First, we will review the simplest initial models of interacting
heterophilic particles in medium. On this basis, we can analyze a series of important phenomena
missed in the classical approach, such as virtual cavitation, two-barrier nucleation, bubble-
bridging, fluctuation capillary-hydrodynamic instability, sound resonances, etc. Then, we will
discuss importance of surface statistics of heterogeneity in theory of coagulation and theory of
surface forces and phenomena. In the frame of this approach, one can derive the exponential law
of hydrophobic attraction of macroscopic particles/membrane in water solutions, as well as some
other exponential laws in surface phenomena. On this way, the physico-chemical theory of
micro-flotation has been advanced. Based on our theoretical estimations and experiments,
we could establish possibility to improve a micro-flotation coefficient of selectivity of anthracite by
its previous heterophilization with methods of radiation chemistry - up to 20%! In conclusion,
one has to note, that completing the current classification of colloids (as lyophilic and lyophobic)
with third class of heterophilic systems is the imperative of our time. Advanced theory of
coagulation/dynamics of heterophilic colloids in media presents a new research paradigm in
modern colloid interface science!

Literature:

   IACIS-2000 Symposium, Bristol, UK}.

Acknowledgements:

The Russian Foundation for Basic Research (grant 12-07-00654).
Light-harvesting Complex II Monolayers in Two Conformational States

Tonya D. Andreeva 1*, Sashka Krumova 1, Ivan Minkov 2, Mira Busheva 1, Stefka Taneva 1

1 – Institute of Biophysics and Biomedical Engineering, Bulgarian Academy of Sciences, Acad. G. Bonchev, bl. 21, 1113 Sofia, Bulgaria
2 – Sofia University, Faculty of Medicine, Department of Chemistry and Biochemistry, Physiology and Pathophysiology, 1 Kozyak Str., 1407 Sofia, Bulgaria.

* - corresponding author’s e-mail

The major light harvesting complex of photosystem II (LHCII) is an important regulatory protein in photosynthetic membranes (Gruszecki, 2010). In vivo it adopts trimeric form and is found either associated to the photosystem II complex or in LHCII-only containing domains (Dekker and Boekema, 2005). It was suggested that in native thylakoid membrane LHCII changes its conformation and macroorganization upon switching to photoprotective state (Johnson et al., 2011).

Monolayers of LHCII were investigated in nonprotonated (nLHCII), pH 7.8, and protonated state (pLHCII), pH 5.2, mimicking the physiological and photoprotective states of the protein. The organization and intermolecular interactions of LHCII trimers in the protein monolayers are studied at the air/buffer interface. The surface pressure/monomer area isotherms of nLHCII and pLHCII monolayers are smooth, without plateaus and kinks. The slow surface-pressure change with area indicates that the LHCII monolayers have a high compressibility and the particles are flexible. pLHCII particles occupy a smaller area and have higher inflection pressure as compared to nLHCII. The increased stability of the protonated monolayer is confirmed by comparison of the time dependencies of the monomer area at two constant surface pressures. Compression–expansion cycles of nLHCII and pLHCII monolayers suggest that during the pLHCII monolayer compression no phase transitions or conformational changes takes place, in contrast to nLHCII films where protein molecules at the air/buffer interface occupy much smaller area (by 500 Å²) at expansion than at compression of the monolayer. The same value of the surface potential at the maximum monolayer density ΔV max = 420 mV, achieved at the inflection points of the π/A curves, was obtained for nLHCII and pLHCII monolayers. Typical surface potentials obtained immediately after spreading range from 100 mV for pLHCII to 140 mV for nLHCII films, suggesting that at the same initial conditions after spreading LHCII complexes assume different molecular orientation and conformation at the interface. This study contributes to better understanding the LHCII conformations in light harvesting and photoprotective states.

Literature:

Solubility Limits and Phase Diagrams for Fatty Acids in Anionic (SLES) and Zwitterionic (CAPB) Micellar Surfactant Solutions

Sylvia Tzocheva1,* , Peter Kralchevsky1, Krassimir Danov1, Gergana Georgieva1, Albert Post2, Kavssery Ananthapadmanabhan2

1Department of Chemical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, J. Bourchier Blvd., 1164 Sofia, Bulgaria
2Unilever Research & Development, 40 Merritt Blvd., Trumbull, Connecticut 06611, USA
* - ssk@lcpe.uni-sofia.bg

The limiting solubility of fatty acids in micellar solutions of the anionic surfactant sodium laurylethersulfate (SLES) and the zwitterionic surfactant cocamidopropyl betaine (CAPB) is experimentally determined. Saturated straight-chain fatty acids with \( n = 10, 12, 14, 16 \) and \( 18 \) carbon atoms were investigated at working temperatures of 25, 30, 35 and 40 °C. The rise of the fatty-acid molar fraction in the micelles is accompanied by an increase in the equilibrium concentration of acid monomers in the aqueous phase. Theoretically, the solubility limit is explained with the precipitation of fatty-acid crystallites when the monomer concentration reaches the solubility limit of the acid in pure water. For ideal mixtures, the plot of the log of solubility limit vs. the chainlength, \( n \), must be a straight line, which is fulfilled for \( n = 14, 16 \) and \( 18 \). For the fatty acids of shorter chains, \( n = 10 \) and \( 12 \), a deviation from linearity is observed, which is interpreted as non-ideal mixing due to a mismatch between the chainlengths of the surfactant and acid. The data analysis yields the solubilization energy and the interaction parameter for the fatty acid molecules in surfactant micelles. By using the determined parameter values, phase diagrams of the investigated mixed solutions are constructed. The four inter-domain boundary lines intersect in a quadruple point. The results can be applied for the interpretation and prediction of the solubility, and phase behavior of medium- and long-chain fatty acids and other amphiphiles that are solubilizable in micellar surfactant solutions, as well as for determining the critical micellization concentration of the respective mixed solution [1].

Fig. 1 Phase diagram of the aqueous solutions of anionic surfactant (SLES) and lauric acid (LA).

Literature:
Foam Flow Behaviour through Two Parallel Channels

Sian Jones 1*, Benjamin Dollet 2, Yves Méheust 3 and Isabelle Cantat 2.

1 – Laboratoire de Physique des Solides, Université Paris Sud, France
2 – Institut de Physique de Rennes, Université de Rennes 1, France
3 – Géosciences, Université de Rennes 1, France
* - sian.jones@u-psud.fr

Flowing foams are used in many engineering and technical applications. For processes such as enhanced oil recovery and soil remediation, foam is injected into rock or soil in order to displace the fluid that initially saturates it or to mobilize pollutant chemical species. As both rocks and soils are both porous materials with inherently complex structures, a knowledge of how a foam will flow in a complex geometry is therefore of great importance.

A study into the behaviour of an aqueous two-dimensional foam flowing through two asymmetric parallel channels (Figure 1a) was carried out as a precursor to the study of foam flow through a porous material. The individual channel widths could be varied, but the total combined width of the two channels was kept constant. The velocity in each channel was measured, and it was found that the velocity ratio between the two channels was not uniquely determined by the ratio of the channel widths, as would be the case for a Newtonian fluid. Instead, there was a strong dependence of the flow behaviour on the foam structure within the narrow channel. In particular, discontinuities in the velocity ratios were observed when the foam structure in the narrow channel transitioned between double and single staircase and between single staircase and bamboo. A theoretical model accounting for the viscous dissipation at the solid wall [Cantat, 2004] and the capillary pressure across a film pinned at the channel outlet predicts the observed non-monotonic evolution of the velocity ratio as a function of the width ratio [Jones et al, 2013].

Following this initial study, preliminary studies have been carried out on foam flow through a simplified, random, two-dimensional porous media created using 7mm diameter obstacles (Figure 1b).

![Fig. 1 Images of foam flowing through (a) two parallel, asymmetric channels and (b) a simplified two-dimensional porous media. In both cases, flow is from left to right.](image)

Literature:

Competitive Adsorption of HFBII Hydrophobin and Surfactant: Sequential vs. Parallel Adsorption and Effect of Surfactant Micelles

Rumyana Stanimirova\textsuperscript{1}, Krastanka Marinova\textsuperscript{1}, Krassimir Danov\textsuperscript{1}, Peter Kralchevsky\textsuperscript{1}, Simeon Stoyanov\textsuperscript{2,3}, Eddie Pelan\textsuperscript{2}

\textsuperscript{1} – Department of Chemical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, 1164 Sofia, Bulgaria
\textsuperscript{2} – Unilever Research & Development Vlaardingen, 3133AT Vlaardingen, The Netherlands
\textsuperscript{3} – Laboratory of Physical Chemistry and Colloid Science, Wageningen University, 6703 HB Wageningen, The Netherlands
* - RS@dce.uni-sofia.bg

Adsorption and displacement of HFBII by the ionic surfactant SDS is studied. The surface properties of solutions containing both HFBII and SDS are compared to those obtained by a consecutive adsorption of the individual components. Phase exchange (PhE) during measurement of the surface tension of a pendant bubble at the tip of a capillary by using the drop shape analysis (DSA) method is applied. The oscillating bubble method (OBM) is used to determine the surface dilatational elasticity and viscosity before and after the exchange. The obtained results show that the adsorption of HFBII is irreversible if the low molecular weight surfactant SDS is added after the HFBII molecules have adsorbed already on the water/air surface, and the effect did not depend on the SDS concentration, i.e. below or above CMC. The HFBII adsorption is irreversible also when it adsorbed from solution containing SDS below CMC. However when HFBII is present in a micellar solution of SDS the protein molecules are not detected to adsorb at the water/air surface: neither the surface tension nor the surface dilatational moduli indicate for possible presence of HFBII at the surface. This result is in agreement with the recently published data by Zhang et al., \textit{Langmuir} 2011, 27, 11316–11323.
Evidence for Electrostatic Interactions Mediating the Affinity of Phosphorylated Lipid for TiO₂ Surface

Quoc-Chon Le1*, Marie-Hélène Ropers2, Hélène Terrisse1, Bernard Humbert1

1 Institut Matériaux Jean Rouxel IMN, UMR 6502 Univ Nantes - CNRS, F-44322 Nantes 3
2 INRA, UR1268 Biopolymères Interactions et Assemblages, F-44300 Nantes, France
* - QuocChon.Le@cnrs-imn.fr

Titanium dioxide nanoparticles are widely used in food industry1-2, cosmetic3, etc. Their interaction with biological materials has been an important concern for scientists because of its safe use and potential environment impact5. Understanding this interaction will help to assess the behaviour of TiO₂ versus biomaterials. The aim of this study was to investigate the electrostatic interaction between TiO₂ particles with selected phospholipids (phophatidic acid, phosphatidylglycerol, phosphatidylycerine, phosphatidylcholine, phosphatidylethanolamine and sphingomyelin) by using Langmuir trough technique coupled with Laser Doppler velocimetry. The pH ranges where the electrostatic interaction is expected to be either attractive or repulsive were deduced from the electrophoretic mobilities measured by Laser Doppler velocimetry. Based on these results, the surface pressure-area isotherms of phospholipid monolayers on subphase containing TiO₂ agglomerates were analysed at constant temperature and at various ionic strengths and pH values. The overall study revealed that the interaction between oxide particles in aqueous suspension with phospholipids is essentially charge-dependent. It was found that two conditions are required to observe attractive interactions between TiO₂ samples and phospholipids: first, charge carried by inorganic particles must be opposite with that carried by phospholipid headgroup; second, both TiO₂ particles and phospholipid headgroup must be charged enough, defined as an absolute value of zeta potential higher than approximately 15 mV.

