Electric Double Layer Forces in Three Phase Contact Formation

Bart Follink [1]*, Marta Krasowska[1], 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-Al_2O_3 surface is negatively charged, while below this value α-Al_2O_3 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-Al_2O_3 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-Al_2O_3 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:

1. C. Yang, T. Dabros, D. Li, J. Czarnecki, J. H. Masliyah '*Measurement of the Zeta Potential of Gas Bubbles in Aqueous Solutions by Microelectrophoresis Method*' Journal of Colloid and Interface Science, 2001, 243, 128–135.

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, Utrecth 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:

1. Philipse Albert, Kuipers Bonny and Vrij Agienus. 2013. Algebraic Repulsions between Charged Planes with Strongly Overlapping Double Layers. Langmuir. 2859-2870.

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:

1. K. Nygård et al., 2012. Anisotropic pair correlations and structure factors of confined hard-sphere fluids: an experimental and theoretical study. Phys. Rev. Lett. 108:037802.

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 measurments 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|SiO$_2$ water interface.

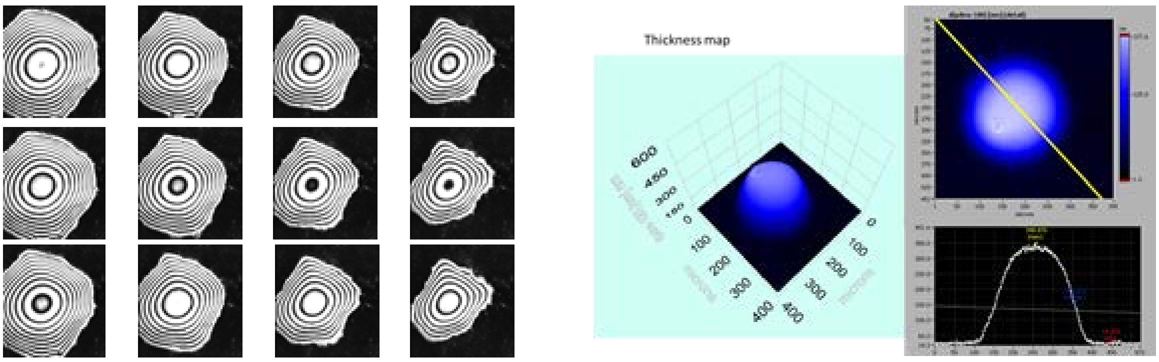
a) b)

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:

1. Oliver AE, Kendall EL, Howland MC, Babak S, Shreve AP, Parikh AN (2008) Protecting, patterning, and scaffolding supported lipid membranes using carbohydrate glasses. Lab Chip 8, 892–897
2. Howland MC, Szmodis AW, Sanii B, Parikh AN (2007) Characterization of Physical Properties of Supported Phospholipid Membranes Using Imaging Ellipsometry at Optical Wavelengths. Biophysical Journal 92, 1306–1317

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.

Coagulation by simple multivalent counterions

Johannes Lyklema.

Department of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6
6703 HB Wageningen, Netherlands
* - Hans.Lyklema@wur.nl

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 ψd of the diffuse part of the double layer is mostly not so high, in fact, at given ψd the dependence is rather as z-2. However, as ψd 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:

1. J.Lyklema, (2013) Coaguation by multivalent counterions and the Schulze-Hardy rule. J.Colloid Interface Sci. 392, 102.
2. M.L.Jiménez, A.V.Delgado and J.Lyklema, (2012). Hydrolysis versus ion correlation models in electrokinetic charge inversion: establishing application ranges. Langmuir 28, 6786.

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-].

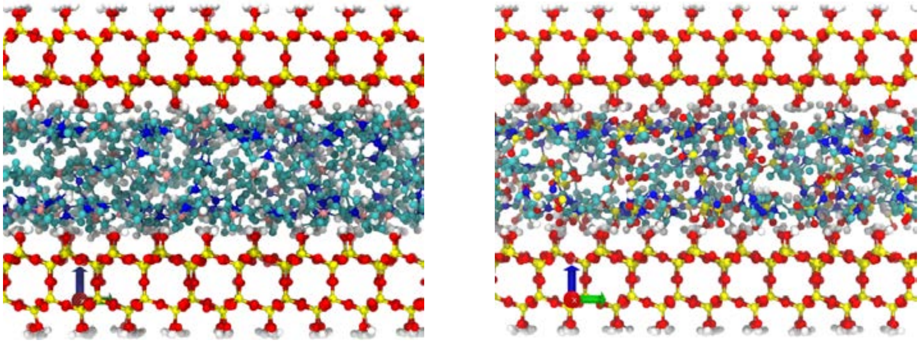

Fig. 1 Snapshot of the confined configurations for [BF4-] and [NTf2-] liquids.

Literature:

1. R. W. Carpick, 2006. Controlling Friction. Science 313: 184.
2. H. Wang, Q. Lu, C. Ye, W. Liu, Z. Cui, 2004. Friction and wear behaviors of ionic liquid of alkylimidazolium hexafluorophosphates as lubricants for steel/steel contact. Wear 256: 44.
3. K. Ueno, M. Kasuya, M. Watanabe, M. Mizukami, K. Kurihara, 2010. Resonance shear measurement of nanoconfined ionic liquids. Phys. Chem. Chem. Phys. 12: 4006.
4. X. Zhong, Z. Liu, D. Cao, 2011. Improved Classical United-Atom Force Field for Imidazolium-Based Ionic Liquids: Tetrafluoroborate, Hexafluorophosphate, Methylsulfate, Trifluoromethylsulfonate, Acetate, Trifluoroacetate, and Bis(trifluoromethylsulfonyl)amide. J. Phys. Chem. B 115: 10027

Aggregation of colloidal particles in ionic liquids

Tamás Szabó[1,2], Anthony Désert[2], Sabine Pita[2], István Szilágyi[2], Gregor Trefalt[2], Michal Borkovec[2,]*

[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 (BF_4) 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.

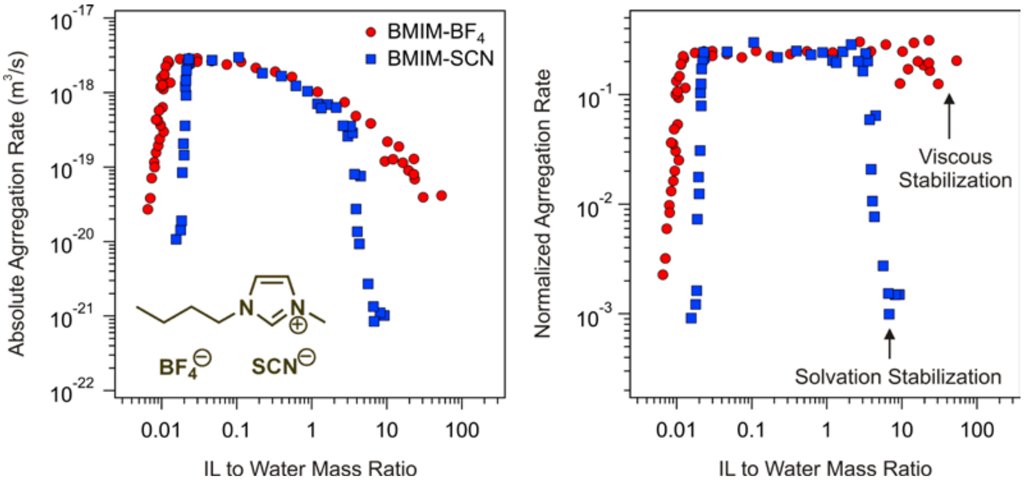

Fig. 1 Absolute (left) and normalized (right) aggregation rates versus the IL to water mass ratio of sulphate latex particles of 530 nm in diameter in BMIM-BF_4 and BMIM-SCN

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 BF_4^- 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.

Development of a System measuring Adhesion Forces in Powder Collectives

Stefanie Wanka[1], Michael Kappl[1]*, Markus Wolkenhauer[2], Hans-Jürgen Butt[1]

[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.

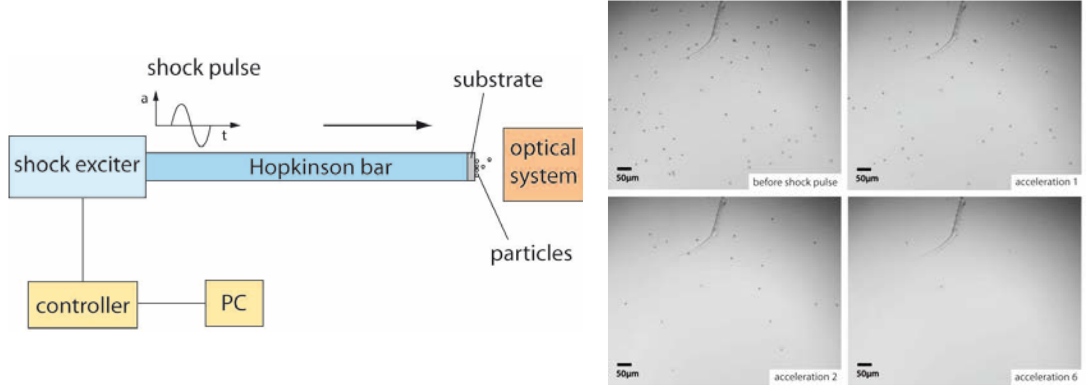

Fig. 1 Schematic of the Hopkinson bar method to measure adhesion forces of particles (left). Microscope images showing detachment of spherical silica particles (5 µm) with increasing acceleration of the substrate (right)

Literature:

1. Heyder, J. 2004. Deposition of Inhaled Particles in the Human Respiratory Tract and Consequences for Regional Targeting in Respiratory Drug Delivey. Proc Am Thorac Soc 1: p. 315-320.

2. Kappl, M., Butt, H.J. 2002. The colloidal probe technique and its application to adhesion force measurements. Particle & Particle Systems Characterization 19(3): p. 129-143.

3. Cappella, B., Butt, H.J., Kappl, M. 2005. Force measurements with the atomic force microscope: Technique, interpretation and applications. Surface Science Reports 59: p. 1-152.
4. Krupp, H. 1967. Adv. Colloid Interface Sci.1: p. 111.
5. Podczeck, F., Newton, J.M., James, M.B. 1995. Adhesion and friction between powders and polymer or aluminum surfaces determined by a centrifuge technique. Powder Technology 83(3): p. 201-209.
6. Nicklich, H., Brucke, M. 2007. Latest Design of Sine and Shock Exciters for Calibration Purposes. In IMEKO 20th TC3, 3rd TC16 and 1st TC22 International Conference, "Cultivating metrological knowledge": Merida, Mexico.
7. Nicklich, H., Brucke, M., Mende, M. 2009. The need for controlled shocks - A new type of shock exciter allows to apply well defined mechanical shocks, in XIX IMEKO World Congress Fundamental and Applied Metrology: Lisbon, Portugal.

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Ion specific structure of nano-confined electrolytes

R.M. Espinosa Marzal[1*], S. Liuzzi[2], S. Chodankar[2], M. Guizar-Sicairos[2], M. Heuberger[1,3] and J. Friso van der Veen[1,2]

[1] – *ETH Zurich, 8093 Zurich, Switzerland*
[2] – *Paul Scherrer Institut, 5232, Villigen PSI, Switzerland*
[2] – *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 (eSFA[1,2]) 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 insights[3]. 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 KNO_3). 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 direction[4]. 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:

1. Heuberger, M., J. Vanicek, and M. Zach, The extended surface forces apparatus. II. Precision temperature control. Review of Scientific Instruments, 2001. 72(9): p. 3556-3560.
2. Heuberger, M., The extended surface forces apparatus. Part I. Fast spectral correlation interferometry. Review of Scientific Instruments, 2001. 72(3): p. 1700-1707.
3. Espinosa-Marzal RM, Drobek T, Balmer T, Heuberger MP (2012a) Hydrated-ion ordering in electrical double layers. Physical Chemistry Chemical Physics 14 (17):6085-6093.
4. Chodankar, S., et al., Density profile of water in nanoslit. EPL (Europhysics Letters), 2012. 99(2): p. 26001.

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.

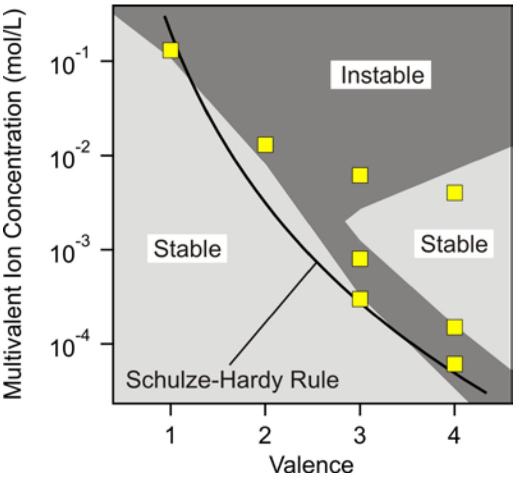

Fig. 1. Location of CCC values obtained from LS (symbols) and AFM (lines) measurements. The thick line indicates the Schulze-Hardy rule.

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 fourvalent 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.

Literature:

1. Prashant Sinha, Istvan Szilagyi, F. Javier Montes Ruiz-Cabello, Plinio Maroni, Michal Borkovec. 2013. Attractive Forces between Charged Colloidal Particles Induced by Multivalent Ions Revealed by Confronting Aggregation and Direct Force Measurements. Journal of Phyisical Chemistry Letters 4: 648-652.

Linear stability of falling films in the presence of soluble surfactants

George Karapetsas[1]*, Vasilis Bontozoglou[1]

[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.

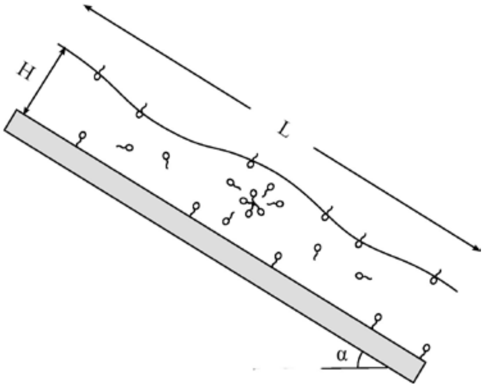

Fig. 1 Schematic of a falling film in the presence of soluble surfactants

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Near Wall Dynamics of Colloidal Suspensions Studied by Evanescent Wave Dynamic Light Scattering

Peter R. Lang[1*], Jan K. G. Dhont[1], Maciej Lisicki[2], Bogdan Cichocki[2], Jerzy. Bławzdziewicz[3], Simon Rogers[4], Benoit Loppinet[5]

[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 DelawareChemical and Biomolecular Engineering,Newark, DE19716, US
[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:

1. Cichocki, B. et al., J. Chem. Phys. 132, 074704 (2010)
2. Lisicki, M. et al., J. Chem. Phys. 136, 204704 (2012)
3. Lisicki, M. et al., in preparation
4. Michailidou. V. N. et al, Phys. Rev. Lett. 102, 068302 _2009_. [5] S. Rogers et al., PRL 109, 098305 (2012)
5. Rogers, S. et al., Phys.Rev. Lett 109, 098305 (2012)
6. Loppinet, B. et al., Eur. Phys. J. E 35, 62 (2012).

Acknowledgements:

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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.

Automated method for measurement of dynamic contact angles of liquid

Mihail Z. Avramov[1]*, Ivan T. Ivanov[1], Borian P. Radoev[1]

[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 liqud 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 hystersis, 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 θ_A,θ_R (Fig 1a). The direct force balance shows proportionality between F, and $\left|\cos\theta_A - \cos\theta_R\right|$. 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 $F \sim \left|H_A - H_R\right|$.

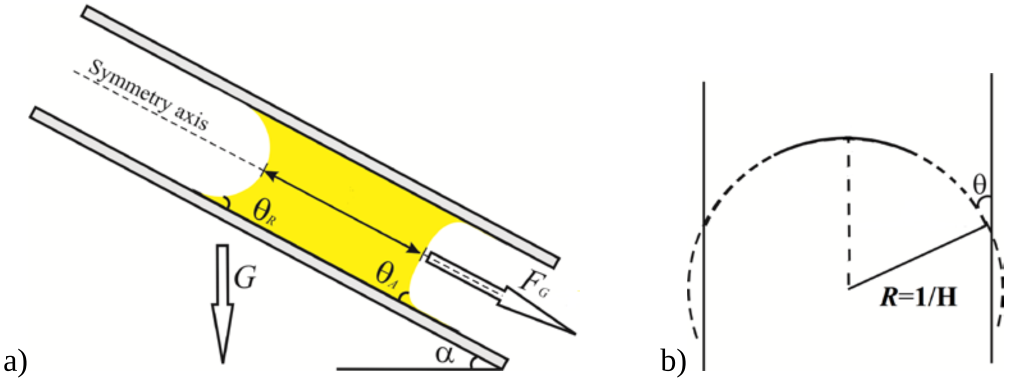

Fig. 1 a) Sketch of an inclined capillary tube partly filled with liquid. b) Scheme of meniscus profile; operative for the curvature determination is only the profile part at the meniscus cap (the solid curve).

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 form optical and mechanical viewpoints.

Acknowledgements:

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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:

1. Plum, Markus A.; Menges, Bernhard; Fytas, eorg.; Butt, Hans-Jürgen.; Steffen, Werner, 2011, Resonance enhanced dynamic light scattering. ;*Review of Scientific Instruments* 82, (1), 015102-015102-11.
2. Plum, Markus A.; Vianna, Sulivan D. B.; Unger, Andreas; Roskamp, Robert F.; Butt, Hans-Jürgen; Menges, Bernhard; Steffen, Werner, 2011, Probing dynamics near surfaces: waveguide enhanced dynamic light scattering.; *Soft Matter* 7, (4), 1501-1505.
3. Haghighi, Maryam, Plum, Markus A., Gantzounis, Georgios, Butt, Hans-Jürgen, Steffen, Werner, and Fytas, George; 2013, Plasmon-Enhanced Dynamic Depolarized Light Scattering; *J. Phys. Chem. C*, 117 (16), 8411–841.

Interfacial Water Studied by Surface Forces Measurement

Kazue Kurihara[1,2]*, Masashi Mizukami [2], and Motohiro Kasuya[2]

[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 ($\gamma = 79.3 \pm 2.0$ mN/m) was estimated from the pull-off force, and was significantly larger than the value for the bulk water/cyclohexane interface ($\gamma = 50.1$ 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:

1. M. Mizukami, A. Kobayashi, K. Kurihara, 2012, Langmuir, **28**,14284.
2. M. Kasuya, M. Hino, H. Yamada, M. Mizukami, H. Mori, S. Kajita, T. Ohmori, A. Suzuki, K. Kurihara, submitted.

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Surface Forces in the Theory of Deliquescence Transition at Nucleation of a Solvent Vapor on Soluble Nanoparticles

Alexander Shchekin[1]*, Ilya Shabaev[1], Olaf Hellmuth[2]

[1] *-St Petersburg State University, Department of Statistical Physics, St Petersburg, Russia*
[2] *-Leibniz Institute for Tropospheric Research, Leipzig, Germany*
* - akshch@list.ru

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:

1. Shchekin A.K. and Rusanov A.I. 2008. Generalization of the Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations for a liquid film on a soluble nanoparticle, *J. Chem. Phys.* **129**: 154116.
2. Shchekin A.K., Shabaev I.V., and Rusanov A.I. 2008. Thermodynamics of droplet formation around a soluble condensation nucleus in the atmosphere of a solvent vapor, *J. Chem. Phys.* **129**: 214111.
3. Shchekin A.K., Shabaev I.V. , and Hellmuth O. 2013. Thermodynamic and kinetic theory of nucleation, deliquescence and efflorescence transitions in the ensemble of droplets on soluble particles, *J. Chem. Phys.*, **138**: 054704.

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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:

1. Schurtenberger, E. and M. Heuberger, *The extended surface forces apparatus. Part IV: Precision Static Pressure Control.* Review of Scientific Instruments, 2011. **82**(103902): p. 8.
2. Schurtenberger, E. and M. Heuberger, *Supercritical Casimir Effect in Carbon Dioxide.* Journal of Supercritical Fluids, 2012. **71**: p. 120-126.

Bubble bouncing and stability of liquid films formed under dynamic and static conditions from n-octanol solutions

Dominik Kosior[1]*, Jan Zawala[1], Roumen Todorov[2], Dotchi Exerowa[2], Kazimierz Malysa[1]

[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 concentration 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 $4{\cdot}10^{-6}$ M n-octanol concentration, respectively) due to diminishing of the bouncing amplitude. Further concentration increase, above a “threshold” value ($5{\cdot}10^{-6}$ 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.

Film hydrodynamic boundary conditions on bubble-surface impact

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

[1] *Institute of High Performance Computing, 1 Fusionopolis Way, 138632 Singapore*
[2] *Physics of Fluids, University of Twente, Enschede 7500 AE, The Netherlands*
[3] *Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore*
[4] *University of Melbourne, Parkville VIC 3010 Australia*
[5] *Swinburne University of Technology, Hawthorn VIC 3122 Australia*
* - D.Chan@unimelb.edu.au

We present a detailed experimental studies [1, 2] 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.

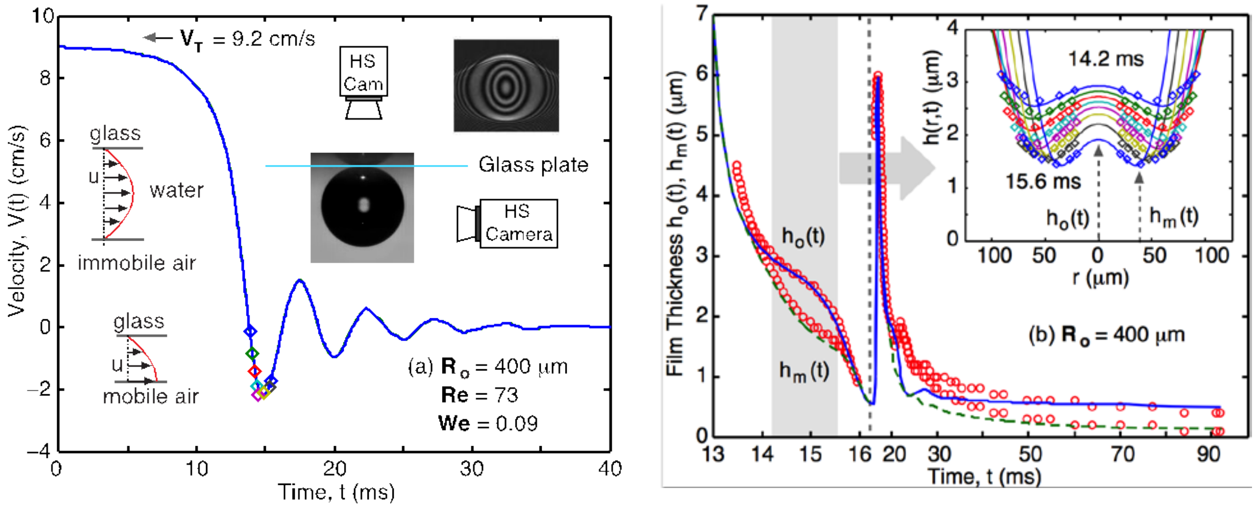

Fig. 1 (a) The experimental setup that measures the velocity, $V(t)$ of the centre of mass of a rising bubble (radius R_o) and the interference pattern of the trapped water film as it collides and bounces against a glass plate after reaching terminal velocity, V_T. The Reynolds, Re and Weber, We numbers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

Literature:

1. M. H. W. Hendrix, R. Manica, E. Klaseboer, D. Y. C. Chan, C.-D. Ohl (2012) Phys Rev Letts 108: 247803.
2. R. Manica, M. H. W. Hendrix, R. Gupta, E. Klaseboer, D. Y. C. Chan, C.-D. Ohl, D. Y. C. Chan (2013) To be published.

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Experimental and Numerical Study of Capillary Transport between Parallel Perforated Plates in Microgravity

Diana Gaulke [1]*, Michael E. Dreyer[1]

[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.

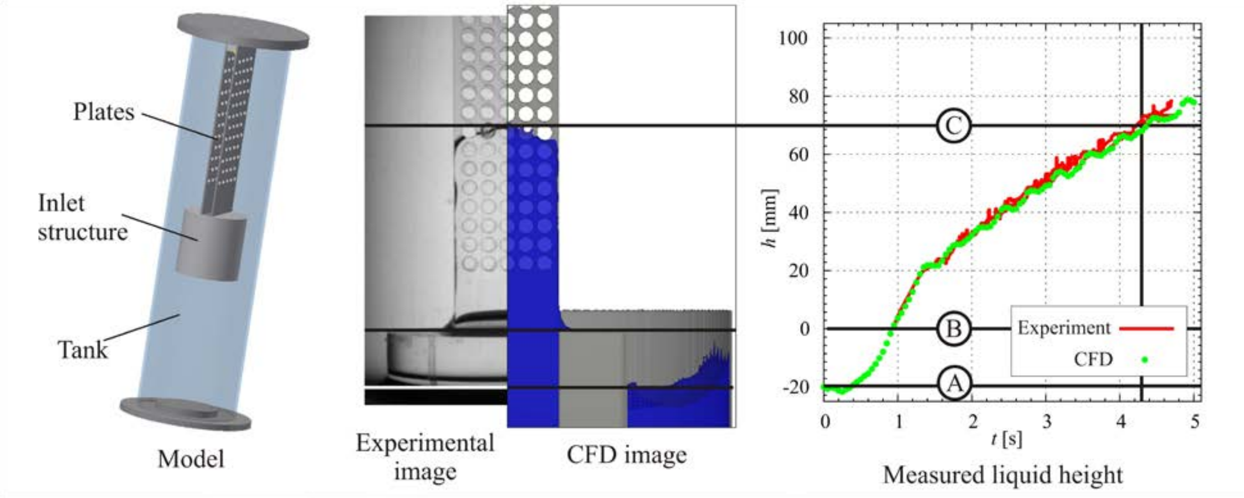

Fig. 1: Image of experimental model, the experimental and the numerical liquid distribution at time $t = 4.25$ s and an example of the measured data of this geometry (Line A: initial fill level, Line B: begin of parallel plates, Line C: liquid height at t)

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.

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Adhesive Behavior of Extracted Latex Polymers Towards Silicon oxide and Cellulose

Cecilia Lidenmark[1], Torbjörn Pettersson[2,3]*, Ola J. Karlsson[4], Shannon M. Notley[5], Magnus Norgren[1], Håkan Edlund[1]

[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.

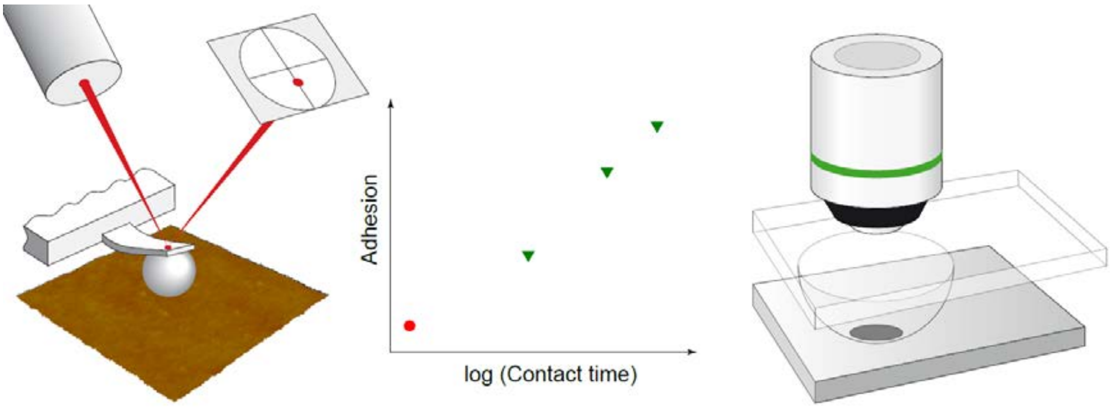


Fig. 1 Adhesion measurements with AFM colloidal probe have been compared with macroscopic JKR-measurements

A New Method for Electro-Microinterferometric Studies of Water-in-Oil Emulsion Films: Development and Application with Natural and Synthetic Surfactants

Nikolay Panchev[1,*], Khristo Khristov[1], Jan Czarnecki[2]

[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:

1. Panchev, N., Khristov, K., Czarnecki, J., Exerowa, D., Bhattacharjee, S., Masliyah, J. 2008. Colloid Surf A 315: 74–78.

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).

Two-component miscibility of partially fluorinated alcohols (*F*6*Hm*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 (π)−molecular area (A) and surface potential (ΔV)−A isotherms were measured for two-component monolayers made of DPPC and partially fluorinated alcohols of (perfluorohexyl)nonanol (*F*6*H*9OH) and (perfluorohexyl)undecanol (*F*6*H*11OH) 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 π–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 *F*6*H*9OH and *F*6*H*11OH 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 *F*6*H*9OH fluidizes DPPC monolayers, whereas *F*6*H*11OH solidifies them. This study provides a fundamental insight into the molecular function of biomembrane components and support for biomedical use of fluorinated materials.

Literature:

1 S. Nakamura, H. Nakahara, M.P. Krafft, O. Shibata, *Langmuir*, 23, 12634-12644 (2007).

2 H. Nakahara, M.P. Krafft, A. Shibata, O. Shibata, *Soft Matter*, 7, 7325–7333 (2011).

3 H. Nakahara, A. Ohmine, S. Kai, O. Shibata, *J. Oleo Sci.*, in press (2013).

Destabilisation of gas condensate-water emulsions and separation by dissolved air flotation using new non ionic surfactants

A.M.Al-sabagh[1], M.R. Noor El-din[1,*], Khaled M. Hussein[2] and A.M. Sharaky[3]

[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*
* - mrned04@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 monoamide to treat gas condensate-in-water emulsion. The chemical structure of the prepared ethoxylated demulsifier was confirmed using FT-IR and ^{1}HNMR 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:

1. H. Al-Zoubi, S. Al-Thyabat, L. Al-Khatib, A hybrid flotation–membrane process for wastewater treatment: an overview, Desalination and Water Treatment, 7 (2009) 60–70.
2. DA Rosa and Rubio J (2005) The FF (flocculation-flotation process).Miner. Eng. 18 (7) 701-707
3. A.A. Al-Shamrania, A. Jamesa,, H. Xiao, (2002) Destabilisation of oil–water emulsions and separation by dissolved air flotation, Water Research 36, 1503–1512.
4. Gregory R, Zabel T. In: Pontius FW, Water quality and treatment, 4th ed. New York: McGraw-Hill, p. 367–453, 1990.
5. Offringa G. (1995) Dissolved air flotation in Southern Africa. Water Sci Technol;31(3-4):159–72.
6. Boyd JL, Shell GL, Dahlstrom DA. Treatment of oily wastewater to meet regulatory standards. AIChE Conference, Toledo, OH, 1971.
7. Takahashi T, Miyahara T, Nishizaki Y. (1979) Separation of oily water by bubble column. J Chem Eng Jpn;12(5):394–9.