Literature:

2. NanoTrust-Dossier No. 004en, (2010), Nanoparticles and nanostructured materials in the food industry, Institute of Technology Assessment, Vienna.
4. Akira Fujishima, Xintong Zhang, Donald A.Tryk, (2008), TiO₂ photocatalysis and related surface phenomena, Surface Science Reports, 63, 515-582.
Role of Gold Nanoparticles on the Photocatalytic Efficiency of ZnO Films

Peter Georgiev1*, Nina Kaneva2, Kristina Mircheva1, Assya Bojinova2, Karolina Papazova2, Konstantin Balashev1

1 – Laboratory of Biophysical Chemistry, Department of Physical Chemistry
2 – Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria

* - peter_g_bg@yahoo.com

Semiconductor photocatalysis has important applications for achieving sustainable energy sources and for the environmental cleaning. ZnO is one of the most widely studied photocatalysts, but its application in practice suffers from low efficiency and narrow light response range. Hence, the research efforts are focused towards overcoming these limitations. One approach which has a prominent potential is the combination of ZnO with gold nanoparticles. Here we report for a simple and inexpensive method for preparation of ZnO/Au nanocomposites by dip-coating technique. It was found that Au deposition plays an important role on the optical and photocatalytical properties. Nanostructured zinc oxide films were obtained on glass substrate via sol-gel method. The sol was prepared using zinc acetate dehydrate as a starting reagent while the gold nanoparticles were obtained by classical citrate synthesis1. Thin ZnO and ZnO/Au films were characterized by Atomic Force Microscopy (AFM) and UV-Vis spectroscopy. The UV-Vis spectra of ZnO/Au films showed two maxima – first exciton peak of ZnO and second small peak due to surface plasmon resonance of gold nanoparticles (Fig. 1). The photocatalytic activity was studied by UV-vis spectroscopy in respect to the photocatalytic degradation of Malachite Green. The experiments were conducted upon UV and visible light illumination. The results showed, that ZnO/Au films have higher photocatalytic efficiency in degradation of the textile dye in comparison to the pure ZnO films.

Fig. 1 Sample illustration: Transmittance spectra of zinc oxide nanoparticle films with increasing gold nanoparticle content and AFM image of gold nanoparticles.

Literature:


Acknowledgements:

The support of FP7 project Beyond Everest and Russian Presidential Program of engineer advanced trading are acknowledged.
Kinetics Studies of Gold Nanoparticle Growth in the Presence of Metal Ions Studied by UV-vis Spectroscopy and Atomic Force Microscopy (AFM)

Peter Georgiev 1* and Konstantin Balashev 1

1 – Laboratory of Biophysical Chemistry, Department of Physical Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1 James Bourchier Blvd., Sofia 1164, Bulgaria

* - peter_g_bg@yahoo.com

The gold nanoparticles were obtained either by classical Turkevich citrate synthesis or by modifying the method with the addition of europium (III), iron (III), copper (II) or silver (I) ions in the initial reaction mixture. At different temperatures we observe acceleration effect of every one of these ions. Particularly, we studied the kinetics of nanoparticles’ growth at two different temperatures with or without metal ions by means of UV-Vis spectroscopy and Atomic Force Microscopy (AFM). We found that the kinetic curves obtained from the nanoparticles plasmon maxima coincide with the kinetic data (i.e. nanoparticles size evolution Fig. 1) extracted from a newly proposed experimental approach which involved AFM imaging1. The obtained nanoparticle growth profiles were fitted with the well established in literature Finke-Watzky model in order to describe the acceleration effect of the metal ions. From the experimental data and the theoretical fits we found that the citrate reduction of tetrachloroauric acid is accelerated by the addition of the metal ions. The addition of the ions at smaller temperatures has also led to an acceleration effect of the reaction rate. Using Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) we compared the morphology and the size distribution of the nanoparticles synthesized by Turkevich method as well as those obtained in presence of metal ions. The results of TEM and DLS were also used to validate the newly proposed experimental approach which involved AFM as a tool for studying the kinetics of gold nanoparticles’ growth.

Fig. 1 AFM imaging and analysis of gold nanoparticles size evolution.

Literature:
1. P.Georgiev, A. Bojinova, B. Kostova, D. Momekova, Th. Bjornholm, K.Balashev
   Implementing atomic force microscopy (AFM) for studying kinetics of gold nanoparticle's growth, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013, DOI 10.1016/j.colsurfa.2013.05.064

Acknowledgements:

The authors are grateful to the FP7 project Beyond Everest.
Specific Effect of Glycyrrhetinic Acid on Lipid Raft Model Membrane: A Langmuir Monolayer Study

Seiichi Sakamoto\textsuperscript{1}, Hiromichi Nakahara\textsuperscript{1}, Osamu Shibata\textsuperscript{1}*  

\textsuperscript{1} – Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, Huis Ten Bosch, Sasebo 859-3298, Japan  
\textsuperscript{*} - wosamu@niu.ac.jp

To elucidate an interfacial behavior of glycyrrhetinic acid (GA), which is aglycon of glycyrrhizin (GC), with lipid raft model consisting of equimolar ternary monolayers of N-palmitoyl-D-erythro-sphingosylphosphorylcholine (PSM), 1, 2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), and cholesterol (CHOL), Langmuir monolayer have been systematically investigated. The surface pressure ($\pi$)–molecular area ($A$) and surface potential ($\Delta V$)–$A$ for ternary PSM/DOPC/CHOL (1/1/1) monolayers on 0.02 M Tris buffer with 0.13 M NaCl (pH 7.4) containing different GA concentrations (0.1, 0.25, 0.5, 1.0, and 5.0 $\mu$M) have been simultaneously measured by an automated homemade Wilhelmy balance. The monolayer was directly visualized by a Brewster angle microscope (BAM) and a fluorescence microscope (FM) coupled with KSV Minitrough. The $\pi$–$A$ and $\Delta V$–$A$ isotherms show that the GA molecules are penetrated from the subphase, and are squeezed out into bulk phase upon compression. Subsequent in situ morphological analysis by BAM and FM revealed that the microdomains corresponding to lipid raft domains become smaller as GA concentration increases. This result suggests that the LE network is promoted by the increment of GA. Interestingly, the distinct striped regions are formed at the 5.0 $\mu$M subphase concentration of GA. As the result, GA divides the ternary PSM/DOPC/CHOL (1/1/1) monolayers showing the stripe region in the FM image. Furthermore, the single-component (PSM, DOPC, and CHOL) and equimolar binary-component (PSM/DOPC, DOPC/CHOL, and PSM/CHOL) monolayer systems on 5.0 $\mu$M GA are studied. It was clarified that CHOL with GA plays an essential role in partitioning of monolayers. It is found that GA interacts more strongly with lipid raft model as compared with GC, which may suggest that the penetration of GA to the membrane regulates the exertion of numerous activities. The present study reveals the specific effect of GA on the lipid rafts model is more effective than the case of GC\textsuperscript{19}.

Literatures:

Miscibility Behavior of Sphingomyelin with Phytosterol Derivatives by a Langmuir Monolayer Approach

Seiichi Sakamoto¹, Hiromichi Nakahara¹, Osamu Shibata¹*

¹ – Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, Huis Ten Bosch, Sasebo 859-3298, Japan
* - wosamu@niu.ac.jp

The miscibility behavior of palmitoyl sphingomyelin (PSM) with phytosterol derivatives of β-sitosterol (SITO), β-sitosteryl glucoside (SG) and β-sitosteryl glucoside palmitate (SGP) has been systematically investigated by the Langmuir monolayer. The surface pressure (π)–molecular area (A) and surface potential (∆V)–A isotherms for the binary PSM/SITO, PSM/SG, and PSM/SGP systems on 0.02 M Tris buffer with 0.13 M NaCl (pH 7.4) have been measured as a function of molar fraction of PSM (XPSM). Surface potentials (∆V) of pure components were analyzed using the three-layer model proposed by Demchak and Fort ¹). The contributions of the hydrophilic D-glucose moiety, the hydrophobic palmitoyl group, and sphingomyelin group to the vertical component of the dipole moment (μ⊥) were evaluated. The thermodynamic quantities based on π–A isotherms reveal that PSM interacts attractively with all the three phytosterol derivatives in the following order; SITO>SGP>SG. In addition, the two-dimensional phase diagram constructed on the basis of phase transition pressure (πeq) from a liquid-expand (LE) to liquid-condensed (LC) state and of collapse (πc) pressure shows that all the two-component systems are miscible with each other. Miscibility manner between PSM/SG and PSM/SGP systems is found to be opposite at large XPSM region, in which the interaction between the same molecules (PSM–PSM or SG–SG) is stronger than that between the different molecules (PSM–SG) in the PSM/SG system and vice versa in the PSM/SGP system. These results suggest that the incorporation of D-glucose and palmitoyl group to SITO molecule dramatically changes the miscibility behavior with PSM. The observations using fluorescence microscopy (FM) image also provide the miscibility behavior in the monolayer state.

Literatures:
Langmuir Monolayer Properties of Egg Yolk Lecithin with Palmitic Acid and Hexadecanol

Hiromichi Nakahara1, Seiichi Sakamoto1, Osamu Shibata1*

1 – Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, Huis Ten Bosch, Sasebo 859-3298, Japan
* - wosamu@niu.ac.jp

Two-dimensional (2D) monolayers at the air-water interface were investigated for the physicochemical interactions of eggPC with PA, HD, and an equimolar PA/HD mixture. The only structural difference between PA and HD is their head group; their monolayer properties are very similar. Thus, in this study, the composition of the PA/HD mixture was kept constant at a 1:1 molar ratio. Our objective was to elucidate the miscibility, interactions, and phase behaviors of the binary and ternary mixtures. The interfacial behavior of eggPC with PA, HD, and their equimolar mixture in the monolayer state was evaluated by surface pressure (π)–molecular area (A) and surface potential (∆V)–A isotherms on 0.15 M NaCl at 298.2 K. The excess Gibbs free energy of mixing was calculated from the isotherm data, and a 2D phase diagram was constructed from the monolayer collapse pressures. In addition, the phase behavior for the monolayers upon compression was examined using in situ fluorescence microscopy (FM). A new finding in the present study is that PA, HD, and the equimolar mixture of PA/HD were partially miscible with eggPC in the binary and ternary monolayer states. In a strict sense, they are considered to interact favorably both thermodynamically and morphologically with certain components containing fatty acid moieties, such as C16:0 in eggPC [1].

Literatures:
Electrohydrodynamic Instabilities in Emulsion Films

Farshid Mostowfi1, Plamen Tchoukov2,4, Nikolay Panchev3,*, Khristo Khristov3, Tadeusz Dabros2, Jan Czarnecki4

1 – Schlumberger-DBR Technology Center, Edmonton, Alberta
2 – CanmetENERGY, Natural Resources Canada, 1 Oil Patch Drive, Devon, Alberta
3 – Bulgarian Academy of Sciences, Institute of Physical Chemistry
4 – Department of Chemical & Materials Engineering, University of Alberta
* - patcho75@yahoo.com

Upon application of an electric field across a water-oil-water emulsion film, instability patterns were observed as small white dots in the film’s microscopic image. The characteristic lengths of these instabilities were measured for constant electric fields of various strengths. The experimental characteristic lengths agreed reasonably well with theoretical predictions for dominant wavelengths based on linear stability model. The linear stability model used in this study took into account experimentally measured disjoining pressure and calculated Maxwell stress. The films were formed in a thin film apparatus (Sheludko-Exerowa cell) modified such that the oil film separated two aqueous phase compartments, each in contact with a platinum electrode. This modification allows measurements of film thickness while applying electric field and external pressure to the film. The films were formed from a solution of a block co-polymer Tegopren (Degussa, Germany) in decane. Electric polarization in the form of step function at various potentials was applied across the film below the critical voltage for film rupture. Electric field induced breakdown of thin films have various applications such as electric field induced dewatering (electrostatic desalting) of petroleum emulsions and electroporation of bilayer lipid membranes. While pore nucleation is a known mechanism for breakdown of bilayer lipid membranes, rupture mechanism of thicker films with substantial solvent core such as those observed in petroleum industry is not well understood yet. The reported results demonstrate that the formation of electro-hydrodynamic instabilities and their growth is a possible mechanism for breakup of thick emulsion films. DC polarization studies of single thin films are promising approach for understanding of electro-induced coalescence and stability mechanisms of W/O emulsions.
Surface Dilatational Properties of Triterpenoid and Steroid Saponins on the Air-Water Interface

Nevena Borisova1*, Konstantin Golemanov2, Slavka Tcholakova1, Nikolai Denkov1, Edward Pelan2, Simeon Stoyanov2

1 – Department of Chemical Engineering, University of Sofia, Bulgaria
2 – Unilever, Research and Development, Vlaardingen, Netherlands

* - nbb@lcpe.uni-sofia.bg

Saponins are a class of natural surfactants, with molecules composed of hydrophobic head group (triterpenoid or steroid) and hydrophilic oligosaccharide chains. In our previous study1 we found that some of the studied triterpenoid saponins - Escin (ESC), Tea Saponin (TS), Berry Saponin Concentrate (BSC) and Ginsenosides (GS) possess very high shear elasticities and viscosities, Quillaja Dry (QD) has intermediate shear elasticity, whereas other studied saponins with triterpenoid and steroid aglycone have zero shear elasticity and negligible shear viscosity – these are Horse chestnut extract (HC), Sapindin (SAP), Ayurvedic Saponin Concentrate (ASC), Tribulus terrestris (TT) and Fenusterols (FEN). In the current study we compare the same saponins with respect to their behavior under dilatational deformation. To characterize the surface dilatational properties of these saponins, we used two methods: (1) Langmuir trough and (2) Oscillating drop method (ODM). Several types of experiments were performed – oscillatory experiments and deformation-relaxation experiments. The obtained experimental data were described by the Burgers model for both compression and expansion of the adsorption layers. From the best fit of deformation and relaxation stages we determined the two elastic moduli in the Burgers model ($E_1$, $E_2$) and the two related relaxation times of the layers ($t_{R1}$ and $t_{R2}$). The ODM method provides complementary information about the surface dilatation moduli and their dependence on the surface deformation. The obtained results revealed that the adsorption layers of ES, TS, BSC and GS have extremely high dilatational and shear elasticities (200-1500 mN/m) at small deformations (ca. 0.1 %). The measured elasticities decrease steeply with increasing the surface deformation for these layers. In contrast, QD adsorption layers have high dilatational elasticity but intermediate shear elasticity which depend weakly on surface deformation, up to 5 %. The adsorption layers of HC, SAP, ASC, TT and FEN exhibit noticeable dilatational elasticity of 20-40 mN/m and negligible shear elasticities. The surface rheological properties of the latter saponins do not depend on deformation and on whether compression or expansion is applied. The lowest dilatational elasticity is measured for Foamation Dry (FD) (10 mN/m). The obtained results are discussed from the view point of the structure of adsorption layers.

Acknowledgements:

The authors are grateful to Mr. Nikola Mirchev from University of Sofia for some of the experiments with Langmuir trough. The study was financially supported by Unilever.
The pH Dependence of Cascade Partial Coalescence at Oil-Electrolyte Interfaces

Natalie Kuznicki 1,2*, Marta Krasowska 2, Zhenghe Xu 1, Jacob Masliyah 1, John Ralston 2, Mihail Popescu 2

1 – University of Alberta, Department of Chemical and Materials Engineering, Edmonton, Canada
2 – Ian Wark Research Institute, University of South Australia
* - Natalie.Kuznicki@ualberta.ca

Determining the value of electric surface potential of liquid-liquid interfaces using currently available colloid methods is very challenging due to surface deformation.1 Recent work from this group utilized a cascade partial coalescence phenomenon, where a “mother” droplet coalesces with the electrolyte-oil interface, while a stable “daughter” droplet is left behind, to overcome the issue of deformation. The number of partial coalescence events and final stable droplet size were employed to develop a simple method to infer the bounds of the absolute value of the surface charge of oil-electrolyte interfaces.2

The current work examines the effect of pH at various salt concentrations on the partial coalescence sequence. Fig. 1 depicts a toluene droplet interacting with a $10^{-2}$ M KCl/toluene interface at pH 4 and 5. The final stable droplet size for the same oil, but different pH and salt concentration differs significantly, most likely due to specific ion adsorption. Estimating the absolute value of the surface potential for a range of salt concentrations and pHs will provide insight into the behavior of oil-electrolyte interfaces and further improve our understanding of their charging mechanism.

Fig. 1 Cascade coalescence process for purified toluene in $10^{-2}$ M KCl at (a) pH 4 and (b) pH 5.

Literature:


Contact Angle Interpretation of CO$_2$-Water-Oil-Sandstone System 
by Surface Free Energy Analysis

N. Shojai Kaveh$^1$*, E.S.J. Rudolph$^1$, W. R. Rossen$^1$, K-H. Wolf$^1$

$^1$ – Department of Geoscience and Engineering, Delft University of Technology, 2628CN Delft, The Netherlands
* - n.shojaikaveh@tudelft.nl

In reservoir engineering, it has been well recognized that interfacial interactions control flow behavior and displacement in porous media. Particularly, wettability is one of the most important factors determining residual saturations and capillary-pressure and relative-permeability functions [1]. Given the importance of the wetting properties of the rock, a correct description and interpretation of the contact angle is crucial. Of special interest are the pressure and temperature conditions where the CO$_2$ phase is supercritical. To describe the wetting properties of the rock surface as a function of pressure, we use surface-free-energy analysis based on an equation of state (EOS) [2]. Following this approach, we propose a modified equation of state to describe the contact angle of a liquid/gas/solid system at various pressures. The method is applied to experimental data for the water/CO$_2$/oil/sandstone system. The experiments were performed in a pendant-drop cell at typical in-situ reservoir pressures, up to 15 MPa. According to our experimental results, the modified EOS is able to reproduce the contact angle data within the range of the pressures studied (Fig. 1(a) and (b)). This modified EOS can only be applied if the solid phase is not altered due to swelling, chemical reaction or mineral dissolution. The equation-of-state method can be used to describe the wetting properties of a specific surface, if a number of reliable contact-angle and interfacial-tension data are available for a system of interest.

Fig. 1 (a) Contact angle as function of pressure for CO$_2$-Water-Oil-Sandstone system at a temperature of 318 K. (b) Point by point comparison. The dashed lines show the 95% confidence interval.

Acknowledgements:
The research reported in this paper is carried out as a part of the CATO2 project (CO$_2$ capture, transport and storage in the Netherlands).

Literature:
Short-range Hydrophobic Attraction between Silanated Silica Surfaces and Solvophobic Attraction

Naoyuki Ishida1*, Yuhei Soga1, Hiroyuki Imanaka1 and Koreyoshi Imamura1

1Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Okayama University, Okayama 700-8530, Japan
* - n-ishida@okayama-u.ac.jp

The origin of the hydrophobic attraction between macroscopic hydrophobic surfaces1 has been under debate for a long time. Almost 10 years ago, it was shown that the bridging of nanobubbles attached to hydrophobic surfaces is attributable to be the origin of long-range attractive forces.2,3 However, this bubble-bridging force is occasionally regarded as not being a ‘true’ hydrophobic force because it is not produced by surface hydrophobicity itself but rather by the bubbles attached to hydrophobic surfaces. To date, it is unclear whether there is an additional attractive force between hydrophobic surfaces when there are no bubbles on the surfaces.

In this study, the interaction forces between hydrophobised silica surfaces were examined in aqueous solutions using atomic force microscopy (AFM). To prevent the attachment of nanobubbles on the silanated surfaces when water is introduced between the surfaces, the AFM fluid cell was first filled with ethanol and the surfaces were then consecutively rinsed with several organic solvents. Finally, the electrolyte solutions were injected into the cell, and the approaching and retracting forces were measured.

In the approaching force curves, no anomalous long-range attractive force was evident; however, the surfaces jump into contact at a distance of 10–20 nm, which indicates the presence of an additional attractive force that is stronger than the van der Waals attraction. This demonstrates the existence of a ‘short-range’ hydrophobic attraction, i.e. a hydrophobic attraction independent of nanobubbles, between the surfaces. We also measured the interaction between fluorinated silica surfaces in organic solvents and found a similar short-range force that is also stronger than the van der Waals attraction; this force can be regarded as a ‘solvophobic attraction’.

![Approaching force curve for silanated silica surfaces with a contact angle of 108° in 1 × 10^-3 M NaNO₃ solution.](image_url)

**Fig. 1** Approaching force curve for silanated silica surfaces with a contact angle of 108° in 1 × 10^-3 M NaNO₃ solution.

**Literature:**
Co-Adsorption of the Proteins β-Casein and BSA in Relation to the Stability of Thin Liquid Films and Foams

Mihail T. Georgiev *, Krastanka G. Marinova, Rumiana D. Stanimirova, Nikola A. Alexandrov, Elka S. Basheva, Peter A. Kralchevsky

Department of Chemical Engineering, Sofia University, Sofia, Bulgaria
* - mtg@dce.uni-sofia.bg

Set of complementary experimental methods is used to determine the properties of adsorption layers from solutions containing two proteins and to analyse qualitatively the impact of the individual components: Phase exchange experiments with (i) rising bubbles to determine the surface tension by the ADSA method, combined with surface dilatational rheology measurements; and (ii) thin films observations for determination of the film thickness and stability.

Two types of mixed adsorption layers and thin films are compared: (i) formed from mixed solutions, i.e. upon parallel adsorption; (ii) a protein initially adsorbed and afterwards exchanged in the bulk by another protein or a surfactant, i.e. by sequential adsorption.

The applied combination of experimental methods and techniques allows detailed analysis of the role of the individual components for the overall stability and surface properties of the mixed system1, and could be further successfully applied to study many other protein and surfactant blends.