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.

Conductivity of Aqueous Wetting Films

Stanislav Itskov[1]*, Vladimir Sobolev[1], Natalia Esipova[1]

[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**.

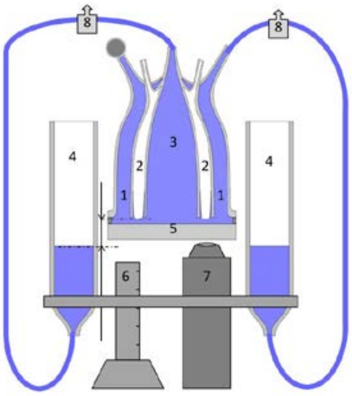


Fig.1. Experimental cell

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 8×10^{-10} Cm and 1.3×10^{-9} Cm that is lower than the previously published data.

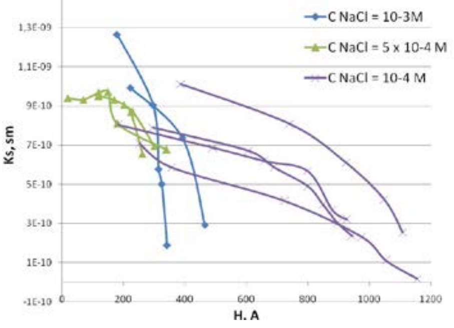


Fig.2. Experimental data of surface conductivity of NaCl solutions on quartz surface.

Literature:

1. Derjaguin B.V., Zorin Z.M., Churaev N.V., Shishin V.A. Examination of thin layersof liquids on various solid substrates. /Wetting, spreading and Adhesion. L.:Acad. Press, 1977, p.201-212
2. Sheludko A., Platikanov D. Untersuchung dunner flussigerschuchten auf Quecksilber./ Kolloid. Zeit. -1961. -B.175 -N2. -S.150

Hydrodynamic Cavitation: A Bottom-Up Approach to Liquid Aeration

Janhavi Raut[1], Simeon D. Stoyanov[2, 3, 4], Charu Duggal[5], Edward G. Pelan[2], Luben N. Arnaudov[2*], and Vijay M. Naik[6]

[1] *Unilever Research & Development, Colworth House, Sharnbrook, Bedfordshire MK44 1LQ, UK*
[2] *Unilever Research & Development, 3133AT Vlaardingen, The Netherlands*
[3] *Laboratory of Physical Chemistry and Colloid Science, Wageningen University, 6703 HB Wageningen, The Netherlands*
[4] *Department of Mechanical Engineering, UCL, Torrington Place, London, WC1E7JE, UKs*
[5] *Unilever Research & Development, 64 Main Road, Whitefield, Bangalore 560066, India*
[6] *Department of Chemical Engineering, Indian Institute of Technology, Bombay, Powai, India*
* - luben.arnaudov@unilever.com

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

Effect of surface diffusivity on the head-on coalescence of viscous drops with insoluble surfactants-Difference between polymeric systems and oil/water emulsions

Carolina Vannozzi [1]*

[1] – *University of California Santa Barbara, Santa Barbara, 93106, CA, USA*
* - carolina.vannozi@gmail.coml

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

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

Literature:

1. Vannozzi C., 2012. Coalescence of surfactant covered drops in extensional flows-Effects of the interfacial diffusivity. Phys. Fluids 24: 082101.
2. Yoon Y., Hsu A., Leal L.G., 2007. Experimental investigation of the effects of copolymer surfactants on flow-induced coalescence of drops. Phys. Fluids 19: 023102
3. Cristini V., Blawzdziewicz J. , Loewenberg M. 1998. Near-contact motion of surfactant-covered spherical drops. J. Fluid Mech. 366:259

Coalescence of Repelling Colloidal Droplets : A Route to Monodisperse Populations

Kevin Roger [1]*, Robert Botet [2] and Bernard Cabane [1]

[1] – *PMMH, ESPCI, CNRS*
[2] – *LPS, CNRS*
* - kevin.roger@espci.fr

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

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

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

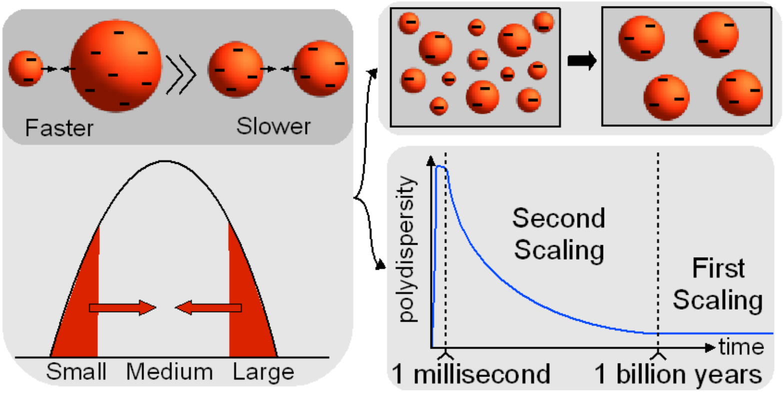


Fig. 1 If coalescence is hindered by repulsions that increase with the size of the droplets, small+large encounters of droplets are favored over medium+medium encounters, which results in a decrease of the polydispersity according to the second-scaling law.

Literature:

1. Kevin Roger[1], Robert Botet[2] and Bernard Cabane[1]. 2013. Coalescence of Repelling Colloidal Droplets : A route to Monodisperse Populations. Langmuir.

Kinetics of drop breakage and drop-drop coalescence in turbulent flow

S. Tcholakova,* N. Vankova, N. Denkov

Department of Chemical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, 1 J. Bourchier Ave.,1164 Sofia, Bulgaria
* - sc@lcpe.uni-sofia.bg

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

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

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

References:

1. S. Tcholakova et al. *Langmuir* **2011**, *27*, 14783–14796.
2. S. Tcholakova et al. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1608-1627.
3. N. Vankova et al., *J. Colloid Interface Sci.* **2007**, *312*, 363-380.
4. N. Vankova et al., *J. Colloid Interface Sci.* **2007**, *313*, 612-629.
5. S. Tcholakova et al., *J. Colloid Interface Sci.* **2007**, *310*, 570-589.
6. S. Tcholakova et al., *Langmuir* **2004**, *20*, 7444-7458.

Shear Stability and Gelation of Inverse Emulsions

Stefano Lazzari, Giovanni M. Maggioni, Miroslav Soos, Hua Wu and Massimo Morbidelli*

Institute for Chemical and Bioenigneering, Department of Chemistry and Applied Sciences, ETH Zurich, 8093 Zurich, Switzerland
* - Massimo.morbidelli@chem.ethz.ch

Inverse emulsions (IE) are of utmost importance in a great variety of industrial areas, such as cosmetics, pharmaceutics and oil industry. Many studies have been devoted to their preparation, stabilization and destabilization mechanisms[1]. Despite this, no investigation has been reported in the literature on the shear-induced aggregation of IEs. Therefore, the aim of this work is *i)* to explore the possibility of the shear-induced gelation in IEs and *ii)* to identify the key parameters that regulate the observed destabilization and gelation phenomena.

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

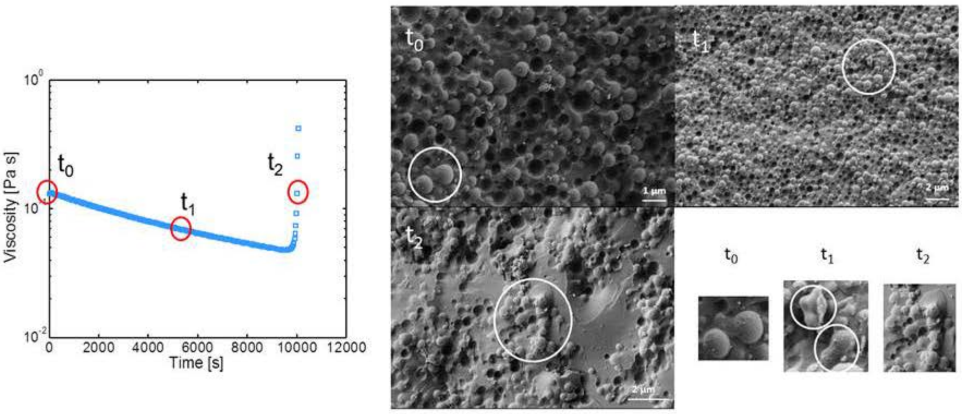


Fig. 1 Viscosity profile of an IE undergoing shear thinning, coalescence and aggregation.

With respect to that of non-coalescing colloidal systems, the shear-induced gelation[2] of the IE systems results clearly from a different mechanism: coalescence slows down the gelation process by reducing the total occupied volume of the clusters. Only when the aggregation rate becomes faster than the coalescence rate, the gelation phenomenon becomes possible. Through the shear-induced gelation, we have identified the main parameters affecting the shear-stability of the IE systems, and their effects can be well interpreted by considering their role in altering the competition between coalescence and aggregation kinetics.

Literature:

1. I. Capek, Adv. Colloid Interface Sci., 2010, 156, 35-61
2. A. Zaccone, H. Wu, D. Gentili and M. Morbidelli, Physical Review E, 2009, 80

Micelle-Like Aggregates in Surfactant-Free Ternary Mixtures

Sebastian Schöttl[1], Werner Kunz[1], Thomas Zemb[2], and Dominik Horinek[1*]

[1] – *Institut für Physikalische und Theoretische Chemie, Universität Regensburg,*
Universitätsstraße 31, 93053 Regensburg, Germany
[2] – *ICSM, Marcoule uMR5257 CEA/CNRS/UM2/ENSCM, 30207 Bagnols sur Cèze, France*
* - dominik.horinek@ur.de

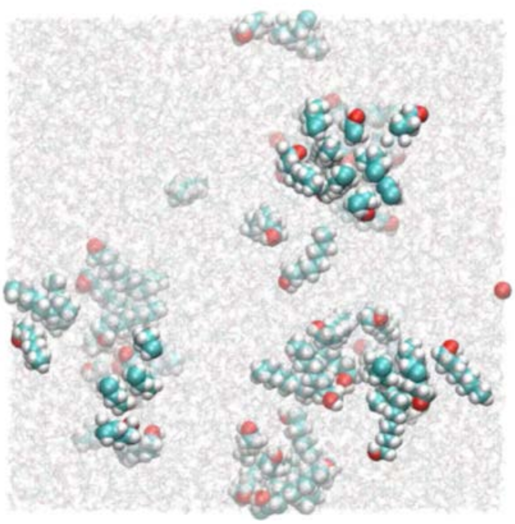


Fig.1. Snapshot of aggregates in an octanol/ ethanol/ water ternary mixture. The mole fractions of ethanol and octanol are 0.2 and 0.007.

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

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

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

Liron Bitan-Cherbakovsky, Abraham Aserin, and Nissim Garti*

The Ratner Chair of Chemistry, Casali Institute of Applied Chemistry, The Institute of Chemistry, The Hebrew University of Jerusalem, Edmond J. Safra Campus, Givat Ram, Jerusalem 91904, Israel.
* - garti@mail.huji.ac.il

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

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

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

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

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

Carlos Bravo-Díaz[1] and Laurence S. Romsted[2]*

[1] – *Universidad de Vigo, Spain*
[2] – *Rutgers, The State University of New Jersey, New Brunswick, NJ USA*
* - romsted@rutchem.rutgers.edu

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

The effect of surfactant on the observed rate constant for reduction of an arenediazonium ion, 16-ArN_2^+, probe by an uncharged antioxidant, AO, e.g., TBHQ (**Fig. 2**), is modeled by assuming that the AO distributes between the oil, interfacial and aqueous regions of an emulsion, but the reactive group of the surfactant like 16-ArN_2^+ is only located in the interfacial region. Values of k_{obs} are obtained by electrochemical and spectrometric methods, physical separation of the phases is not required, and the data are fit with a kinetic model that provides estimates of the partition constants, P_O^I and P_W^I, for the distribution of the AO and of k_I, for reaction in the interfacial region.

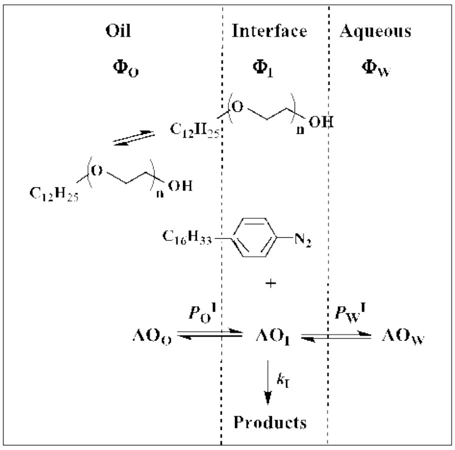
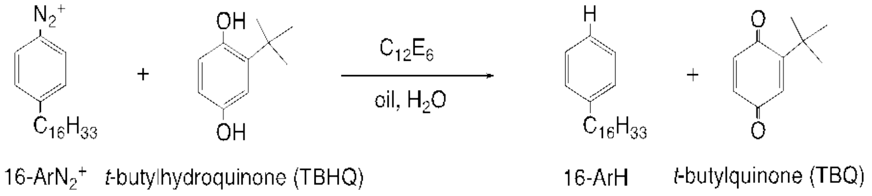


Fig. 1. Emulsion regions➔

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



↑Fig. 2. TBHQ/16-ArN_2^+ reaction.

Literature:

(1) Romsted, L. S.; Bravo-Diaz, C. 2013. Modeling chemical reactivity in emulsions, *Current Opinion in Colloid and Interface Science* **2013**, *18*, 3. **Overview**.

(2) Romsted, L. S. "Introduction to Surfactant Self-Assembly," In *Supramoleular Chemistry from Molecules to Nanomaterials*; 2012. Gale, P. A., Steed, J. W., Eds.; John Wiley & Sons: Chichester, Vol. 1, p 181. **Encyclopedia Chapter**.

Connecting fundamental phenomena and the characteristics of emulsions produced by microfluidics

Claire C. Berton-Carabin and Karin Schroën*

Wageningen University, The Netherlands
* - karin.schroen@wur.nl

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

Recent work has focused on characterizing the formation of emulsion droplets in microfluidic systems, *e.g.*, T-junctions[1], flow focusing devices[2], and microchannels[3]. In the case of small, food relevant-sized droplets, *i.e.*, typically of a few µm, the known scaling relations describing the formation of millimetre-scale droplets no longer apply directly. In fact, the interfacial tension can then no longer be approached by values measured under equilibrium conditions.