Literature:

Membrane Emulsification as a Method to Form Liquid Core Polyelectrolyte Microcapsules

Małgorzata Adamczak1*, Ewelina Jarek1, Krzysztof Szczepanowicz1, Christian Simon2, Piotr Warszyński1

1 – Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Krakow, Poland
2- SINTEF Materials and Chemistry, Forskningsveien 1, NO-0314 Oslo, Norway
* - ncmadame@cyf-kr.edu.pl

The layer-by-layer adsorption of polyelectrolytes (PE) is considered as a convenient method to obtain microcapsules’ shells on colloidal cores. Solid particles (polystyrene latex, silica, CaCO3) are most often used as cores for formation of capsules, which may contain some active ingredient. Alternatively the solid core can be dissolved to leave the hollow shell, which can be then refilled with the desired composition. The disadvantage of this method can be traces of the destructed core trapped in the capsule and low efficiency of loading the active substance into the hollow shells. Use of emulsions droplets as liquid cores provides possibility to encapsulate oil soluble active components with control of size and shell properties of obtained capsules, that opens perspectives for application in many fields such as cosmetic, medicine, pharmacy and food industry. Membrane emulsification is a two-liquid phase flow process, in which a dispersed phase is pressed through the membrane pores to a continuous phase. Droplets grow at the membrane pore, and after reaching a certain size, they are detached by the shear force of the continuous phase flow. Membrane emulsification has received increasing attention over the last 10 years, with potential applications in many fields where the monodisperse emulsions is required. One of them is the fabrication of monodisperse polymer microcapsules.

In this work we were focused on the preparation of o/w emulsion as cores for microencapsulation by sequential adsorption of polyelectrolytes (layer-by-layer method). The emulsions of squalene stabilized with AOT/PAH interfacial complex (AOT-Docusate sodium salt, PAH poly(allylamine hydrochloride)) were prepared on membrane emulsification unit. The influence of AOT and PAH concentration on the size and zeta potential of obtained emulsions was investigated. Size of the emulsion droplets was correlated with the dependence of the interfacial tension at squalene/water interface. The emulsion droplets were used as a cores for further layer-by-layer encapsulation within PAH/PSS (PSS-poly(styrene sulfonate) polyelectrolytes (up to 10 layers) using the saturation technique. A growth of the polyelectrolyte shell was followed with the electrophoretic mobility and light scattering measurements. A hydrophobic drug (Naproxen) and oil-soluble witamin D were encapsulated within the cores and their presence was confirmed by UV-vis measurements.

Acknowledgements:

This work was supported by the "Krakow Interdisciplinary PhD-Project in Nanoscience and Advanced Nanostructures", which is operated within the Foundation for Polish Science MPD Programme co-financed by the EU European Regional Development Fund, by NCN project NN209 757340 and the Marian Smoluchowski Krakow Research Consortium - a Leading National Research Centre KNOW supported by the Ministry of Science and Higher Education and the COST Action CM1101.
Effect of Solid Surface Modification on the Formation of Supported Lipid Bilayers

Magdalena Włodek 1*, Marta-Kolasińska - Sojka 1, Piotr Warszyński 1

1 Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Krakow, Poland
* - ncwlodek@cyf-kr.edu.pl

Supported lipid bilayers (SLBs) are commonly used as models of cell membranes with potential biotechnological applications such as biochips and biosensors. One of two main pathways, which are usually used to form SLBs is spreading of the small unilamellar vesicles (SUV) on the solid supports. It is an attractive and simple route to form thermodynamically stable bilayers on these substrates.

Our study aims at understanding how the modification of surfaces by adsorption of polyelectrolytes influences the process of vesicle adsorption and SLB formation on various supports. For the preparation of lipid vesicles following lipids were used: zwitterionic 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine, positively charged 1-palmitoyl-2-oleoyl-sn-glycero-3-ethylphosphocholine (chloride salt) and negatively charged 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-L-serine (sodium salt). Small unilamellar vesicles were prepared by the extrusion method using polycarbonate membranes with the defined pore size of 100nm. For the characterization of the obtained lipid vesicles dynamic light scattering and zeta potential measurements were applied.

We examined the formation of SLBs by quartz crystal microbalance with dissipation monitoring (QCM-D), which provided information about the mass and the structure of adsorbed material during the deposition. We investigated the effect of polyelectrolyte multilayers of various thickness and surface charge, used for the modification of QCM crystal surface, on the vesicle fusion and the formation of supported lipid bilayers. Modification of sensors was done by using the layer-by-layer deposition of polyelectrolytes. Cushion thickness was regulated by the number of polyelectrolyte layers used and its surface charge – by the proper terminating layer: either positively or negatively charged.

Acknowledgements:

The work presented was financed by the National Science Centre, Contract No. DEC-2011/01/DST5/04913the Marian Smoluchowski Krakow Research Consortium - a Leading National Research Centre KNOW supported by the Ministry of Science and Education and the COST Action CM1101.
Relation between Surface Rheological Properties and Foam Film Behavior of Saponin Solutions

Kristina Neshkova1*, Konstantin Golemanov,2 Slavka Tcholakova1, Nikolai Denkov1, Edward Pelan2, Simeon Stoyanov2

1 – Department of Chemical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, J. Bourchier Ave., 1164 Sofia, Bulgaria
2 – Unilever, Research and Development, Vlaardingen, Netherlands
* - kn@lcpe.uni-sofia.bg

Saponins are natural surfactants, whose molecules are composed of hydrophobic steroid or triterpenoid group, and one or several hydrophilic oligosaccharide chains attached to the hydrophobic group. In our previous study1 we found that the saponin extracts of Escin, Tea Saponin, Berry Saponin Concentrate and Ginsenosides exhibit very high shear elasticities and viscosities, Quillaja Dry has intermediate shear elasticity, whereas the other studied saponins with triterpenoid and steroid aglycone have zero shear elasticity and viscosity – these are Horse chestnut extract, Sapindin, Ayurvedic Saponin Concentrate, Tribulus terrestris and Fenusterols. The major aim of the current study is to characterize the foam film behavior of these saponins and to relate this behavior to the surface rheological properties of the saponin solutions. Foam films were studied in the Sheludko-Exerowa capillary cell at capillary pressure of 50 Pa. We measured the drainage time and the equilibrium thickness of the foam films, formed from the various saponin solutions. The obtained results show that all studied saponins with triterpenoid aglycon formed films which thin down more slowly than the films stabilized by typical low molecular-mass surfactants, whereas two of the three steroid saponins formed films with typical drainage behavior of low molecular mass surfactants. The comparison of the film drainage time and the surface rheological properties of the saponin adsorption layers showed that the saponins which lead to slowest thinning of the foam films are those with very high surface shear and dilatational elasticities - Escin, Berry saponins, Quillaja Dry 100 and Ginsenosides. Saponins with intermediate dilatational elasticity and zero shear elasticity showed intermediate drainage time. The fastest drainage is observed with saponins which exhibit no shear and dilatational elasticity.

Literature:

Bacterial Adhesion to Metal Surfaces

Klemen Bohinc*1, Damijan Nipič1,2, Karmen Godič Torkar1, Goran Dražič3, Peter Raspor2

1 – Faculty of Health Sciences, University of Ljubljana, Ljubljana, Slovenia
2 – Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, Slovenia
3 – Institute of Science and Technology, Jamova 39, Ljubljana, Slovenia
* - klemen.bohinc@fe.uni-lj.si

Interactions between bacteria and material surfaces play an important role in biology and different process technologies. The aim of this study is to investigate the influence of material surface roughness on the degree of bacterial adhesion. Two different stainless steel materials AISI 304 and AISI 316TI are used. The surface roughness is adjusted as needed by brushing, 3D polishing and electropolishing. The roughness, morphology and texture of the material surfaces was measured and evaluated by Atomic force microscopy (AFM) [1]. The adhered cells are stained and detected spectrophotometrically and consequently compared with the results obtained by scanning electron microscopy [2]. For experiments we will use one Gram-positive bacterium (Staphylococcus aureus) and two Gram-negative bacteria (Pseudomonas aeruginosa and Escherichia coli). Finally, the influence of bacterial shape on the adhesion will be studied.

Literature:

Control of the Bubble Departure Diameter by Saw-tooth Surfaces

Ken Yamamoto* and Satoshi Ogata

1 – Department of Mechanical Engineering, Tokyo Metropolitan University, Tokyo, Japan
* - yamamoto-ken@ed.tmu.ac.jp

Controlling the bubble diameter departing from the wall is highly important for the performance improvement of the boiling systems, but the mechanism of the bubble detachment is still open issue due to the complexity of the phenomenon. In this study, the control of the bubble departure diameter is achieved by equipping saw-tooth surfaces, which can enhance the relative influence of the surface tension in the bubble detachment mechanism.

The bubble generation process in the liquid–gas micro mixing system is dominated by the surface tension and the pressure difference between two phases [1]. Although other forces such as the drag force due to the bubble growth and buoyancy force may attract the bubble detachment in boiling systems, it is anticipated that the surface tension may still have large influence on the phenomenon. Therefore, if the relative influence of the surface tension can be enhanced, the phenomenon may be considered to be dominated by the surface tension. Since the inner pressure of bubbles in microscale are considerably high and hence bubbles tend to form the spherical shape, four different microscale saw-tooth surfaces were fabricated in order to interfere the bubble to grow in a spherical shape at the nucleation site (Fig. 1).

Carbonated water were chosen as the test liquid because of the similarity of the bubble generation process and the easiness of the experiment, and it was observed that the generated bubbles (Fig. 2a) immediately departed from the nucleation sites as they grew and touched the opposite wall (Fig. 2b). The bubbles then kept growing and slid the wall (Fig. 2c), and completely departed from the wall (Fig. 2d). The bubble departure diameters on Surface A were constant and they were altered when different saw-tooth surfaces were equipped. On the contrary, departure diameters were not constant for bubbles generated from a flat surface.

Literature:


Acknowledgements:

We would like to express our appreciation for the financial support by the Japan Society for the Promotion of Science through the Research Fellowship for Young Scientists.
Influence of Cationic Surfactant on Kinetics of the Three Phase Contact Formation at mica and Teflon Surfaces

Dominik Kosior 1, Anna Niecikowska 1, Jan Zawala 1*, Kazimierz Malysa 1

1 - Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland
* - nczawala@cyf-kr.edu.pl

Probability and kinetics of the three phase contact (TPC), gas-liquid-solid, formation and the bubble attachment to solid surface depends on many interrelated factors among which properties and drainage kinetics of the separating liquid film are the factors of crucial importance. Properties of the thin liquid film (TLF) formed by the colliding bubble are strongly affected by hydrophobicity and roughness of solid surface, the bubble impact velocity, size and degree of the bubble shape deformation, presence of surface active substances (SAS), properties of the SAS adsorption layers, and also on a dynamic architecture of the adsorption layer (DAL) formed. A preferential adsorption of ionic surfactant at surface of the colliding bubble can modify electrostatic interactions and stability of the TLF formed. It can either (i) lower or (ii) increase stability of the film formed. In the case (i) we should observe a facilitation of the TLF rupture and the TPC formation, while in the case (ii) the time of the TPC formation and the bubble attachment should be prolonged.

Results of studies on influence of n-hexadecyltrimethylammonium bromide (CTABr) on time of the TPC formation (t_{TPC}) at model surfaces; hydrophilic mica and hydrophobic Teflon, are presented. In the case of mica plate immersed in distilled water, both the solid and the bubble surface were negatively charged (zeta potentials: ca. -100 mV and -65 mV, respectively), what caused formation of stable thin liquid film due to electrostatic repulsion between similarly charged film interfaces. Presence of CTABr (cationic surfactant) in solution and its preferential adsorption at bubble surface caused electrical charge reversal at gas/solution interface from negative to positive. As a consequence, destabilization of the wetting film and attachment of the colliding bubble to mica surface occurred. The time-scale of this phenomenon depended on CTABr solution concentration and distance (L) between the mica surface the bubble formation point (capillary orifice). For example in the case of L= 100 mm, increase of the CTABr concentration, from 1\times10^{-6} M to 1\times10^{-5} M, resulted in shortening of time of the TPC formation (t_{TPC}) from 577± 121 ms to 365±127 ms. In the case of 1\times10^{-6} M, the t_{TPC} for different mica locations, i.e. L = 100 mm and L = 3 mm, was 577±121 ms and 161±97 ms, respectively. The obtained results clearly indicate the importance of the CTABr concentration over the DAL formation over the bubble surface and for kinetics of the TPC formation at mica surface. In the case of the smooth Teflon surface (zeta potentials: ca. -40 mV), addition of CTABr should lead to shortening of the t_{TPC} due to mentioned above charge reversal of the bubble surface. However, opposite phenomena, for both studied distances, i.e. 3 and 250 mm, was observed. Increases of CTABr concentrations from 1\times10^{-6} M to 1\times10^{-5} M caused prolongation of the t_{TPC} from 90 ±17 ms to 260± 25 ms and from 141±14 ms to 240±36 ms, for L=3 mm and L=250 mm, respectively. Prolongation of the t_{TPC} on Teflon surface indicates that air, in a form of nano- and micro-bubbles, was attached to hydrophobic solid surface. Thus, preferential adsorption of CTABr on liquid/air interface led to prolongation of the t_{TPC} due to increased stability of foam films formed locally between colliding macro-bubble and air "captured" at the Teflon surface.

Acknowledgements:

Financial support from Ministry of Science and Higher Education (Grant 1794/B/H03/2010/39) is gratefully acknowledged.
Kinetics of the Bubble Collisions at Hydrophilic Fritted Glass with Controlled Air Presence – Experiments and Numerical Simulations

Jan Zawala*, Dominik Kosior, Kazimierz Malysa

* - nzawala@cyfronet.pl

Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Krakow, Poland

Kinetics and outcome of the rising bubble collisions with liquid/solid interfaces depends on many interconnected factors, like: bubble size, shape deformations, impact velocity, hydrophobic/hydrophilic properties of solid surfaces, solid surface roughness, air presence at solid surfaces, presence and state of adsorption layer at the interacting surfaces and properties of the liquid film formed during the collisions, etc. During the very short collision time (millisecond time-scale), the liquid film needs to drain to its critical thickness of rupture, otherwise a bubble rebounds from the surface. It is well known that the kinetic of the liquid film drainage depends mainly on its radius, kinetic energy and a size of the colliding bubble, solid surface roughness, mobility of the film interfaces, presence and state of the adsorption layer at the film interfaces. Moreover, recently we showed that air presence at solid surface in form of nano- and micro-bubbles affects significantly stability of the liquid films formed and the bubble attachment to hydrophobic surfaces.

The paper presents the computational fluid dynamics (CFD) simulations and experimental results on the bubble collisions with hydrophilic fritted glass filter immersed in distilled water. The filter was connected to a closed system consisting of: (i) syringe (ii) one-way valve and (iii) precise pressure analyser. The syringe was used to have an overpressure (< 1 kPa) in the system in order to force the presence of air in the pores and at surface of the hydrophilic fritted glass filter. The collision of the bubble with filter surface was monitored using high-speed camera (1000 Hz). The surface was immersed in the liquid either (i) with overpressure (case 1) or (ii) equilibrium (atmospheric) one (case 2). For case 2 the filter surface was additionally immersed several times (quite vigorously) in water to get rid of air, which could be potentially present at the surface. It was found that the outcome of the bubble collisions and dissipation of kinetic energy associated with its motion was significantly affected by the procedure of surface preparations. Comparison of variations in position of the bubble centre and local velocities during collisions showed that a characteristic phase-shift of the bubble oscillations period occurred. The period was shifted towards smaller values for case 1. For example in the air absence (case 2) the second collision occurred at t = 23 ms after the first one, while in the air presence (case 1) this time period was shortened to 19 ms. Additionally, the number and amplitude of the bubble bouncing was smaller for case 1. The results obtained indicate that rupture of water film formed by the colliding bubble and submicroscopic bubbles, present in pores of the fritted glass filter in case 1, was responsible for changes of the bubble bouncing kinetics. The CFD simulations results were compared to the experimentally obtained data. The bubble behaviour during collision with hydrophilic solid surface was calculated numerically by solving the governing equations, describing the conservation of momentum and mass of an incompressible liquid. Two cases were considered in numerical simulations: (i) collision of the bubble with smooth, hydrophilic wall, and (ii) collision of the bubble with the wall having a hole (80×160 µm) filled with air in a form of small bubble. The height of this micro-bubble was equal 31 µm. Very good agreement between the experimental data (phase shift, changes in the bouncing amplitude, the energy exchange rate) and the numerical results were found.
Bubble-bubble Interaction in Aqueous β-lactoglobulin Solutions

Jooyoung Won¹,* Jürgen Krägel¹, Georgi Gochev¹, Vamsee Ulaganathan¹, Aliyar Javadi¹, Alexander V. Makievski² and Reinhard Miller¹

¹ - Interfaces, Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam-Golm, Germany
² - SINTERFACE Technologies, Volmerstrasse 5-7, D-12489 Berlin, Germany
* - Jooyoung.Won@mpikg.mpg.de

The presented drop and bubble micro manipulator (DBMM, SINTERFACE Technologies, Berlin) is a new experimental tool for the quantitative analysis of the interaction between two drops or two bubbles or even between a single drop and a single bubble in a liquid medium [1]. We used DBMM to analyse the stability of bubbles, having protein absorbed on their surfaces. The stability of the liquid films between bubbles depends on the β-Lactoglobulin (BLG) solution concentrations, the ageing time [2] and the solution pH. A threshold concentration of BLG is required to prevent immediate coalescence. The longer the ageing time above this threshold concentration of BLG is the longer is the lifetime of the liquid film between the bubbles. The adsorbed amount of BLG determined as a function of time and concentration by bubble profile tensiometry correlates with the observed coalescence behaviour of the two contacting bubbles.

Fig. 1 Sudden pressure changes registered for both sides of DBMM and estimation of coalescence time for solutions of BLG concentrations of 10⁻⁶ M and 2×10⁻⁶ M at a fixed ageing time of 40 s

Literature:


Tensiometric Investigation on Adsorption of Oil–soluble Emulsifiers at w/o Interfaces

Brankica Marčeta, Jaroslav Katona *, Sandra Njaradi, Lidija Petrović, Jadranka Milanović.

University of Novi Sad, Faculty of Technology, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia
* - jkatona@uns.ac.rs

Polyglycerol polycinyloleate (PGPR) and distilled monoglycerides (DMG) are oil–soluble emulsifiers which are often used for emulsification of water droplets in triglyceride oils. PGPR and DMG adsorb at w/o interface and stabilize the droplets. Unhydrogenated vegetable fats (UVF), having relatively high melting temperature, are commonly used as ‘oil adsorbers’ and rheology modifiers, and are normally poor emulsifiers. Formation of good adsorption layers at w/o interface are especially required in w/o emulsions with high concentration of dispersed phase, such as low–fat spreads, where the water droplets are more susceptible to coalescence. The objective of this work was to investigate adsorption of PGPR, DMG and UVF at w/o interface, when used alone or as their mixtures. The oil phase was prepared by dissolving PGPR, DMG, UVF or their mixtures, at different concentrations, in sunflower oil. Deionized water was used as the water phase. Interfacial tension measurements were performed at 40 °C, and for selected compositions at 15 °C. PGPR and DMG adsorb at the w/o interface, as evidenced by decrease in interfacial tension. UVF is not surface active. Binary PGPR/DMG mixtures give lower interfacial tension when compared to the single component solutions, indicating a synergistic adsorption. Finally, ternary PGPR/DMG/UVF mixtures gives even lower interfacial tension, indicating that UVF influence properties of PGPR/DMG adsorption layers, even though it does not adsorb at w/o interface when used alone.

Acknowledgements:

This work was financially supported by Ministry of education, science and technological development of Republic of Serbia grant No. III 46010/3.
Co-adsorption of Bovine Serum Albumin in n-dodecyl-β-D-maltoside Foam Films

Jana Angarska1* Anelia Gerasimova2, Dilyana Ivanova1 and Konstantin Balashev3

1 - Faculty of Natural Sciences, University of Shumen, Shumen, Bulgaria
2 - Faculty of Pharmacy, Medical University -Varna, Varna, Bulgaria
3 - Faculty of Chemistry and Pharmacy, Sofia University, Sofia, Bulgaria

* - angarska@shu-bg.net

The co-adsorption of Bovine Serum Albumin (BSA) in n-dodecyl-β-D-maltoside (C12G2) foam films formed from mixed solutions with a composition (BSA:C12G2 = 1:7.5; 1:50; 1:100) was experimentally investigated. In order to answer the question which one of the surfactants or both of them is/are adsorbed on the film surfaces data for: (i) the kinetics of surface tension of the single surfactants and their mixtures; (ii) the AFM pictures of BSA surface layer and its mixed layers with C12G2; (iii) the viscosity in the foam film determined from its thinning before 100 nm; (iv) the kinetics behavior of foam films at pH = 4.9, 3.8; (v) the BSA concentration in the solution obtained by dissolving of a dry foam were obtained.

Data for the surface activity of investigated solutions showed that in the mixed adsorption layers from solutions with molar ratio BSA:C12G2=1:50 and 1:100 C12G2 molecules predominate. This conclusion is supported by AFM pictures. The lower viscosity calculated from the thinning of foam films stabilized by these mixtures than this for the films from individual BSA solution is explained with the less aggregation between albumin molecules due to their hydrophilization by bind C12G2 molecules. The stable foams produced from the above mixtures were dried to such an extent enough for black foam films formation in them. Quantitatively, it was found that the concentration of BSA in the solution obtained after dissolving of the dry foam is an order lower than the concentration of the solution drained from the foam during its drying.

The thinning evolutions of the films from pure and mixed solutions, recorded at pH = 4.9 showed that C12G2 films thin up to 90 nm, while the thinning of films from the mixture (1:100) depends on the time of film interfaces aging: the films with fresh interfaces have a similar drainage as the pure C12G2 films; the films with intermediate times of aging become unstable or stable ones when black spots (mobile or frozen) formed in them; the aged films thin fastest and they jump to NBF as the films from C12G2 solution but with pH =3.8 or with 10^{-1} M NaCl. It means that the films electrostatics stabilization is screened which can be due to BSA adsorption. This suggestion was checked by an estimation based on the surface charge density of the following interfaces: air/water; air/C12G2 solution and air/C12G2+BSA solution. It was found that the number of OH^- ions expelled by BSA is two orders smaller that those by C12G2. The values of films equilibrium thickness and surface potential in the case when pH of the mixed solution is 3.8 indicate that the films are common ones. This finding demonstrates again that BSA molecules adsorb on the film interfaces. At pH=3.8 BSA molecule is charged positively that is why the film interfaces are recharged.