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

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

Literature:

1. Van der Graaf S., Nisisako T., et al. 2006. Lattice Boltzmann simulations of droplet formation in a T-shaped microchannel. Langmuir 22: 4144-4152.
2. Ganan-Calvo A. 1998. Generation of steady liquid microthreads and micron-sized monodisperse sprays in gas streams. Physical Review Letters 80: 285-288.
3. Van Dijke K., Schroën C., et al. 2008. Microchannel emulsification: from computational fluid dynamics to predictive analytical model. Langmuir 24: 10107-10115.
4. Steegmans M., Warmerdam A., et al. 2009. Dynamic interfacial tension measurements with microfluidic Y-junctions. Langmuir 25: 9751-9758.

Water in Oil Emulsions either regularly cooled or stored at sub ambient temperatures. Determination of the amount of ice formed.

Danièle Clausse[1] *, Jean Louis Lanoisellé[2]

[1] - Université de Technologie de Compiègne, TIMR. [2] – Université de Bretagne Sud, LIMATB
* - daniele.clausse@utc.fr

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

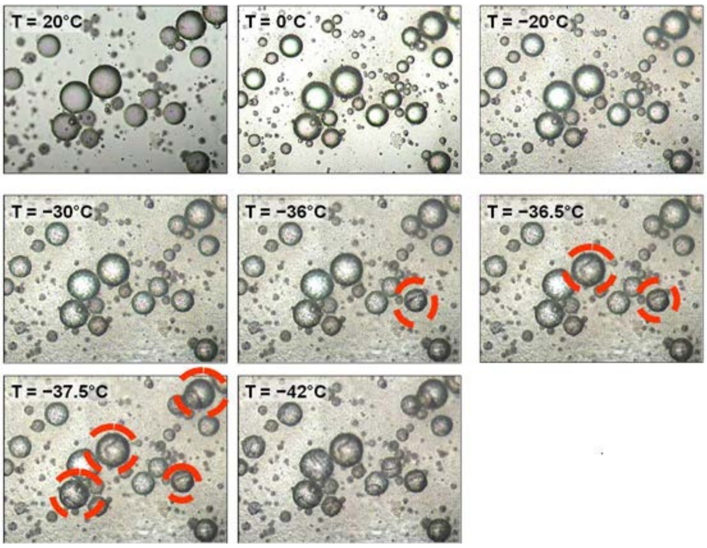


Figure 1: Photography of an emulsion showing the progressive freezing of the droplets during cooling. At – 42°C all the droplets are frozen.

Literature:

1. **Clausse D**.,Gomez F., Pezron I., Komunjer L. Morphology characterization of emulsions by differential scanning calorimetry. Advances in Colloid and Interface Science. 2005, 117, 59-74.

Acknowledgements: thanks to the European projects FASES supported by ESA

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

David Schäffel, Roland Staff, Hans-Jürgen Butt, Katharina Landfester, Daniel Crespy and Kaloian Koynov*

Max Plack Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
* - koynov@mpip-mainz.mpg.de

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

Literature:

1. Schwille P., Meyer-Almes F.-J., Rigler R. 1997. Dual-color fluorescence cross-correlation spectroscopy for multicomponent diffusional analysis in solution. Biophys. J. 72: 1878-1886.
2. Schaeffel D., Staff R.-H., Butt H.-J., Landfester K., Crespy D., Koynov K. 2012. Fluorescence correlation spectroscopy directly monitors coalescence during nanoparticle preparation. Nano Letters 12: 6012-6017.
3. Staff R., Schaeffel D., Turshatov A., Donadio D., Butt H.-J., Landfester K., Koynov K., Crespy D. 2013. Particle Formation in the Emulsion-Solvent Evaporation Process. Small DOI: 10.1002/smll.201300372.

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

Piotr Korczyk, Marine Jacquet, Mihail Popescu, Marta Krasowska, and David A. Beattie*

Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095
* - David.Beattie@unisa.edu.au

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

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

Acknowledgements:

PK acknowledges the support of a Marie Curie Actions IOF award. DB acknowledges the support of the Australian Research Council for his Future Fellowship award.

Adsorption Layers and Foam Films from β-Lactoglobulin

Georgi Gochev[1,2*], Dotchi Exerowa[2], Reinhard Miller[1]

[1] *Max-Planck-Institute for Colloid and Interface Science, D-14476 Golm, Germany*
[2] *Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
* - Georgi.Gochev@mpikg.mpg.de

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

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

Literature:

References should be placed immediately below end of main text according to citation below:

1. Exerowa D and Kruglyakov PM, *Foam and Foam Films.* Elsevier, 1998.
2. Krasowska, M., Hristova, E., Khristov, Khr., Malysa, K., Exerowa, D, 2006, *Isoelectric state and stability of foam films, bubbles and foams from PEO-PPO-PEO triblock copolymer (P85).* Colloid Polymer Sci 284:475-481.
3. Alahverdjieva, V.S., Khristov, Khr., Exerowa, D., Miller, R., 2008, *Correlation between adsorption isotherms, thin liquid films and foam properties of protein/surfactant mixtures: Lysozyme/C10DMPO and lysozyme/SDS.* Colloids Surfaces A, 323:132-138.
4. Kotsmar, Cs., Arabadzhieva, D., Khristov, Khr., Mileva, E., Grigoriev, D.O., Miller, R., Exerowa, D., 2009, *Adsorption layer and foam film properties of mixed solutions containing β-casein and C12DMPO.* Food Hydrocolloids 23:1169-1176.

Acknowledgements:

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On the Elasticity of Liquid Marbles

Samuel Asare-Asher, Jason Connor & Rossen Sedev

[1] *Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia*
* - rossen.sedev@unisa.edu.au

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

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

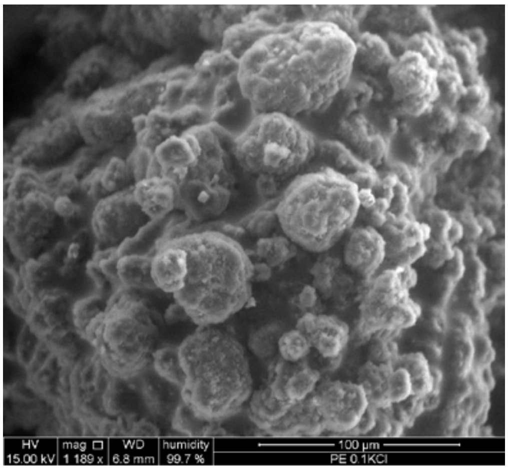

Fig. 1 The surface of a millimeter-size liquid marble seen with an ESEM.

Literature:

1. Aussillous P. and Quere D. (2001) Liquid Marbles, *Nature*, 411, 924.
2. McHale G. and Newton M.I. (2011) Liquid Marbles: Principles and Applications, *Soft Matter*, 7, 5473.

Protein microgels stabilize water-in-water emulsions by absorbing at the interface.

Bach T. Nguyen, Taco Nicolai *, Lazhar Benyahia

LUNAM, Université du Maine, IMMM UMR CNRS 6283, PCI, 72085 Le Mans cedex 9, France
* - Taco.Nicolai@univ-lemans.fr

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

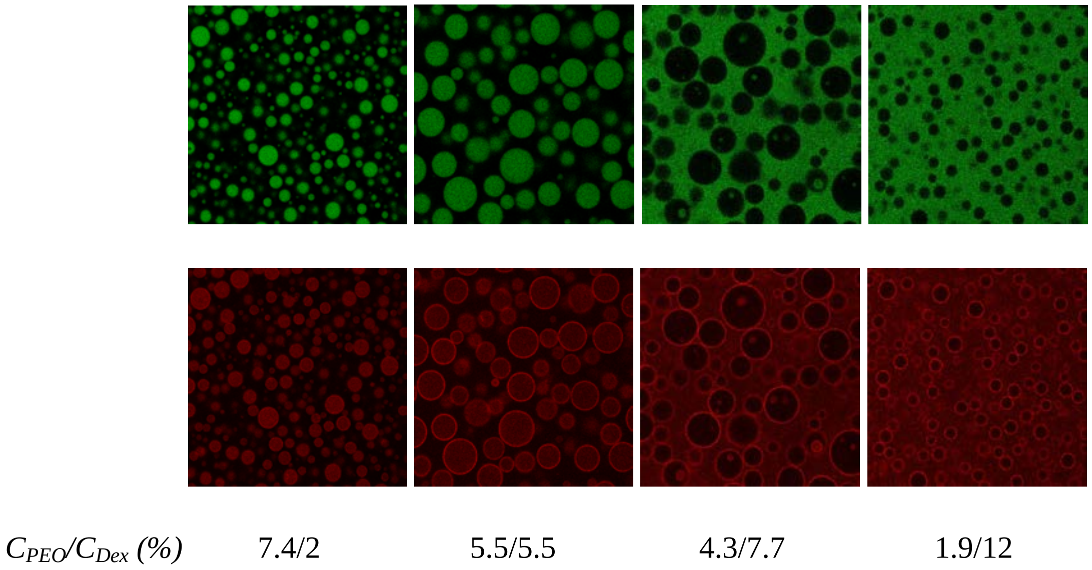

Fig. 1 Confocal microscopy images (160x160µm) of the dextran signal (green, top) and the protein signal (red, bottom) for PEO/dextran mixtures in the presence of 0.5wt% protein particles (R_h=150nm) for different polymer compositions on the same tie-line indicated in the figure.

Numerical simulation of bubble dissolution and Ostwald ripening in paint films

Tatiana Gambaryan-Roisman [a,b]*, Quinglu Lin [a,b], Joachim Venzmer[c], Michael Klostermann[c]

[a]*Institute of Technical Thermodynamics, Technische Universität Darmstadt, Petersenstr. 17, 64287 Darmstadt*
[b]*Center of Smart Interfaces, Technische Universität Darmstadt, Petersenstr. 17, 64287 Darmstadt*
[c]*Evonik Industries AG, Goldschmidtstr. 100, 45127 Essen*
* - gtatiana@ttd.tu-darmstadt.de

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

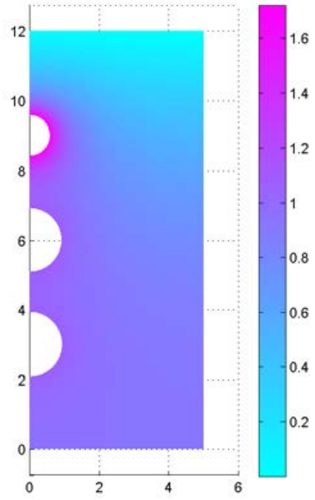

Fig. 1 Dimensionless concentration distribution of dissolved gas

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

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

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

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

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

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

Literature:

1. Ostwald W. 1896. Lehrbuch der allgemeinen Chemie. Vol 2, Part 1.

Particle stabilized foams – a journey through length scales

Adrian Carl*, Anne Bannuscher, Regine von Klitzing

TU Berlin, Institut für Physikalische Chemie, Straße des 17. Juni 124, 10623 Berlin
* - adrian.carl@mailbox.tu-berlin.de

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

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

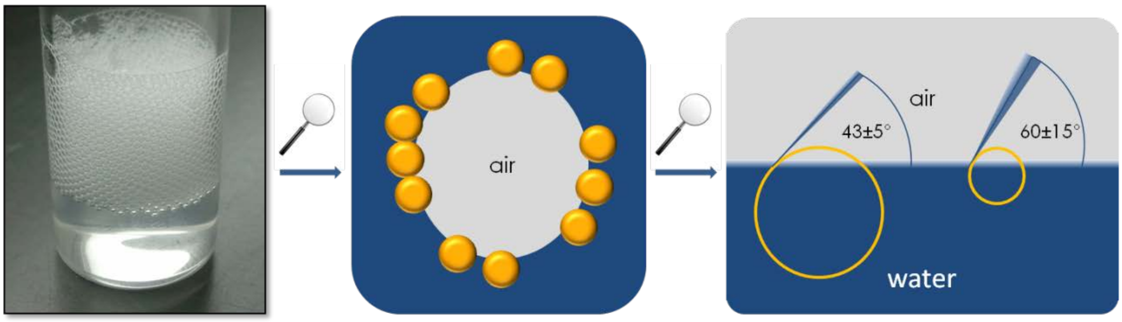

Fig. 1 Foam stabilization by nanoparticles – a multi-scale problem

1. Gonzenbach, Urs T.; Studart, André R.; Tervoort, Elena; Gauckler, Ludwig J. (2006). Ultrastable Particle-Stabilized Foams. Angew. Chem. Int. Ed 45 (21): 3526–3530.
2. Carl, Adrian; von Klitzing, Regine (2011). Smart Foams: New Perspectives Towards Responsive Composite Materials. Angew. Chem. Int. Ed 50 (48): 11290–11292

Pickering emulsions stabilized by nanoparticles of bare silica. Adsorption of nanoparticles and emulsion stability

Laure Ridel [*], Marie-Alexandrine Bolzinger, Yves Chevalier

University of Lyon 1, LAGEP, CNRS UMR 5007, 69622 Villeurbanne, France.
* - ridel@lagep.univ-lyon1.fr

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

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

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

Emulsification of diisopropyladipate oil droplets using Ludox™ AS40 silica stabilizing nanoparticles was successful up to 60% oil content (Fig. 1). An unusual dependence of the oil droplet diameter with respect to silica content occurs. The linear dependence $D = \frac{6}{\rho_{\mathrm{oil}}\, a_{\mathrm{SiO_2}}} \frac{M(\mathrm{oil})}{M(\mathrm{SiO_2})}$ expected for full adsorption of solid particles was not followed, although it is generally followed over a wide silica concentration domain [2],[3].

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

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

1. Frelichowska J., Bolzinger M.-A., Chevalier Y. 2009. Pickering emulsions with bare silica. Colloids Surfaces A 343:70-74.
2. Frelichowska J., Bolzinger M.-A., Chevalier Y. 2010. Effects of solid particle content on properties of o/w Pickering emulsions. J. Colloid Interface Sci. 351: 348-356.
3. Arditty S., Whitby C.P., Binks B.P.,Schmitt V., Leal-Calderon F. 2003. Some general features of limited coalescence in solid-stabilized emulsions. Eur. Phys. J. E 11, 273–281.

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

Rafael Muñoz-Espí,* Viktor Fischer, and Katharina Landfester

Max Planck Institute for Polymer Research, Ackermannweg 10, 55118 Mainz, Germany
* - munoz@mpip-mainz.mpg.de

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

Our work focuses on the versatility of heterophase systems like miniemulsions in the synthesis of multifunctional nanoparticles. We have shown that inorganic/polymer hybrids can be prepared by in-situ formation of metal oxide (CeO_2, Fe_2O_3, Fe_3O_4, ZnO) nanocrystals on the surface of polystyrene particles functionalized with hydrophilic groups [2]. The approach can be carried out in both aqueous and alcoholic media, which implies that it can be extended to a wide range of inorganic materials, including different chalcogenides. By combining the in-situ precipitation at the surface of particles with an additional encapsulation of previously formed inorganic nanoparticles in the polymer core, we have succeeded on preparing a “second generation” of multifunctional particles containing a magnetoresponsive inorganic component (Fe_3O_4) on the core and a light-responsive functionality (CdS) on the surface [3].