Acknowledgment:

This study was realized by the financial support through the Project No. RD-08-264/14.03.2013 and Project BG051PO001-3.3.06-0003 “Building and steady development of PhD students, post-PhD and young scientists in the areas of the natural, technical and mathematical sciences” which is realized by the financial support of the Operative Program “Development of the human resources” of the European social found of the European Union.
Impinging Jet Study of the Deposition of Colloidal Particles on Synthetic Polymer (Zeonor) and Glass Surfaces

Jakub Vlček 1*, Lubomír Lapčík 1**, Jiří Čech 2

1 – Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacky University, 17 Listopadu 1192/12, 771 46 Olomouc, Czech Republic
2 – DTU Nanotech, Department of Micro- and Nanotechnology, Technical University of Denmark, Building 345 East DK-2800 Kongens Lyngby, Denmark
* - jakub.vlcek@upol.cz; ** - lapcikl@seznam.cz

Adsorption, deposition and removal of colloidal particles and bioparticles on/off a solid/liquid interface is of a high scientific and industrial importance, e.g. for better understanding of filtration processes, water treatment, microfluidic devices construction, paper making, biofouling of membranes and artificial organs etc. For detailed and exact understanding of the latter mentioned phenomena well defined hydrodynamic and physicochemical conditions during experiments are required. These conditions are met in Impinging Jet technique. In our study, Impinging Jet deposition experiments were performed on microscopic glass and on synthetic polymer (Zeonor) original and by micro-embossing modified substrates with exactly defined topology as confirmed by AFM, SEM and TEM. Deposition experiments were performed at ambient temperature and at selected flow regimes (Re ranging from 10 to 20). As a particles deposited the PS 1,1 µm diameter particles (Sigma-Aldrich) were used having negative charge of -20 mV as observed by zeta potential experiments. There was found gradual increase of total number of deposited particles with time reaching steady state number. Obtained kinetic curves were fitted to the theoretical blocking model where characteristic time required to reach the steady state (blocking time) as well as steady state number of deposited particles were calculated.

Literature:


Acknowledgements:

Financial support from the Operational Program Research and Development for Innovations – European Regional Development Fund (Grant CZ.1.05/2.1.00/03.0058) and of internal grant of Palacky University in Olomouc (Grant Prf_2013_028) are gratefully acknowledged.
Wetting Properties of Ionic Liquids

Ivan T. Ivanov*, Milen G. Bogdanov, Mihail Avramov, Boryan Radoev

Faculty of Chemistry and Pharmacy, University of Sofia “St. Kliment Ohridski”, 1, J. Bourchier Blvd., 1164 Sofia, Bulgaria.
* - fhiivanov@gmail.com

One of the interesting discoveries in the field of chemistry in the last two decades turns to be the room-temperature ionic liquids (RTIL). They are liquid salts at low temperature (room temperature or below), consist entirely of ions – organic cations and organic or inorganic anions, i.e. electrolytes without solvent. These liquids reveal many useful properties. In this study we investigated the wetting properties of series of six RTILs in contact with solid (glass) surfaces. Particularly, we studied the RTIL adhesion on glass via influence on the three-phase contact (TPC) hysteresis. This was carried out by means of two independent methods – the conventional small droplet on flat inclined plane (Fig.1a) and a method developed by us, named as „capillary tube method” here and afterwards (Fig.1b).

**Fig. 1** Sketches of the measuring element of the methods used in this study: **Left**: droplet on flat inclined plane; **Right**: droplet in a capillary tube; $G$ – the droplet weight; $F_G$ – the driving force (projection of $G$ along the plate surface/tube axis). $v$ – the rate of propagation of the TPC line; $\theta_{A/R}$ – TPC advancing/rececing contact angle.

One of the most informative parameter, characterizing the TPC hysteresis is the so-called critical angle of inclination $\alpha_{cr}$. This is the angle $\alpha_{cr}$ at which the droplet is set in motion. Experimental results for both wetting statics and dynamics of ionic liquids and pure water hysteresis are given and discussed.
Emulsion (oil/water/oil and water/oil/water) Films from Polyoxyalkylated Dietylenetriamine Polymeric Surfactant Solutions: Molecular Structure Effect.

Hristina Petkova*,1, Khristo Khristov1, Dotchi Exerowa1.

1-Institute of Physical Chemistry, Bulgarian Academy of Science, 1113 Sofia, Bulgaria  
* - hpetkova@ipc.bas.bg

The present study explores four polyoxyalkylated dietylenetriamine polymeric surfactants (A, B, C and D), products of Champion Technologies (USA). Surfactant A is an industrially applied agent, while surfactants B, C and D have been recently synthesized. The molecule of each polymer consists of two parts: a more hydrophobic one, where polypropylene oxide (PPO) blocks are predominant and a more hydrophilic one, where polyethylene oxide (PEO) blocks are predominant. Surfactants A, B, C have a similar structure and belong to the group of the so-called “star-like” polymers, differing only in the number of polymeric branches: 4, 6 and 9 in the mentioned order. Surfactant D is of a dendrites type and its molecule consists of 4 to 6 primary and 2-3 secondary branches. (Fig.1)

![Fig.1 Sketch of Polyoxyalkylated Dietylenetriamine Polymeric Surfactants](image)

The differences in surfactants’ ability to stabilize oil/water/oil and water/oil/water emulsion films are evaluated. Emulsion films stabilized by the surfactants also show different behaviour regarding some specific parameters such as surfactant concentration for obtaining a stable film, critical pressure of a single film rupture, etc.

These observations give reasons to believe that model studies can support a comprehensive understanding of how the change in polymeric surfactants’ molecular structure can impact the emulsion films properties. This may enable a target design of the macromolecular architecture depending on the polymeric surfactant purpose to stabilize or destabilize different types of emulsions.

Acknowledgements:

The authors gratefully acknowledge the financial support of Project BG 051PO001-3.3.06-0038
Poisson-Boltzmann Description of Interactions and Aggregation in Charged Colloidal Suspensions in the Presence of Multivalent Ions

Gregor Trefalt*, Istvan Szilagyi, Tamas Oncsik and Michal Borkovec

Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, 30 Quai Ernest-Ansermet, 1205 Geneva, Switzerland

* - gregor.trefalt@unige.ch

The DLVO theory is able to explain the interactions between the charged colloidal particles in the presence of ions. From the interactions one can also predict the aggregation rates at different conditions and thus the stability of the suspensions [1,2]. Within the DLVO the interactions are explained as a sum of the van der Waals and electrostatic forces. The latter can be described by the Poisson-Boltzmann (PB) theory which usually involves a numerical solution of the non-linear differential equation. On the other hand Debye-Hückel (DH) approximation leads to a linear differential equation and therefore in many cases permits an analytical solution.

We numerically study the forces and aggregation rates between spherical colloidal particles in the presence of multivalent ions. The electrostatic interactions are treated at full PB level as well as within the DH approximation. The DH model is valid for weakly charged particles and in the presence of ions of low valence. Furthermore within this approximation the ionic composition is not important, because the ion valence enters in the equations only through the ionic strength. On the other hand, the full PB approach discriminates between electrolytes with different ion valence but the same ionic strength.

The DH approximation predicts the decrease of the critical coagulation concentration (CCC) with the square of the valence, $z^{-2}$, whereas in the case of the full PB approach the dependence of CCC on the valence is stronger and it enhances with increasing the surface charge of the particles. However even at unrealistically high surface charge densities the classical Schulze-Hardy rule, which predicts the $z^{-6}$ dependence, is not recovered by PB.

For the prediction of the CCCs, the DH approximation can be used, because at CCC the diffuse layer potentials are small. We derive a simple analytical expression for calculating the CCCs within the DH approximation and compare it to the experimental results. By using the surface charge densities of the particles, that are calculated from the electrophoretic mobility data, very good agreement with the experimentally determined CCCs [2,3] is observed.

Literature:


Acknowledgements:

This research was supported by the Swiss National Science Foundation and the University of Geneva.
Dendritic Nanofluids Mediating Surface Forces: A Combined SAXS and SFA Study

Georgia A. Pilkington* and Wuge H. Briscoe

1 – School of Chemistry, University of Bristol, Bristol, Avon BS8 1TS
* - georgia.pilkington@bristol.ac.uk

Fluids containing nano-sized structures are increasingly employed in modern technologies, ranging from cooling fluids to drug delivery systems. However, despite their numerous applications, our fundamental understanding of the surface forces mediated by nanofluids is still limited. In particular, due to their nanosize and related characteristics, applicability of established surface force theories, such as the DLVO theory is unclear. With several tunable parameters such as the size, surface and interior chemistry, dendritic macromolecules (or dendrimers), offer a unique model nanofluid for investigating the effect of nanostructures on classic colloidal phenomena – for instance, how they may mediate surface forces or interact with lipid mesophases. Recently we have performed complementary small angle X-ray scattering (SAXS) and surface force apparatus (SFA) measurements in aqueous solutions of anionic polyamidoamine (PAMAM) dendrimers to study their interactions in the bulk and when under nano-confinement. Furthermore, we have studied how the interactions mediated by the dendrimers would be modified by the presence of a number of ionic surfactants, including cationic surfactant dodecyltrimethylammonium bromide (DTAB) and anionic surfactant sodium dodecyl sulfate (SDS).

We find in the bulk that the presence of cationic surfactant DTAB, at concentrations just above its cmc, the adsorption of the surfactant monomers to the dendrimer surfaces leads to the formation of a new dendrimer-surfactant complex. Under nano-confinement in the SFA under similar conditions, we observe short range interactions between confining surfaces relating to structuring of the dendrimer-surfactant complexes. For anionic surfactant SDS which is similarly charged to the dendrimers, the dendrimers and surfactant remain non-interacting which leads to a binary depletion interaction between when confined in the SFA.

From these SAXS and SFA measurements, we have gained insight into the complex effects of nanofluids on surface interactions. Such interactions between nanofluids and soft matter structures bear fundamental relevance to how nanostructures interact with lipid mesophases encountered in complex biological tissue surfaces such as cell membranes, as well as to the design of drug delivery systems employing dendrimers where such interactions are an important consideration.

Literature:

Acknowledgements:
M. Malfois, A. Smith and N. Terrill (Diamond I22, UK); B. Sironi and T. Snow (Bristol Chemistry). Funding from the Engineering and Physical Science Research Council (EPSRC; EP/H034862/1) and support from the School of Chemistry, University of Bristol are also gratefully acknowledged.
The Effect of Varying Substrate Wettability on the Thermocapillary Motion of Droplets

Kirti C. Sahu 1, George Karapetsas 2*, Omar K. Matar 3

1 – Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Yeddumailaram 502 205, Andhra Pradesh, India
2 – Department of Mechanical Engineering, University of Thessaly, Volos 38334, Greece
3 – Department of Chemical Engineering, Imperial College London, London SW7 2AZ, U.K.

* - gkarapetsas@gmail.com

We study the two-dimensional dynamics of a droplet moving on a non-isothermal, inclined solid substrate, heated with constant temperature gradients. We use lubrication theory to derive a single evolution equation for the gas-liquid interface. Our model takes into account the presence of dynamically-varying substrate wettability brought about by local temperature variations. This important feature of the model has, to the best of our knowledge, not been taken into account by previous models in the literature in which the contact angles were typically kept constant. The evolution equation is solved numerically using the finite element method and an implicit Euler method in time. A full parametric study is carried out that focuses on the interplay between the effects of the magnitude of the substrate temperature gradient, substrate wettability, Marangoni stresses, and gravity. The results show that in the presence of temperature-induced wettability variations, the dynamics are rather complex. This is characterised by a non-monotonic dependence of the droplet centre-of-mass velocity on the magnitude of the substrate temperature gradient for horizontal substrates, and situations wherein, for inclined substrates, this monotonicity persists even when the thermal gradient is such that Marangoni stresses are expected to reinforce the action of gravity. We have also found evidence of ‘stick-slip’ contact line motion that arises in cases in which the initial contact angles are between the corresponding temperature-varying equilibrium values. These results show collectively that it is essential to account for variations of the substrate wettability in models of droplet motion over non-isothermal walls.