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

References

1. Muñoz-Espí, R.; Mastai. Y; Gross, S.; Landfester, K. *CrystEngComm* **2013**, *15*, 2175–2191.
2. Fischer, V.; Lieberwirth, I.; Jakob, G.; Landfester, K.; Muñoz-Espí, R. *Adv. Funct. Mater.* **2013**, *23*, 451–466.
3. Fischer, V.; Bannwarth, M. B.; Jakob, G.; Landfester, K.; Muñoz-Espí, R. *J. Phys. Chem. C* **2013**, *117*, 5999–6005.

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

Manoni Kurtanidze, Tinatin Butkhuzi, Rusudan Chaladze, Manuchar Gvaramia, Nino Lominadze and Marina Rukhadze*

Faculty of Exact and Natural Sciences, Ivane Javakhishvili Tbilisi State University, 3, I.Chavchavadze ave, Tbilisi, 0179, Georgia
* - marina_rukhadze@yahoo.com; * - marina.rukhadze@tsu.ge

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

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

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

Literature:

1. Chang G., Huang T., Hung H. 2000. Reverse Micelles as Life-Mimicking Systems. Proc. Natl. Sci. Counc. ROC (B), 24 (3), 89-100.

2. Itri R., Caetano W., Barbosa L.R.S., Baptista M.S. 2004. Effect of Urea on Bovine Serum Albumin in Aqueous and Reverse Micelle Environments Investigated by Small Angle X-Ray Scattering, Fluorescence and Circular Dichroism. Brazilian Journal of Physics, 34(1), 58-63.

New Strategies for the Microencapsulation of Healing Agents

Roberto F. A. Teixeira[1,2]*,Xander K. D. Hillewaere[1,2], Le-Thu Nguyen[1,2], Filip E. Du Prez[1,2].

[1]_ *Department of Organic Chemistry, Polymer Chemistry Research Group, Ghent University,*
Krijgslaan 281 S4-bis, B-9000 Ghent, Belgium.
[2]_ *SIM vzw, Technologiepark 935, B - 9052 Zwijnaarde, Belgium.*
* - Roberto.Teixeira@UGent.be

Microcapsules can represent reservoirs of healing agents that are dispersed into materials. Matrixes such as thermoset materials undergo damages over time due to external forces such as cyclic stresses and climate conditions. This can eventually lead to the formation of cracks, thereby deteriorating and weakening the materials. Upon crack formation, the microcapsules present in the matrix should break (and not debond) and release their reactive liquid content, allowing the material to recover its strength.[1,2,3] The development of self-healing materials has gained considerable attention over the last decade. This is driven by the replacement of heavy materials by lightweight high performance materials. The application fields include building and construction, automotive and aerospace, industrial applications, wind energy and marine applications.Our research aims at the encapsulation of newly developed self-healing agents. Different synthetic routes for the formation of core-shell structures, well known in literature, are applied and adapted to our targeted systems. In self-healing composites, for capsules to rupture in a reliable fashion, they must have an effective embedded modulus lower than that of the surrounding polymer matrix. Typical compositions used for the shell material are poly(urea-formaldehyde) (PUF), poly(melamine-formaldehyde), polyurethane (PU) and acrylates.

This study describes the complexity of having a reactive core system, such as multi-thiols or multi-isocyanates. Moreover our newly developed microcapsules hold the ability to comprise different functionalities on the shell, allowing easy post-functionalization, making the capsules more compatible with the surrounding matrixes. Furthermore, a novel approach for the encapsulation of reactive ingredients, beyond the classical approaches and based on a highly efficient chemistryreaction, will be presented. This original approach allows straightforward functionalization of the shell and can be applied to a vast number of highly reactive core materials.

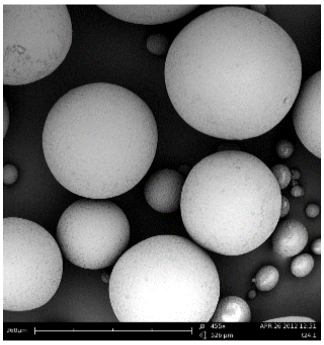

Fig. 1 Microcapsules filled with highly reactive self-healing agents.

1. Roberto F. A. Teixeira, Xander K.D. Hillewaere, Stijn Billiet, Filip E. Du Prez,2013,Chemistry of crosslinking processes for self-healing polymersin *Self-Healing Polymers* (ed. W.H. Binder), Wiley & Sons Inc., NY, ASAP.
2. Stijn Billiet, Xander K. D. Hillewaere, Roberto F. A. Teixeira, Filip E. Du Prez,2013,Chemistry of crosslinking processes for self-healing, Macromol. Rapid Comm., 34, 290-309.
3. Scott R.White, Nancy R. Sottos, Jeff Moore, Philippe Geubelle, Michael Kessler, E. Brown, S. Suresh, S. Viswanathan, 2001,Autonomic healing of polymer composites, *Nature*, 409,794-797.

Aqueous foams and aerated emulsions partly stabilized by calcium carbonate particles

Bernard P. Binks and Saeed Mashinchi*

Surfactant & Colloid Group, Department of Chemistry, University of Hull, Hull. HU6 7RX. UK.
* - s.mashinchi@2008.hull.ac.uk

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

Literature:

1. Bernard P. Binks, Tommy S. Horozov. 2005. Aqueous Foams Stabilized Solely by Silica Nanoparticles. Angewandte Chemie 117: 3788.

Effects of density difference between oils and water on stabilization of powdered o/w emulsions

Ryo Murakami[1,2]*, Hiroshi Moriyama[1], Masahiro Yamamoto[1,2], Bernard P. Binks[3]

[1]*Department of Chemistry of Functional Molecules, Konan University, Kobe 658-8501, Japan.*
[2]*Japan Science and Technology Agency, CREST, Kobe 658-8501, Japan.*
[3]*Department of Chemistry, University of Hull, Hull HU6 7RX, U.K.*
* - murakami@konan-u.ac.jp

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

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

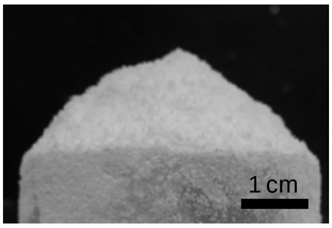

Fig. 1 Photograph of powdered emulsion ($\Delta\rho$ = 0.03 g cm^{-3}).

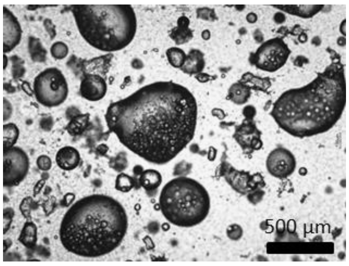

Fig. 2 Optical photograph of powdered emulsion, dispersed in oil ($\Delta\rho$ = 0.03 g cm^{-3}).

Literature:

1. Binks, B. P. and Murakami, R. 2006. “Phase inversion of particle-stabilized materials from foams to dry water” *Nat. Mater.* 11, 865-869.
2. Murakami, R., Moriyama, H., Yamamoto, M. Binks, B. P., Rocher, 2012. “Particle stabilization of oil-in-water-in-air materials: powdered emulsions” *Adv. Mater.* 24, 767-771.

Acknowledgements: We thank JSPS KAKENHI (Grant-in-Aid for Young Scientists (B), 12018977) and the Cosmetology Research Foundation for funding.

SWOP^{TM}: A Microgel Stabilised, Low-HLB O/W Emulsion Concept

Björn Klotz [1]*, Thomas Albers [1], Marta Domingo [2], Cristina Amela [2],
Jordi Esquena [3], Maria Homs [3], Conxita Solans [3]

[1] – *BASF Personal Care & Nutrition GmbH, Henkelstr. 67, 40589 Düsseldorf, Germany*
[2] – *BASF Española S.L., Sector E, Calle 42, Zona Franca, 08040 Barcelona, Spain*
[3] – *Institute for Advanced Chemistry of Catalonia (IQAC), Calle Jordi Girona 18-26, 08034 Barcelona, Spain*
* bjoern.klotz@basf.com

SWOP^{TM} (**SW**itch-**O**il-**P**hase Technology) is an emulsion concept that combines a W/O emulsifier with a mild surfactant, giving a low-HLB O/W emulsion (HLB ~ 6-7) stabilized by a polyacrylate microgel. Such emulsions can be formulated as lotions and creams for skin care applications.

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

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

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

In addition, the influence of oil polarity, NaCl content and addition of various polymers on the phase diagrams of SWOP^{TM} emulsions will be reported.

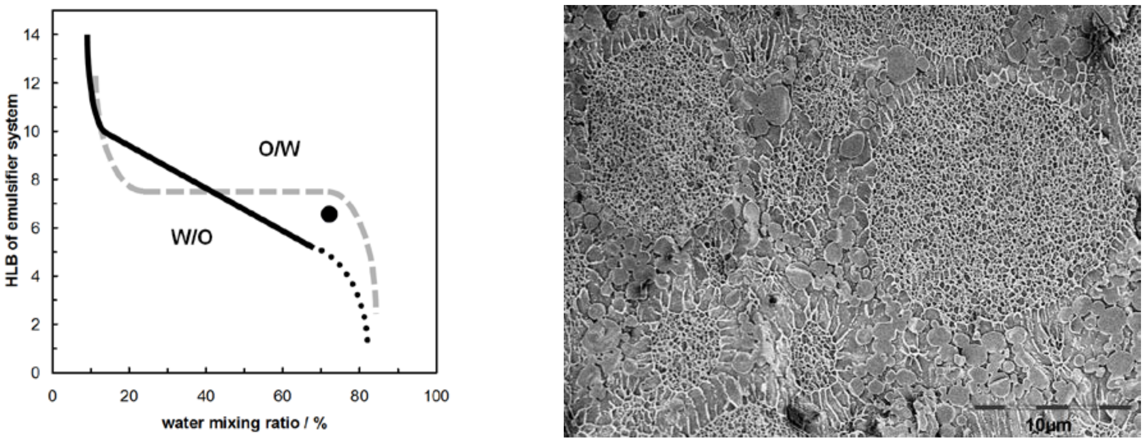

Fig. 1 Left: Schematic phase diagram of a SWOP^{TM} (black solid line) and a "classical" emulsion (grey dashed line), the black dot represents a typical SWOP^{TM} formulation. Right: Freeze-etched cryo-SEM image of a SWOP^{TM} emulsion.

Control of Size and Stability of Unilamellar Vesicles by Modification of the Kinetic Pathway by Amphiphilic Copolymer

Michael Gradzielski [1]*, Katharina Bressel [1], Michael Muthig [1], Jeremie Gummel [2] and Theyencheri Narayanan [2]

[1] – *Institut für Chemie, Stranski-Laboratorium for Theoretical and Physical Chemistry, Technische Universität Berlin, Germany*
[2] – *European Synchrotron Radiation Facility (ESRF), Grenoble, France*
* - michael.gradzielski@tu-berlin.de

Unilamellar vesicles are a class of self-assembled aggregates that are interesting of purposes of encapsulation or as delivery systems. They may form spontaneously when mixing cationic or zwitterionic with anionic surfactants. However, often it is difficult to control their size and structure and in general they are prone to ageing, i.e., the structure is not well-defined over time [1]. In our experiments the fast formation process was studied by coupling the stopped-flow technique to high-flux SANS/SAXS instruments, allowing to obtain detailed structural information with a time-resolution of 5-50 ms. This was done on a model system composed of perfluorinated anionic and zwitterionic hydrocarbon surfactant, showing that it proceeds via a disk-like intermediate state, yielding very monodisperse unilamellar vesicles, due to the kinetic control of this proess. The size of the vesicles formed is determined by the ratio of bending constants and the line tension of the system [2]. However, these vesicles age rather quickly afterwards. Based on detailed knowledge of the formation process it was possible to manipulate it by admixing amphiphilic copolymers. This leads to larger and very monodisperse vesicles, which now in addition are long-time stable. Accordingly by this shaping approach one can obtain unilamellar vesicles with tunable radii in the range of 20-70 nm and with polydispersity indices of 0.04-0.06, which are attractive for a number of applications [3]. This means that by knowing the pathway of forming vesicles this process can be controlled by the presence of copolymers, which allows for shaping them in a systematic fashion. These well-defined and stable vesicles then are not only very interesting model systems but also attractive for a number of applications.

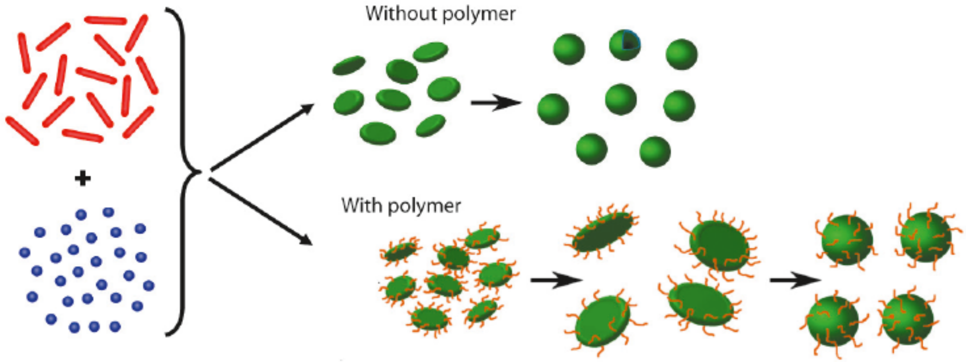

Fig. 1 Structural progression occurring in the solutions as a function of time.

Literature:

1. T.M. Weiss, T. Narayanan, M. Gradzielski, Langmuir 24, 3759 (2008)
2. K. Bressel, M. Muthig, S. Prévost, I. Grillo, M. Gradzielski, Colloid Polym. Sci. 288, 827 (2010)
3. K. Bressel, M. Muthig, S. Prévost, J. Gummel, T. Narayanan, M. Gradzielski, ACS Nano 6, 5858 (2012)

Acknowledgements: The DFG is thanked for funding of this project with the priority program SPP 1273 “Kolloidverfahrenstechnik” (GR1030/7-1 and 2).

Phase transition from sponge phase to lamellar phase of aqueous solution of non-ionic surfactant induced by adding antagonistic salt

Hideki Seto [1]*, Michihiro Nagao [2], Koichiro Sadakane [3], Hitoshi Endo [1] and Yuri B. Melnichenko [4]

[1] –*Institute of Materials Structure Science, High Energy Accelerator Research Organization*
[2] – *NCNR, National Institute of Standards and Technology*
[3] – *College of Science and Engineering, Ritsumeikan University*
[4] – *Oak Ridge National Laboratory*
* - hideki.seto@kek.jp

Effect of electrostatic interaction is sometimes drastic in the ordering of softmatters because this force is rather stronger than another (entropic) interaction, which governs structural formations in softmatters. However, the effects of salt on structural formations in softmatters are not truly understood; these are not explained in terms of ionic strength nor ionic radius. The ability of ions to salt out or salt in proteins is classified as the Hofmeister series, but it is just an empirical classification and not explained from the basic level.

Recently, we showed several experimental evidences of nano-scale structures in liquids induced by adding an antagonistic salt composed of hydrophilic cations and hydrophobic anions. In the water-rich mixture of deuterated water (D_2O), 3 methylpyridine (3MP) and sodium tetraphenylborate ($NaBPh_4$), we showed experimental evidences of the formation of ordered lamellar structure. [1] A precise data analysis and a theoretical consideration indicate that planar layers of 3MP are stabilized by pairs of hydrophilic cations and hydrophobic anions, which play a similar role as surfactant molecules. These results suggest that the heterogenous distribution of anions and cations is important for the ordering of softmatters.

In this respect, we have done further small-angle neutron scattering (SANS) experiments to investigate the effect of antagonistic salt on the structure of 10 wt % of $C_{12}E_5$ (10 vol%) and D_2O. Figure 1 shows a typical example of the SANS profiles. In a binary mixture without salt, the structure at 60°C is interpreted as a sponge phase. By adding small amount of $NaBPh_4$, the SANS spectra drastically changes and becomes multi-peak profile corresponding to the lamellar structure. The first peak position shifts to lower-Q at lower salt concentration, while it shifts to higher-Q at higher salt concentration. This behavior is also observed by adding another antagonistic salt ($RbBPh_4$ or PPh_4Cl), while no effect was found when we added a normal (hydrophilic) salt.

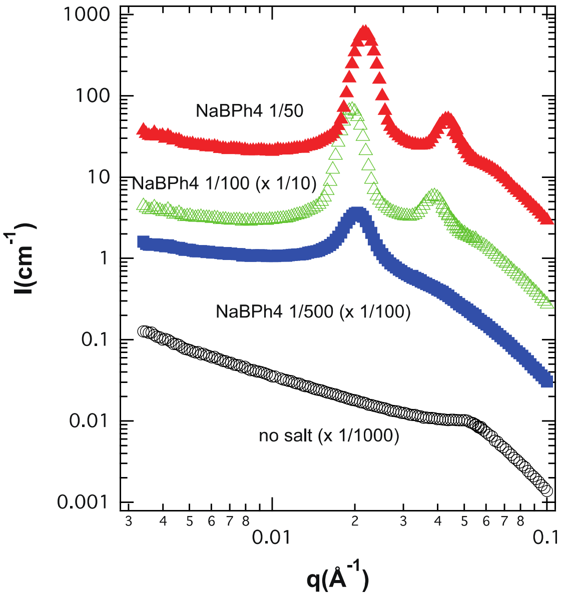

Fig. 1 Salt concentration dependence of the SANS profile from $C_{12}E_5/D_2O$ (black circles) and those from $C_{12}E_5/D_2O/NaBPh_4$ (others). The lamellar structure becomes more distinct by increasing the salt concentration.

Literature:

1. Sadakane Koichiro, et al., 2009 Phys. Rev. Lett., 103: 167803.

Aggregation Behaviors of Gemini Cationic Surfactants in a Protic Ionic Liquid EAN

Xudong Wang, Qintang Li and Xiao Chen*

Key Laboratory of Colloid and Interface Chemistry, Shandong University, Jinan, 250100, China
* - xchen@sdu.edu.cn

The aggregation behaviors of a series of symmetric and dissymmetric cationic Gemini surfactants, $[C_mH_{2m+1}(CH_3)_2N\text{-}(CH_2)_2\text{-}N(CH_3)_2C_nH_{2n+1}]Br_2$, designated as m-2-n (m = n with m = 10, 12, 14; or m ≠ n with a fixed m + n = 24, m = 16, 14, 12) have been investigated in a protic ionic liquid, ethylammonium nitrate (EAN). Surface tension, polarized optical microscopy (POM), small-angle X-ray scattering (SAXS), and rheological measurements are adopted to investigate the micellization and lyotropic liquid crystal (LLC) formation. Compared to LLCs formed in aqueous environment, the normal hexagonal (H_I) and lamellar (Lα) phases are found to disappear with a new reverse hexagonal (H_{II}) phase instead. The structure dissymmetry plays an important role in aggregation process of m-2-n. With increasing degree of dissymmetry, the critical micellization concentration, the maximum reduction of solvent surface tension, and the minimum area occupied per surfactant molecule at the air/EAN interface all become smaller. The thermostability of formed LLCs is therefore improved because of the more compact molecules. These characteristics can be explained by the enhancement of solvophobic effect due to the increased structure dissymmetry of Gemini surfactants.

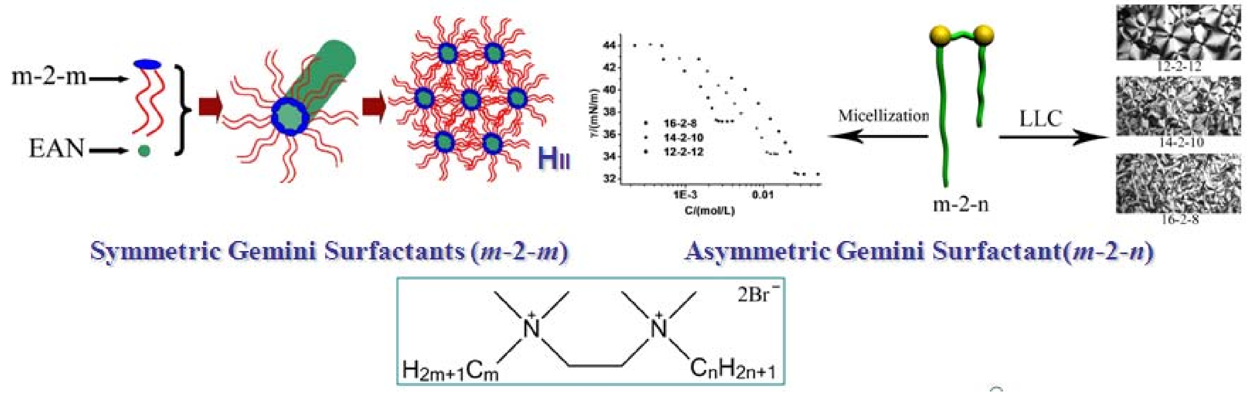

Fig. 1 Chemical structures of Gemini surfactants and their aggregates formed in EAN.

Literature:

1. Xudong Wang, Xiao Chen*, Yurong Zhao, Xiu Yue, Qiuhong Li, and Zhihong Li, **2012,** Nonaqueous Lyotropic Liquid-Crystalline Phases Formed by Gemini Surfactants in a Protic Ionic Liquid, *Langmuir*, 28, 2476-2484.
2. Xudong Wang, Qintang Li, Xiao Chen*, and Zhihong Li, 2012, Effects of Structure Dissymmetry on Aggregation Behaviors of Quaternary Ammonium Gemini Surfactants in a Protic Ionic Liquid EAN, *Langmuir*, 28, 16547-16554.

Acknowledgements:

The financial supports from the National Natural Science Foundation of China (20973104, and 21033005) and the SAXS station with the Beijing Synchrotron Radiation Facility (BSRF) in China are acknowledged.

Self-organization of particles with heterogeneously charged surfaces under confinement

Emanuela Bianchi [1]*, Christos N. Likos [2], and Gerhard Kahl [1]*

[1] – *Institut für Theoretische Physik, TU Wien, Wien, Austria*
[2] – *Fakultät für Physik, Universität Wien, Wien, Austria*
* - gerhard.kahl@tuwien.ac.at

Heterogeneously charged particles are multipolar units characterised by a competitive interplay between attractive and repulsive anisotropic interactions. We consider a selection of axially symmetric quadrupolar colloids - first introduced in Ref. [1] and referred to as *inverse patchy colloids* (IPCs) - in a confined planar geometry; the role of both the overall particle charge and the patch extension as well as the effect of a neutral or possibly charged substrate are studied in thermodynamic conditions such that the formation of extended structures is favoured. A general tendency to form quasi two-dimensional aggregates composed by particles with their symmetry axis oriented within the plane is observed irrespective of the confinement size; among these planar self-assembled scenarios, a clear distinction between the formation of microcrystalline gels -- branched networks consisting of extended purely crystalline domains - as opposed to disordered aggregates is possible based on the specific features of the interparticle interaction [2]. The competition of particle-particle and particle-substrate interactions significantly affects the size and the internal structure of the aggregates and can even inhibit the aggregation process [2,3].

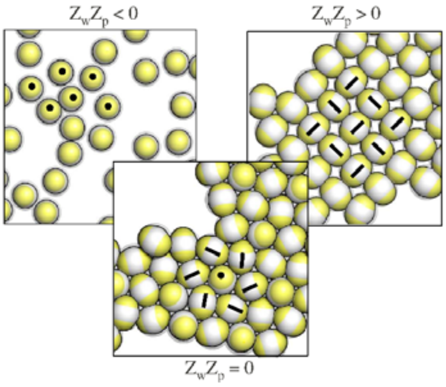

Fig. 1 Magnified views of typical simulation snapshots for one of the investigated IPC systems under planar confinement [3]; black bars and points indicate the particle orientational vectors; the wall and the patch charges are labeled as Z_w and Z_p, respectively; the top wall is always neutral, while the bottom wall can be either neutral (central-bottom panel) as well as charged (side-top panels).

Literature:

1. Bianchi E., Kahl G., and Likos C.N., Soft Matter, 7: 8313 (2011)
2. Bianchi E., Likos C.N., and Kahl G., ACS Nano (in press; DOI: 10.1021/nn401487m)
3. E. Bianchi, C. N. Likos, and G. Kahl, in preparation

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Membrane wetting, budding and tube formation in vesicles enclosing two aqueous phases

Rumiana Dimova *

Max Planck Institute of Colloids and Interfaces, Science park Golm, 14424 Potsdam, Germany
* dimova@mpikg.mpg.de

The interior of living cells is crowded with macromolecules. In such a concentrated environment, local phase separation may occur, involving local composition differences and microcompartmentation. Recently, giant vesicles loaded with polymer solutions were reported to exhibit spatial compartments formed by phase separation within the vesicle. We employed these artificial cell systems to study various phenomena related to molecular crowding and microcompartmentation in cells. We demonstrate that similarly to the wetting behavior of liquid droplets in contact with surfaces, different polymer aqueous phases in contact with membranes as a substrate can undergo complete to partial wetting transition [1]. We find that the degree of wetting is characterized by a hidden material parameter - the intrinsic contact angle, which can be determined from effective contact angles observed by optical microscopy [2]. Upon osmotic deflation of vesicles enclosing two aqueous phases that partially wet the membrane, one can observe vesicle budding [3] and/or tube formation [4] (see Fig. 1) depending on the competition between the spontaneous curvature of the membrane and the wetting properties of the aqueous phases [5]. Phase separation in the interior of vesicles can lead to stable and retractable membrane nanotubes, which is relevant for membrane area storing and regulation in cells.

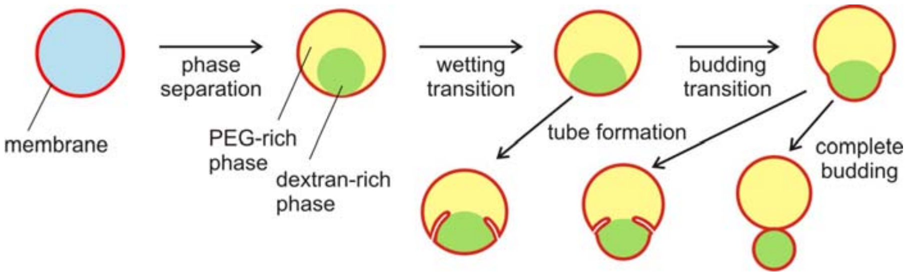

Fig. 1 Lipid membranes in contact with aqueous phases of polymer solutions can undergo wetting, budding, and tube formation processes.

Literature:

1. Li Y., Lipowsky R., Dimova R. 2008. Transition from complete to partial wetting within membrane compartments. J. Am. Chem. Soc. 130:12252-12253.
2. Kusumaatmaja H., Li Y., Dimova R., Lipowsky R. 2009. Intrinsic Contact Angle of Aqueous Phases at Membranes and Vesicles. Phys. Rev. Lett. 103:238103.
3. Li Y., Kusumaatmaja H., Lipowsky R., Dimova R. 2012. Wetting-Induced Budding of Vesicles in Contact with Several Aqueous Phases. J. Phys. Chem. B 116:1819-1823.
4. Li Y., Lipowsky R., Dimova R. 2011. Membrane nanotubes induced by aqueous phase separation and stabilized by spontaneous curvature. Proc. Natl. Acad. Sci. USA. 108:4731-4736.
5. Dimova R., Lipowsky R. 2012. Lipid membranes in contact with aqueous phases of polymer solutions. Soft Matter 8:6409-6415.

Controlled Size and Loading of Block Copolymer Micelles for Encapsulation

J. G.J.L. Lebouille [1]*, L.F.W. Vleugels [1], M.A. Cohen Stuart [2], F.A.M. Leermakers [2], R. Tuinier[1,3]

[1] *DSM ChemTech, Advanced Chemical Engineering Solutions (ACES), PO Box 18, 6160 MD Geleen, the Netherlands*
[2] *Laboratory for Physical Chemistry and Colloid Science, Wageningen University, Drijenplein 6, 6307 HB Wageningen, the Netherlands*
[3] *Van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, the Netherlands.*
* - jerome.lebouille@dsm.com

We report on the formation of polymeric micelles in water using triblock copolymers with a polyethylene glycol middle block and various hydrophobic outer blocks prepared with the precipitation method [1]. Micelles form in a reproducible manner with a narrow size distribution. By comparison with self-consistent field calculations we find that the hydrodynamic size and the loading of the micelles are consistent with experimental findings [2]. This enables to design nanoparticles/micelles with defined size and loading that are able to encapsulate hydrophobic compounds [3].

Literature:

1. Niwa T., Takeuchi H., Hino T., Kunou N., and Kawashima Y., 1993. Preparations of biodegradable nanospheres of water-soluble and insoluble drugs with D,L-lactide/glycolide copolymer by a novel spontaneous emulsification solvent diffusion method, and the drug release behavior. J. Controlled Rel., 25, 89-98.
2. Lebouille J.G.J.L., Tuinier R., Vleugels L.F.W., Cohen Stuart M.A. and Leermakers F.A.M., 2013. Self-consistent field predictions for quenched spherical biocompatible triblock copolymer micelles. Soft Matter, submitted.
3. Lebouille J.G.J.L., Vleugels L.F.W., Dias A.A., Leermakers F.A.M., Cohen Stuart M.A. and Tuinier R, 2013. Controlled block copolymer micelle formation for encapsulation of hydrophobic ingredients. Soft Matter, submitted.