Fig. 1 Schematic diagram of the drop on an inclined plate. $T_w = T_0 + \Gamma x$, where $\Gamma$ is the constant temperature gradient applied at the solid wall

Acknowledgements:

GK acknowledges the support by the General Secretariat of Research and Technology of Greece under the action "Supporting Postdoctoral Researchers" (grant number PE8/906), co-funded by the European Social Fund and National Resources. OKM acknowledges the support of the Engineering and Physical Sciences Research Council, UK, through grant numbers EP/K003976/1 and EP/J010502/1.
Self-Assembled Bilayers from the Protein HFBII Hydrophobin: 
Nature of the Adhesion Energy

Elka Basheva, Peter Kralchevsky, Krassimir Danov, Simeon Stoyanov, Theo Blijdenstein, Eddie Pelan, Alex Lips

1Department of Chemical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, 1 J. Bourchier Blvd., 1164 Sofia, Bulgaria 
2Unilever Research & Development, 3133AT Vlaardingen, The Netherlands 
3Unilever Research & Development, Port Sunlight, Wirral, Merseyside CH63 3JW, UK 
* - eb@lcpe.uni-sofia.bg

The hydrophobins are a class of amphipilic proteins, which spontaneously adsorb at the air/water interface and form elastic membranes of high mechanical strength as compared to other proteins [1]. The mechanism of hydrophobin adhesion is of interest for fungal biology and for various applications in electronics, medicine and food industry. We established that the drainage of free foam films formed from HFBII hydrophobin solutions ends with the appearance of a 6 nm thick film, which consists of two layers of protein molecules (Fig. 1), i.e. it is a self-assembled bilayer (S-bilayer), with hydrophilic domains pointing inward and hydrophobic domains pointing outwards. Its formation is accompanied with a considerable energy gain, which is much greater than that typically observed with free liquid films. The experiments at different pH show that this attraction between the “hydrophilic” parts of the HFBII molecules is dominated by the short-range hydrophobic interaction rather than by the patch-charge electrostatic attraction [2].

Fig. 1 Two photographs of the process of S-bilayer formation, and sketch of its structure.

Literature:


Quantitative Evaluation of Surfactant Adsorption from Kinetic Interfacial Tension Data

Dora T. Dimitrova¹*, Theodor D. Gurkov¹

¹ – Department of Chemical Engineering, University of Sofia, Faculty of Chemistry & Pharmacy, James Bourchier Avenue 1, 1164 Sofia, Bulgaria
* - dt@lcpe.uni-sofia.bg

In this work we discuss experimental data for dynamic interfacial tension (O/W), measured at different surfactant concentrations, $\sigma(c,t)$. A procedure for interpretation of such data is proposed – we show how to determine the adsorbed amount per unit area ($\Gamma$), and obtain useful information for the surface equation of state and the time evolution of $\Gamma$. The method for data processing is based on the theory described in Ref. [1]; currently, it is applicable to relatively short times and/or low bulk concentrations. An example of results is shown in Fig. 1, for the cationic surfactant cetyl trimethylammonium bromide, in the presence of salt. One observes that the experimental points at different times and concentrations lie on a “master curve”; the latter can be fitted with a suitable equation of state. This gives values for some characteristic parameters, e.g., $\Gamma_{\infty} = 5.69 \times 10^{-4}$ µmol/cm² (the limiting adsorption). Another outcome from the processing operations is the time dependence of the adsorption, $\Gamma$ (presented in Fig. 2). The calculations might be useful for analysis of measured data in the case of fast adsorption dynamics in undersaturated surfactant layers.

Fig. 1 Data for $\sigma(c,t)$, extracted from the kinetic curves and fitted with an isotherm.

Fig. 2 The short-time adsorption kinetics, obtained for the system in Fig. 1.

Literature:

Adsorption on Solid Surfaces: Effect of Surfactant and Calcium

Dilek Gazolu1*, Slavka Tcholakova1, Nikolai Denkov1

1 – Department of Chemical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, Sofia
* - dg@lcpe.uni-sofia.bg

The surface energy of solids and the solid-liquid interfacial tension are two important characteristics, governing the behaviour of solid materials in practically important processes, such as adhesion and wetting. In the approach proposed by van Oss1, the interfacial tension is decomposed into three components: Lifshitz-van der Waals (γLW), electron-acceptor (γ+) and electron-donor (γ−) components. To determine the aforementioned components for a given surface, one should measure the three-phase contact angles of at least three liquids with known surface properties. The major aims of the current study are: (1) to characterize the surface properties of a series of solid substrates by using van Oss approach and (2) to evaluate how these energies depend on the presence of surfactant and calcium ions in the liquid phase. To achieve our goals we determined γLW, γ+ and γ− by measuring the contact angle of water, formamide and diiodomethane on the studied substrates. Then we examined the effect of surfactant concentration on the solid-water interfacial energy, as well as on the contact angle of oily drops placed on a given solid surface. The obtained results demonstrate that the contact angle of oily drops may pass through a maximum, whereas the surface tension may go through a minimum, with the increase of surfactant concentration for anionic surfactants in the presence of calcium ions. These unexpected results are explained with the competitive adsorption of the calcium ions on the surface of the anionic surfactant micelles and in the surfactant adsorption layer.

Fig. 1 Oily drop deposited on solid substrate in presence of anionic surfactant and calcium ions.

Literature:

Surfactant Transport onto a Foam Lamella

Denny Vitasari*, Paul Grassia, Peter Martin

School of Chemical Engineering and Analytical Science, The University of Manchester Sackville Street, Manchester M13 9PL
* - denny.vitasari@manchester.ac.uk

The evolution of surfactant on a foam film interface determines the efficiency of separation obtained by a foam fractionation column used e.g. for purifying/enriching that surfactant. Therefore, a study of the surfactant evolution on the film surface coupled to lamellar film drainage has been carried out to understand the performance of a foam fractionation column. This study simulates the surfactant transport onto a lamella in a foam fractionation column with reflux, since such columns offer greater control over enrichment and recovery.

Assumptions made for the simulation are that the lamella is flat due to the bubble shape in a dry foam – a common situation in a foam fractionation column, the initial surfactant concentration on the film surface is uniform and the surfactant concentration at the Plateau border is held fixed at the value set by the reflux. Insoluble surfactant is assumed during the simulation as such surfactants derive more benefit from a reflux system. There are two terms involved in the equation for surfactant flux which are the Marangoni flow – from the Plateau border to the centre of the lamella – and the film drainage – which is directed from the centre of the lamella to the Plateau border. The extent of film drainage is bounded using two extremal assumptions of mobile [1] or rigid [2] interfaces. On a mobile interface, the film drainage dominates the Marangoni effect, while on a rigid interface, the Marangoni effect is dominant. The numerical simulation was carried out using a material point method [3] followed by a bookkeeping operation to regrid the film. Analytical solutions for the case of no drainage and for a (quasi) steady state for the case of a rigid film – in which Marangoni flows and drainage are balanced – as well as the asymptotic solution for the case of a mobile film – where there is a boundary layer near the Plateau border, were used to verify the numerical simulation. From the simulations, it can be concluded that the film drainage obtained using surfactant with a mobile interface is much faster than that modelled using surfactant with a rigid interface, meaning that surfactant is washed out of the film in the mobile case. The desirable condition in a foam fractionation column is however where the Marangoni flow dominates the liquid drainage which can be achieved when using surfactant that gives a rigid interface. The (quasi) steady state solution verifies the simulation result at later time for the case of film with a rigid interface. An asymptotic solution in the case of film with a mobile interface gives a good prediction of the surface concentration of surfactant at the centre of the film as well as that within the Boundary layer.

Literature:

The Impact of Water on a Range of non-aqueous Colloidal Suspensions

Clare Mayes ¹*, Francois Ricard ², Paul Luckham¹.

¹ – Imperial College London
² – GlaxoSmithKline R&D
* - Clare.E.Mayes@gsk.com

Water has for many years been known to have a significant impact on the behaviour of non-aqueous colloidal systems[1]. There are two potential impacts of water. It will either a. destabilise the system due to the formation of water bridges [2] and capillary action, or b. stabilise the system due to an increase in the surface potential of the particles resulting in repulsion [3]. The majority of the published research has focused on inorganic solids suspended in non-aqueous media, however there is growing interest within the pharmaceutical industry as much of primary processing (processes up to the isolation of the pure active pharmaceutical ingredient – API) is carried out in non-aqueous systems where the water levels may vary.

The aim of this work was to investigate correlations between the physical properties of the solid and the suspending media and the impact water has on the suspension properties. A range of solvents have been investigated with varying water miscibility and dielectric constants, coupled with a range of APIs with varying hygroscopic nature, wettability and solubility. Additionally lactose (a more wettable organic compound) and Calcium carbonate (a comparably wettable inorganic compound) have been investigated. A relative prediction of the impact of water on the colloidal properties is suggested with reference to the physical properties of both the solids and the liquids investigated.

Literature:

The Effects of Reactive Oxygen Species on Single Polycation Layers

Florian Berg\textsuperscript{1}, Stephan Block\textsuperscript{2}, Steffen Drache\textsuperscript{1}, Rainer Hippler\textsuperscript{1} and Christiane A. Helm\textsuperscript{1}\textsuperscript{*}

\textsuperscript{1} Institut für Physik, Ernst-Moritz-Arndt Universität, D-17487 Greifswald, Germany
\textsuperscript{2} ZIK HIKE, D-17475 Greifswald, Germany.
\textsuperscript{*} helm@uni-greifswald.de

Positively charged, branched polyethylenimine (PEI) adsorbed onto silicon wafers and silica surfaces are attacked by free hydroxyl radicals.\textsuperscript{[1]} With AFM colloid probe technique, the surface forces between the PEI layers are measured.\textsuperscript{[2]} Force profiles show that between freshly deposited PEI layers electrostatic repulsion dominates the surface forces. After radical attack both, surface potential and surface charge density, are reduced by a factor of about two, while the Debye length remains unchanged. Adsorbed gold nanoparticles and force volume measurements show a homogeneous distribution of the surface charge on length scales between 40 nm and 30 \( \mu \)m. For radical attacked PEI layers we find a 10 \% decrease of saturation coverage of gold nanoparticles. This is consistent with the decreased surface charge density when the electrostatic three-body interaction is considered. Nevertheless, the NP adsorption kinetics is slowed down suggesting that the PEI layer is inhomogeneous on the nm-scale after radical attack.

\textbf{Fig. 1.} Left: Surface Forces before and after exposure to free oxygen radicals. Right: Schematic of the partial decomposition of the surface layer.