Phospholipid Bicelles to Generate Magnetically Switchable Material

Marianne Liebi [1]*, Joachim Kohlbrecher [2], Peter Fischer [1], Peter Walde [3], Simon Kuster [1], Erich J. Windhab [1]

[1] – *Laboratory of Food Process Engineering, ETH Zurich, Switzerland*
[2] – *Laboratory for Neutron Scattering, PSI Villigen*
[3] – *Department of Materials, ETH Zurich, Switzerland*
* - marianne.liebi@hest.ethz.ch

With the goal of producing smart hydrogels, magnetically alignable bicelles were embedded into a gelatin matrix, generating a temperature responsive magnetically switchable structure. This results in nanometer-scaled switches operable by an external magnetic field for the anisotropy conferred by bicelles as functional ingredient. Bicelles are a self-assembly structure based on phospholipids with a disk-like shape. The bicelles studied in this work were composed of DMPC, cholesterol and DMPE-DTPA with complexed lanthanide ions (i.e. Tm^{3+} or Dy^{3+}) [1]. Magnetic alignment was caused by an anisotropic magnetic susceptibility $\Delta\chi$ of the phospholipids and the complexed lanthanide ions, leading to a preferred orientation of the molecular assembly parallel (with Tm^{3+}) or perpendicular (with Dy^{3+}) as shown in Fig. 1 with birefringence and SANS measurements conducted in a magnetic field.

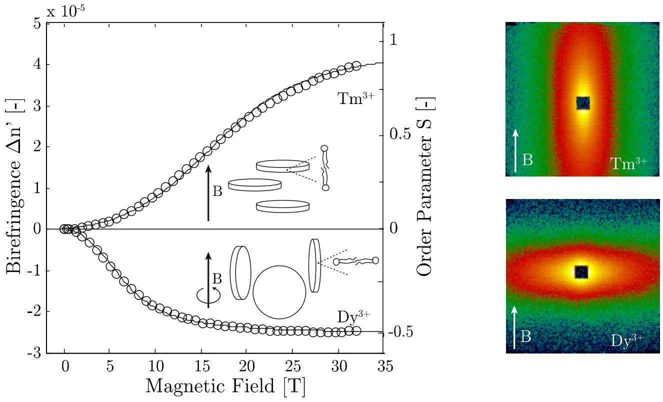

Fig. 1 Magnetically induced birefringence measurements (left) and SANS measurements in a magnetic field of 8 T (right) showing the different orientation direction of bicelles with Tm^{3+} and Dy^{3+}. [2]

The formation process of bicelles was investigated and optimized to yield a maximum magnetic alignment. The disk-like aggregates were preserved after embedding into gelatin and the magnetic orientation of the bicelles could be entirely fixed by gelation of the matrix. The resulting gel cubes showed an anisotropic transfer for electromagnetic waves, i.e. a different birefringence in all three orthogonal directions. Cycling through the melting point of gelatin set the bicellar alignment back to its isotropic state.

Literature:

1. Liebi, M., Kohlbrecher, J., Ishikawa, T., Fischer, P., Walde, P., Windhab, E. J. 2012. Cholesterol Increases the Magnetic Aligning of Bicellar Disks from an Aqueous Mixture of DMPC and DMPE–DTPA with Complexed Thulium Ions. Langmuir 28:10905-10915.
2. Liebi, M., van Rhee, P. G., Christianen, P. C. M., Kohlbrecher, J., Fischer, P., Walde, P., Windhab, E. J. 2013. Alignment of Bicelles Studied with High-Field Magnetic Birefringence and Small-Angle Neutron Scattering Measurements. Langmuir 29:3467-3473.

Permeable shells acting as containers

Nina Elbers[1]*, Jissy Jose[1], Marlous Kamp[1], Arnout Imhof[1], Alfons van Blaaderen[1]*

[1] – *Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University,*
Utrecht, The Nederlands, www.colloid.nl
* - A.vanBlaaderen@uu.nl, N.A.Elbers@uu.nl

The aim of this research is to develop permeable shells that can act as ‘containers’ for certain chemicals. By manipulating the absorption and desorption behaviour of these shells one could release the contents of the shells in a controlled and localized way. These systems are for instance interesting for drug delivery purposes and for surfactant flooding, an enhanced oil recovery (EOR) technique, in which surfactants are used to reduce the interfacial tension between oil and water still remaining in the rocks.

In our study, permeable monodisperse silica-siloxane shells are synthesized using a method that was developed in our group [1]. By labelling the shells with a fluorescent dye, the system can be monitored with Confocal Laser Scanning Microscopy (CLSM). Empty shells buckle in a dried state, but they remain spherical in presence of a fluorescently labelled liquid surfactant phase as a result of shell filling (Fig. 1). In preliminary experiments, the behaviour of these surfactant-filled shells is examined at oil-water interfaces. Previous experiments have indicated that filling and emptying of oil-filled shells can be regulated by surfactants.

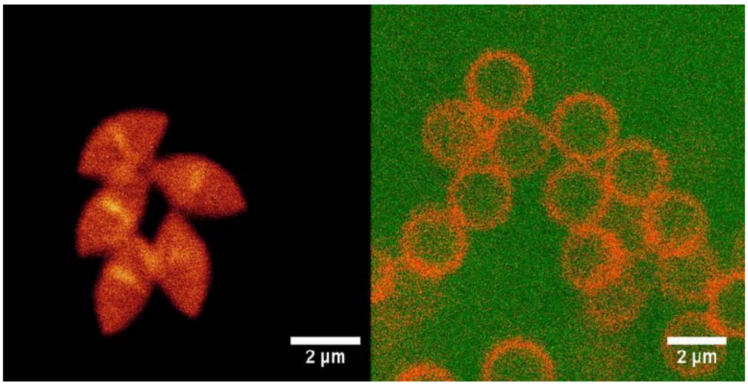

Fig. 1: Confocal microscopy images of silica-siloxane shells in absence (left) and in presence (right) of a fluorescently labelled liquid surfactant phase.

Literature:

1. Carmen Zoldesi, Arnout Imhof. 2005. Synthesis of monodisperse colloidal spheres, capsules, and microballoons by emulsion templating. Advanced Materials 17: 924-928.

Acknowledgements:

This work is part of the Industrial Partnership Programme (IPP) Innovatie Physics for Oil and Gas (iPOG) of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is supported financially by Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). The IPP iPOG is co-financed by Stichting Shell Research. We would like to thank Esther Vermolen from Shell for useful discussions.

Dissociation dynamics of clusters of colloidal spheres

Johan Bergenholtz[1]*

[1]*Department of Chemistry and Molecular Biology, University of Gothenburg, Sweden*
* - jbergen@chem.gu.se

First passage time theory is used to analyze the dissociation behavior of doublets of colloidal particles. The distribution of first passage times for particles interacting via, e.g., a DLVO potential is determined numerically. For strongly attractive particles the distribution becomes broad such that the mean first passage time becomes a poor measure of the first passage time dynamics. In spite of this, use can be made of the mean in a matching condition, which allows for reproducing first passage time distributions of strongly attractive doublets by an analytical solution for particles interacting only through surface adhesion. The smallest eigenvalue in the analytical solution, which governs the long-time asymptotic behavior of the first passage time distribution, is identified analytically for strongly attractive pairs of particles. In addition, in this limit, the first passage time distribution is shown to asymptote to an exponential distribution, which means that the dissociation process can be simply captured by a stochastic two-state model, without sacrificing the effect of the surface chemistry, with a constant probability for dissociation. This probability is simply related to the surface adhesive parameter and the separation distance at which the pair of particles ceases to be considered a doublet.

About the origin of “synergism” in ion selectivity in metal salt extraction by microemulsions

S. Dourdain[1]*, I. Hofmeister[1], O. Pecheur[2], J-F. Dufrêche[1], R. Turgis[1], A. Leydier[1], J. Jestin[3], F. Testard[4], S. Pellet-Rostaing*[1], T. Zemb*[1]

[1] – *ICSM/LTSM, CEA/CNRS/UM2/ENSCM UMR5257, Site de Marcoule, Bat 426, 30207 Bagnols sur Ceze, France*
[2] – *CEA, Nuclear Energy Division, RadioChemistry & Processes Department, 30207 Bagnols sur Cèze, France*
[3] – *Laboratoire Léon Brillouin CEA/CNRS, CEA Saclay, 91191 Gif-sur-Yvette, France*
[4] – *DSM/IRAMIS/SIS2M/LIONS, CEA Saclay, Bat 125, 91191 Gif-sur-Yvette, France*
* - sandrine.dourdain@cea.fr

In solvent extraction, a concentrated solution of mixed salts is contacted with a reverse microemulsion. Some salts are selectively extracted. When mixed surfactants are used in the formulation of the microemulsion, “synergism” of yet unknown origin emerges: when, for a defined formulation of the solvent phase, there is an increase of distribution coefficients for some salts from a mixture. The origin of synergism is a mystery in chemical engineering because modelling implies complexation and not micellisation. In order to achieve predictive modelling, aggregation number, coordination numbers and complexation numbers must be distinguished.

To determine the origin of this synergism, we determine free energy of co-assembly in mixed aggregates. Aggregation in any point of a phase diagram is followed not only structurally by SANS, SAXS and SLS, and also thermodynamically by determining the concentration of monomers coexisting with reverse aggregates. Using the industrially used couple HDEHP/TOPO forming mixed reverse aggregates, and the representative couple U/Fe[1], we show that there is no peculiarity in the aggregates microstructure when the maximum of “synergism” is obtained. We compare for the first time the free energy of aggregation necessary to form mixed aggregates containing extracted ions in their polar core, and the free energy of extraction difference between target and non-target ions, as deduced from the synergistic selectivity peak.[2] This allows us to propose a general mechanism at the basis of ion selectivity used industrially for metal recovery.

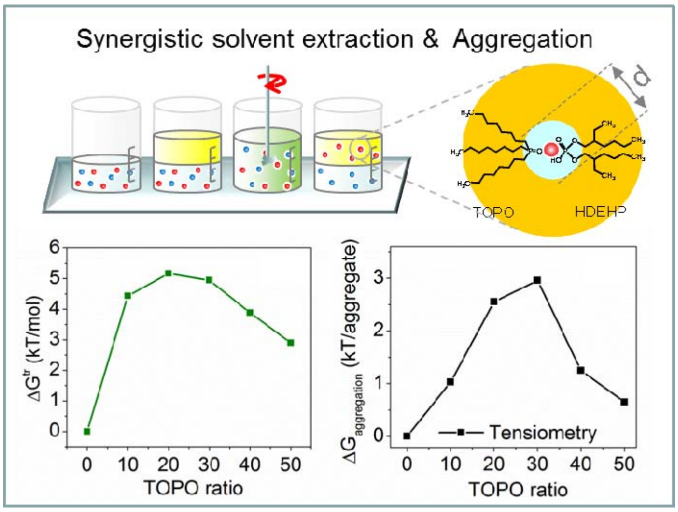

Fig. 1 Aggregation and transfer energy correspondence in and out of synergism.

References:

1. C.K. Gupta, G. Gupta, H. Singh, Uranium resource processing, - secondary resources, Springer Berlin, 2003.
2. S. Dourdain, I. Hofmeister, O. Pecheur, J-F. Dufrêche, R. Turgis, A. Leydier, J. Jestin, F. Testard, S. Pellet-Rostaing,and T. Zemb, Langmuir 2012, 28, 11319−11328

Carbon nanospheres and their interactions with lipid membranes

Arben Jusufi[1]*, Russell H. DeVane[2], Michael L. Klein[2]

[1] – *Department of Chemistry, College of Staten Island, City University of New York, New York, NY 10314, USA*
[2] – *Institute for Computational Molecular Science, Temple University, Philadelphia, PA , USA*
* - arben.jusufi@csi.cuny.edu

Carbon nanoparticles (CNS) are promising drug carrier particles and are also utilized for medical cell imaging. Here we investigate the effect of CNS on membrane stability. We study the translocation mechanism of CNS of different sizes through lipid bilayers. Various fullerenes serve as model systems for CNS. Using all-atom (AA) and coarse-grained (CG) Molecular Dynamics (MD) simulations, we calculated the free energy change when C60, C180, and C540 fullerenes are transferred from bulk water to the interior of a dioleoylphosphatidylcholine (DOPC) bilayer. Upon entering the lipid bilayer, the larger fullerene (2.4 nm in diameter) causes local distortions in the bilayer surface, see Fig. 1, similar to distortions previously observed in carbon nanotube simulations. These local distortions, however, do not lead to any free energy barriers. From the free energy profiles we deduce spontaneous absorption of all three fullerene types. In contrast to these nonspecific single fullerene properties, extensive CG-MD simulations of fullerene rich lipid bilayers reveal substantial fullerene-size effects on the bilayer stability. We found that multiple fullerenes, irrespective of their size, self-aggregate within the bilayers. However, while the C60 aggregates have little effect on the bilayer structure, C540 clusters cause substantial membrane distortion. This membrane destabilization might have implications for potential cytotoxicity of CNS of sizes close to that of C540 fullerenes upon their uptake by biological cells.

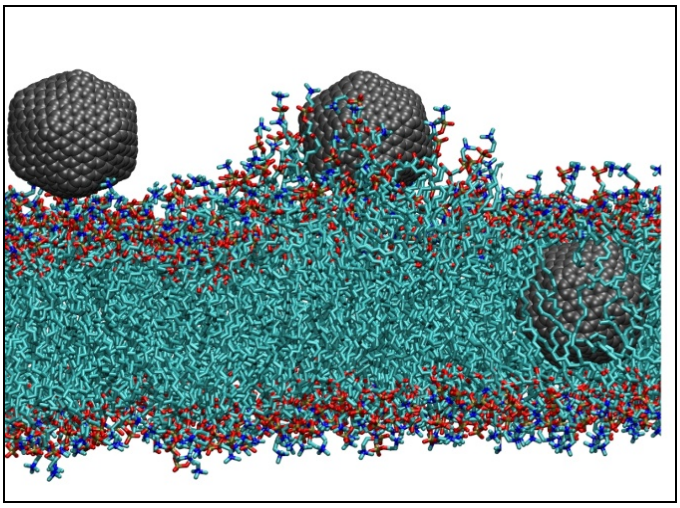

Fig. 1: Molecular Dynamics simulation of a C540 fullerene entering a lipid membrane.

Literature:

1. Jusufi, Arben; DeVane, Russell H.; Shinoda, Wataru; Klein, Michael L., Nanoscale carbon particles and the stability of lipid bilayers, Soft Matter 7, 1139 (2011)

Nanopore formation and reconstruction of small unilamellar vesicles consisting of long- and short-chain phospholipids

Norifumi L. Yamada [1]*

[1] *High Energy Accelerator Research Organization, Tokai, Ibaraki 319-1106, Japan*
* - norifumi.yamada@kek.jp

Cells and their organelles are enclosed by biomembranes consisting of phospholipid bilayers, where biomolecules, such as cholesterol, membrane proteins, *etc*., are embedded. These molecules have different amphiphilic properties, and this variety affects the structure of biomembranes. From this point of view, this study shed the light on the effect of phospholipids with short-hydrocarbon chains on the structure in the mixture with normal phospholipids. On the analogy of surfactant mixtures, the molecular shape and phase separation of the molecules play a key role on the structural formation mechanism. Concerning the molecular shape, short-chain phospholipids are corn-like, that is, the cross section of the hydrophilic part is larger than that of the hydrophobic part, whereas normal phospholipids are cylindrical. This means that normal phospholipids and short-chain phospholipids tend to form bilayers and their rims in the mixture, respectively. In fact, the mixture spontaneously forms bilayered micelles (bicelles) with stable rims below the chain melting temperature of the long-chain lipid, T_c. On the other hand, the phospholipids tend to mix each other above T_c, because both of them are in disordered-phase and the phase separation becomes weak. Then, the rim of bicelles becomes unstable, they fuse each other, and transform into small unilamellar vesicles (SUVs). However, the behavior of short-chain phospholipids on the SUV structure has not been investigated so far.