\textbf{Literature:}

2. Florian Berg, Stephan Block, Steffen Drache, Rainer Hippler, Christiane A. Helm, subm.
Parabolic and Linear Growth Regime of PDADMAC/PSS Multilayers

Peter Nestler, Malte Pasvogel and Christiane A. Helm

* - helm@uni-greifswald.de

The buildup of polyelectrolyte multilayers is investigated in solution with multiple angle null ellipsometry. Polyanion poly(styrenesulfonate) (PSS) and polycation poly(diallyldimethylammonium) (PDADMAC) are adsorbed sequentially from 0.1 M NaCl solution. First the films grow parabolically. After $N_{\text{trans}}$ deposited PDADMAC/PSS layer pairs a transition from a parabolic to a linear growth occurs.

For large molecular weight ($M_n$(PSS) > 25 kDa and $M_n$(PDADMAC) > 80 kDa), $N_{\text{trans}}$ is fifteen, the thickness per layer pair in the linear growth regime is 12.3 nm. But if either the PDADMAC or the PSS molecular weight is decreased, $N_{\text{trans}}$ either falls (down to 8) or rises (highest value observed 33), respectively. Simultaneously, in the linear growth region the thickness per layer pair decreases down to 4.3 nm or exceeds 25 nm. If the PSS molecular weight is decreased below 20 kDa, three growth regimes are observed: first exponential, then parabolic and finally linear. The opposite influence of PSS and PDADMAC molecular weight is attributed to different polymer conformations during adsorption. The data suggest that molecular weight provides a way to control growth and internal structure of polyelectrolyte multilayers.

**Fig. 1** Thickness of polyelectrolyte multilayer as function of the number of deposited layer pairs for three different combinations of PDADMAC/PSS molecular weight.

**Acknowledgements:**

We thank DFG for financial support (He 1616/14-1).
Disjoining Pressure of Core-shell Particle Stabilized Thin Films

Carolina Vannozzi \textsuperscript{1*}

\textsuperscript{1} – University of California Santa Barbara, Santa Barbara CA 93106

* - carolina.vannozzi@gmail.com

An analytical expression to determine the disjoining pressure (van der Waals interaction force per unit area) of a thin film stabilized by core-shell particles straddling a thin film interfaces is presented. The method used is similar to the Hybrid-Hamaker approach employed in Ref. [1] for Janus particle or bear particle stabilized films. The expression finds application in the stability of thin films for electronic devices and the stability against coalescence of drop in polymeric blends for producing advanced functional materials.

Literature:

Stability of Foam Films under Dynamic Conditions

Boryana Ralcheva 1*, Borislava Damyanova 1, Slavka Tcholakova 1, Nikolai Denkov 1

1 - Department of Chemical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, Bulgaria
* - br@lcpe.uni-sofia.bg

We have developed a new procedure, which allows us to form foam films, from a limited surface of surfactant solution. With this procedure we studied the stability of dynamic foam films, formed by rapidly stretching the solution surface (viz. under dynamic conditions). This procedure mimics the surface expansion of newly formed bubbles during foaming. This procedure was used to study the effect of surfactant type and concentration on the stability of dynamic foam films. The effect of some basic electrolytes (NaCl and CaCl₂) was also studied. The obtained results were compared to the foamability of the same surfactant solutions, as well as with the results from several other “classical” methods for studying foam films – vertical films withdrawn from large solution surface, capillary cell of Scheludko-Exerowa, and bubble under air-water interface. For most of the studied systems we observed a good correlation between the stability of the dynamic films and the foamability of the respective solutions. In contrast, no such correlation was seen with the results from the “classical” methods.

Fig. 1 Thinning of a foam film under dynamic conditions. This film ruptures 113 s after its formation, immediately after the third frame shown on the right-hand-side of this figure.
Adhesion Improvement of Electroless Copper Coatings by Thixotropic Additives

M. Radoeva¹, G. Georgiev² and B. Radoev²*

¹ – Bulgarian Academy of Science
² – Faculty of Chemistry and Pharmacy, University of Sofia
* - fhbr@chem.uni-sofia.bg

The problem with the adhesion of metal coatings is well known, but its solution, especially at smooth substrate surfaces in great extend remains open till nowadays. The standard way for adhesion improvement is substrate roughening but there are objects, where the roughening is unsuitable or even impossible (e.g. glass, steel, decoration surfaces). Adhesion increasing in such cases requires other methods. Encouraging results in this respect shows addition of the so-called thixotropic substances in metallization solutions. In our experiments we have used ethyl cellulose (EC) and a polyzwitterion polymer poly(dimethyaminoethykmethacryloyl propanesulfonate) (PDMAPS) showing pronounced stickering properties. Utilized was a standard copper bath, pure and with added thixotropic substances. Metalized were smooth epoxy fiber glasses, glass and stainless steel substrates. The deposition rate was 2-3 µm/h and the deposition thickness about 0.1÷0.3 µm. The thixotropic additives changed not substantially the deposition rate, in the same time they have shown stabilizing action on the electroless bath. At all cases thixotropic additives improved substantially the adhesion especially on smooth surfaces. The sticking mechanism has been investigated via analysis of viscous, wetting, electrochemical properties and EPR-spectrums. Most interesting correlations have been shown with respect to the viscous and wetting properties. So for instance it has been found, a drastic increase of the relative viscosity (up to 236%) of the bath solution by adding EC. Not so drastic, but enough expressive influence has been observed by the wetting properties: the solutions with EC/PDMAPS additives have shown highest degree of three phase contact angle hysteresis, compared with the bath solutions without thixotropic additives. The experimental results are qualitatively, quasi-quantitatively interpreted and discussed.

Acknowledgements:

The authors gratefully acknowledge the financial support of the National Bulgarian Scientific Fund (Grant No DDVU 02/43).
Capillary bridges (CB) are systems of liquid droplets wetting two other interfaces. Most popular CB variant is a droplet between two parallel plates. Even this relative simple system reveals number of interesting and non-trivial behaviors part of which are experimentally demonstrated and theoretically analyzed in the present study. The experimental setup consists of two plates parallel fixed at a micrometer with the help of which the two plates can be drawn nearer and apart. The processes taking part within BCs are recorded by a camera. Experiments are carried out with BCs of pure water between hydrophilic and hydrophobic surfaces. One of the most informative static parameters obtained from these measurements is the upper limit of distance at which a CB can be stretched, i.e. the upper CB’s stability limit. These experimental data are interpreted from the viewpoint of Rayleigh stability theory. The CB’s dynamic concerns the kinetics of capillary attraction. For that purpose the lower plate (the plate with the droplet on it) is mobile (not fixed) and when the upper plate touches the droplet cap, the droplet together with the adhered (lower) plate are set in motion. Actually the two plates are pressed together until a thin (less than 0.5 mm) liquid film between the plates is formed. The attraction kinetics is recorded and the corresponding rates are evaluated. The experimental data are interpreted as a balance of capillary inertia and viscose forces.
Low-frequency Shear Viscoelastic Relaxation in Liquids

Bair B. Damdinov\textsuperscript{1,2*}, Tuyana S. Dembelova\textsuperscript{2}, Dagzama N. Makarova\textsuperscript{2}

\textsuperscript{1} – Buryat State University, 670000, Russia, Ulan-Ude
\textsuperscript{2} – Institute of physical materials science of RAS (Sib. Div), 670047, Russia, Ulan-Ude
* - bdamdinov@bsu.ru

Micro inhomogeneous structure of liquids has been suggested. It is assumed that the liquid structures are fluctuating clusters which form and break. High- and low-viscosity liquids have no fundamental difference. They differ in quantity, namely the lifetime of clusters which in simple liquids is much smaller than that of high-viscosity liquids.

The low-frequency relaxation process in liquids and slow relaxation process in amorphous polymers have analogy. The mechanism of low-frequency viscoelastic relaxation in liquids associated with the decay of the cluster, which is a multi-step process with a relatively long relaxation time.

The activation energy of the low-frequency viscoelastic relaxation and the number of kinetic units in the cluster has been estimated by the cluster modeling.

This work is concerned to studying of the low-frequency viscoelastic relaxation in liquids by an acoustic resonance method. The cluster model has been carried out for the interpretation of low-frequency viscoelastic relaxation in liquids. The study of low-frequency elasticity of liquids may be important for understanding of the boundary layers of liquids and their structural features, stability of colloids, for the theory of structural component of the disjoining pressure, etc.

Acknowledgements:

Supported by Russian Foundation for Basic Research, project №12-02-98012-r_sibir_a.
Investigating Electro-steric Interactions of Weak Polyelectrolytes on Particle Surface through Monitoring Their Aggregation Kinetics

Baptiste Jaquet, Hua Wu and Massimo Morbidelli

Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland
* - baptiste.jaquet@chem.ethz.ch

The well-known use of polyelectrolytes1,2 to stabilize soap-free polymer particles is a very active area of industrial interest. The lack of quantitative kinetic model for fed-batch emulsion copolymerization processes with monomers of very different hydrophilicity and reactivity gives rise to a significant uncertainty about the detailed monomer distribution and architecture of the obtained particles. The synthesis of polyelectrolyte-covered particles using non-core-shell methods usually results in hydrophilic, pH- and salt-sensitive swellable layers of relatively small thickness, because they are used as additive in the material. This prevents the direct measurement of their physical properties using the usual techniques such as TEM or light scattering. It is therefore challenging to characterize the resulting particles and to predict trends in particle colloidal stability.

In this work, we use the particle aggregation kinetics obtained experimentally using various light scattering techniques as a tool to investigate steric interaction potential of weak polyelectrolytes on the particle surface. Our methodology is based on modelling of the measured Fuchs stability ratio, which links the aggregation kinetics to the interparticle potential. The interparticle potential is resulting from both charges and hydrophilicity of the polyelectrolyte layer. Therefore, modeling the potential using experimentally measured stability under various conditions provides a reliable insight into the mechanism of steric stabilization and general trends with polymerization conditions and particle composition. The investigated systems are various combinations of neutral acrylic monomers and weakly acidic acrylic monomers3.

Literature:


Acknowledgements:

Financial supports from the Swiss National Science Foundation (Grant No. 200020_147137/1) and BASF SE (Germany) are gratefully acknowledged.
Nanoscale Droplets and Thin Films of Ionic Liquids on Mica Surface

Zhantao Wang 1*, John Ralston 1

1 – Ian Wark Research Institute, UniSA, Mawson Lakes, SA5095, Australia
* wanzy044@mymail.unisa.edu.au

Ionic liquids (ILs) are promising candidates for wetting study due to their non-volatility and tunable physical properties [1]. In our study, nanoscale droplets of ionic liquid [bmim][TFSI] were produced by depositing the solution of this ionic liquid (IL) and extracting the solvent (ethanol) through evaporation [2]. By imaging these tiny droplets using tapping mode AFM, we revealed the coexistence of solid and liquid phases of [bmim][TFSI] on mica, similar to what was previously reported for another IL [bmim][PF6] [3]. The solid-like thin film between the tiny IL droplets was correlated with the precursor film in partial wetting and the possible autophobicity of this IL on mica. In addition, these nanoscale droplets of IL appeared to be nearly spherical (cap) on mica. By assuming an even distribution of this film, an attempt was also made to extract the line tension exhibited by these nanoscale droplets. The order of line tension obtained using the modified Young’s equation is in agreement with theoretical approximations.

Fig. 1 2-D and 3-D images of [bmim][TFSI] droplets on mica surface from tapping mode AFM.

Literature:

Acknowledgements:
Discussions with Dr Mihail Popescu and Dr Marta Krasowska are gratefully acknowledged.