In this study, the effect of the short-chain phospholipids on the SUV structure was investigated with taking the phase separation of phospholipids into account. With decreasing temperature from a value far above T_c, nanopore formation was enhanced on the surface of SUVs. Furthermore, a sequential transformation of small SUVs to small bicelles, small bicelles to large bicelles, and large bicelles to large SUVs occurred when the temperature approaching to the value slightly above T_c. By considering the bending energy of the membrane, the line tension of the rim, and the rim domain growth due to the phase separation, the mechanism of the nanopore formation and reconstruction of SUVs were clarified.

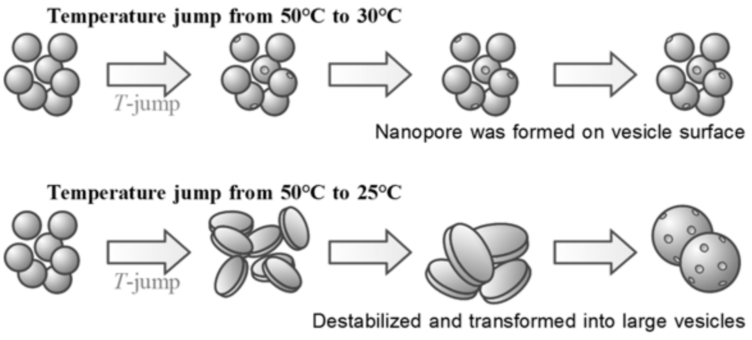

Fig. 1 Schematic illustration of nanopore formation and reconstruction of SUVs at the temperature jump**.**

Literature:

1. N. L. Yamada, M. Hishida, and N. Torikai, 2009, “Nanopore formation on unilamellar vesicles of long- and short-chain lipids”, Phys. Rev. E 79: 032902.
2. N. L. Yamada, 2012, “Kinetic process of formation and reconstruction of small unilamellar vesicles consisting of long- and short-chain lipids”, Langmuir 28: 17381.

A synchrotron radiation study on the structural evolution of weakly amphiphilic block copolymers monolayers at the air/water interface

Giovanni Li Destri [1]*, Oleg Konovalov [1].

[1] – *European Synchrotron Radiation Facility (ESRF)*
* - giovanni.lidestri@esrf.fr

Langmuir monolayers of amphiphilic block copolymers [1-2] represent a very interesting model case of soft matter confined systems since their thickness approaches the single molecule one, thus depicting the extreme case of confined environment, and since their dynamics are governed by few very specific interactions.

However, the need of a liquid interface for their formation has made difficult their in situ characterization so far. The use of high brilliance synchrotron radiation sources may overcome this problem enabling to study the structural reorganization of such systems during the spreading and the eventual compression.

Here we report a full in situ characterization of a model weakly amphiphilic block copolymer, polystyrene-b-polymethylmethacrylate (PS-PMMA), which is known to form characteristic quasi 2D surface micelles when spread at the air/water interface [3]. Langmuir monolayers of PS-PMMA were studied directly at the air/water interface by means of Grazing Incidence X-Ray Scattering (GISAXS) and X-Ray Reflectivity (XRR) at ID10 beamline of the European Synchrotron Radiation Facility. Three different macromolecules, bearing three different relative block lengths, were characterized. As expected the interfacial behaviour of the polymer, especially in terms of collapse pressure and compressibility, was observed to be strongly dependent on the chemical composition but all the three macromolecules showed the same, unique, phase transition at 12 mN/m.

The X-Ray data were also different for the three macromolecules since GISAXS was observed to be more sensitive to the PS blocks while XRR gave more intense signal for macromolecules bearing longer PMMA blocks. The GISAXS pattern confirmed the presence of surface micelles with minor structural changes during compression. XRR showed instead a more gradual transition toward more dense films with increasing the surface pressure and, in addition, a sharp PMMA structural transition at the surface pressure corresponding to the observed phase transition. Finally, by developing a new fitting model taking into account the peculiar nanostructure of these monolayers (namely, micelles scattering density, height, size and coverage density), it was found that XRR data were also influenced by the packing, upon compression, of the PS blocks.

Literature:

1. Perepichka Iryna I., Lu Qing, Badia Antonella, Bazuin C. Geraldine. 2013. Understanding and Controlling Morphology Formation in Langmuir–Blodgett Block Copolymer Films Using PS-P4VP and PS-P4VP/PDP. Langmuir 29: 4502-4519
2. Bosker Wouter T.E., Cohen Stuart Martien A., Norde Willem. 2013. (Quasi-) 2D Aggregation of Polystyrene-b-Dextran at the Air–Water Interface. Langmuir 29: 2667-2675
3. Seo Yongsok, Paeng Keewook, Park Sangwook. 2001. Molecular Weight Effect on the Behaviors of Polystyrene-block-poly(methyl methacrylate) Diblock Copolymers at Air/Water Interface. Macromolecules 34: 8735-8744

Collapse of lipid monolayers with phase coexistence

Svetlana Baoukina, Eduardo Mendez-Villuendas, Dmitri Rozmanov, and D. Peter Tieleman.

*Department of Biological Sciences and Institute for Biocomplexity and Informatics,
University of Calgary, 2500 University Dr. NW, Calgary, AB, Canada, T2N 1N4.*

Lateral compression of a surfactant monolayer at an air-water interface increases its surface density and reduces the surface tension. Compression is possible until a certain threshold, below which the monolayer becomes unstable at the interface and collapses. For homogeneous monolayers, collapse has been characterized to proceed via wrinkling (buckling) followed by folding into bilayers. For monolayers separated into coexisting phases, the mechanism of collapse is not fully understood. The effect of phases in monolayer stability, the sites for formation of bilayer folds, and the distribution of phases between the monolayer and the folds, remain unclear.

In this work, we used computer simulations to investigate collapse of lipid monolayers with coexisting phases. This is important for understanding the role of lateral organization in the function of biological membranes, and is directly relevant for the regulation of surface tension by lung surfactant. Molecular dynamics simulations with the coarse-grained force field MARTINI were employed to achieve large length (~80 nm) and time (tens of microseconds) scales. Lipid mixtures containing saturated and unsaturated lipids and cholesterol were investigated under varying surface tension and temperature. We reproduced the coexistence of LE and LC phases, and Lo and Ld phases, and simulated formation of bilayer folds on monolayer collapse (Fig. 1). We investigated the properties of monolayers connected to bilayers at and below the equilibrium surface tension. Domains of LC phase increase the monolayer stability; bilayer folds nucleate in the LE phase. Domains of Lo phase with spontaneous curvature reduce the monolayer stability; bilayer folds nucleate in the Ld phase close to phase boundary. Percolation of LC domains slows monolayer collapse below the equilibrium surface tension.

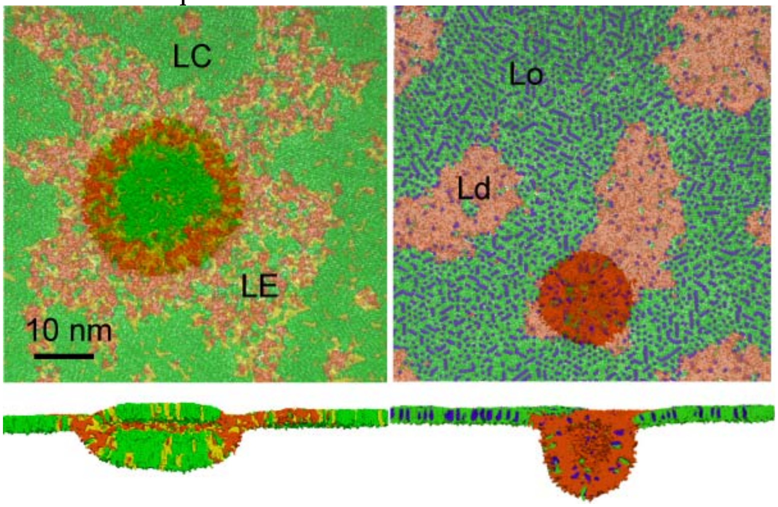

Figure 1. Lipid monolayers with coexisting phases connected to bilayer folds, top and cross-section view.

Adsorption of polyallylamine hydrochloride/sodium dodecylsulphate mixtures at water/tetradecane interface. Effect of adding of the salt.

A. Sharipova[1,2]*, S. Aidarova[1], R. Miller[2]

[1] *International Postgraduate Institute "Excellence Polytech" of Kazakh National Technical University, Almaty, Kazakhstan*
[2] *Max-Planck Institute of Colloids and Interfaces, Potsdam, Germany*
*Altynay.sharipova@mpikg.mpg.de

To study the behaviour of polyelectrolyte/surfactant mixtures is important because of their industrial, technological and domestic applications. To understand their behavior different techniques are used at the interfaces, such as surface and interfacial tension, dilational and shear rheology, ellipsometry, and in the bulk, methods such as DLS and zeta potential measurements. The properties of polyelectrolyte/surfactant mixtures and effect of different solution conditions like effect of surfactant chain length, effect of ionic strength, pH and temperature are studied so far mainly at the water/air interface. In contrast, there are only very few works dedicated to the adsorption of these systems at the water/oil interface, in particular at the water/hexane, octane or hexadecane interfaces [1]. These works also include investigations of the influence of chain length of sodium alkyl sulphates to the adsorption of polyelectrolyte/ surfactant mixed systems [2]. That is why the present work is devoted to the study of interfacial tension and dilational rheology of polyallyl amine hydrochloride /sodium dodecylsulphate mixtures at the water/tetradecane interface with and without adding of salt. Also DLS and zeta potential measurements were carried out for the same systems.

The results shows that with added salt the polyelectrolyte/surfactant mixtures becomes more surface active which can be seen in the interfacial tension isotherm measured at the water/tetradecane interface. The values of dilational reology for the polyallyl amine hydrochloride/sodium dodecyl sulphate mixture with salt are higher than for those without salt. This indicates a strengthening of the Rehbinder structur-mechanical factor which means a significant strengthening of the mixed interfacial adsorption layers built up by surfactants and polyelectrolyte.

Literature:

1. Tucker Ian M., Petkov Jordan T., Jones Craig, Penfold Jeffrey, Thomas Robert K., Rogers Sarah E., Terry Ann E., Heenan Richard K. and Grillo Isabelle. 2012. Adsorption of Polymer−Surfactant Mixtures at the Oil−Water Interface. Langmuir. 28:14974−14982.
2. Sharipova A., Aidarova S., Cernoch P., Miller R. 2013. Effect of surfactant hydrophobicity on the interfacial properties of polyallylamine hydrochloride/sodium alkylsulphate at water/hexane interface. Colloids Surf. A: Physicochem. Eng. Aspects, http://dx.doi.org/10.1016/j.colsurfa.2012.12.013.

Acknowledgements

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Surface Freezing of Binary Mixtures of Hydrocarbon and Fluorocarbon Compounds

Takanori Takiue*, Miyako Tsuura, Mayuko Shimasaki, Hiroki Matsubara, and Makoto Aratono

Department of Chemistry, Faculty of Sciences, Kyushu University, Fukuoka, Japan

* - t.takiue@chem.kyushu-univ.jp

Surface freezing (SF) is the phenomenon of the two-dimensional condensed film formation at liquid surface at temperature T_s which is a few degrees above the bulk freezing temperature T_b. Deutsch *et al.* have claimed that liquid alkanes with 16~50 carbon atoms and alkanols with 10~28 ones exhibit SF phenomena.[1] In this study, we aim at discussing the miscibility of molecules at the surface of the binary liquid mixture of hydrocarbon and fluorocarbon compounds from the viewpoint of the mutual interaction between the film forming molecules. We employed two kinds of mixtures; 1-perfluorooctyl decane (F8H10) – octadecane (C18) and 6-perfluorohexyl hexanol (F6H6OH) – 1-dodecanol (C12OH) mixtures.

The surface tensions (γ) of these mixtures were measured as a function of temperature (T) and composition of the second component (C18 and C12OH) in the liquid mixture (x_2) under atmospheric pressure. X-ray reflectivity (XR) measurement was performed at BL37XU in SPring-8 as a function of scattering vector along the interface normal Q_z.

The γ vs. T curves of pure C18, F8H10, and C12OH systems except the one of F6H6OH show a sharp break point at T_s corresponding to the surface liquid (SL) – SF phase transition. The entropy of surface formation Δs and the electron density profile showed that C18 and F8H10 molecules form SF monolayer and C12OH ones form SF bilayer stabilized by the hydrogen bonding between OH groups facing each other through water molecule intercalated in between them.

In the F8H10 C18 system, the estimation of surface composition suggested that both components are more miscible in the SL layer than in the SF layer. The SL layer is enriched in F8H10 with lower surface tension than C18 compared to bulk liq The excess entropy of the surface $s^{\sigma,E}$ at high x_2 is negative due to domain formation of F8H10 at the surface. In case of F6H6OH C12OH system at high x_2, SL layer is enriched in F6H6OH than b liquid. The negative $s^{\sigma,E}$ value in SL layer also suggests F6H6OH molecules form domain at the surface. Furthermore surface composition and electron density profile (Fig.1) indica that a small amount of F6H6OH mix with C12OH in the SF bila in which F6H6OH molecules preferentially exist in the upper layer of the bilayer.

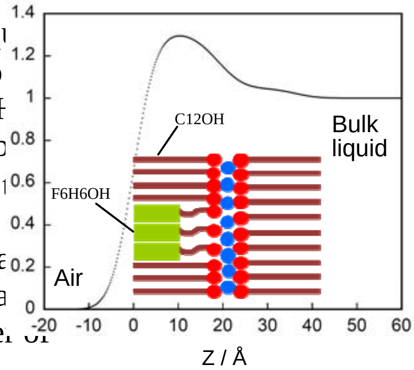

Fig.1 Electron density profile of SF layer of F6H6OH – C12OH system

Literature:

1. O. Gang, X.Z. Wu, B.M. Ocko, E.B. Sirota, M. Deutsch, *Phys.Rev. E,* **58**, 6086 (1998).

Lyotropic lamellar phase made of monolayered θ-shaped amphiphiles

Pierre Bauduin*, Damien Brusselle, Luc Girard, Clara Viñas, Francesc Teixidor, Thomas Zemb, Olivier Diat

[1] – ICSM, UMR 5257 (CEA,CNRS,UM2,ENSCM), BP 17171, 30207 Bagnols-sur-Cèze, France
[2] – CSIC/ICMAB Barcelona, Spain
* - pierre.bauduin@cea.fr

Lyotropic lamellar phases are ubiquitous in the high concentration range of binary surfactant/water mixtures. The present contribution shows that the formation of lamellar phases is not exclusive to alkyl chain based surfactants with a well-defined amphiphilic structure but can also be obtained with metala-carborane clusters, described previously as theta-shaped amphiphiles. As for classical surfactants the lamellae formed can exist both in the liquid and in the solid states depending on temperature. It was concluded from the 2D molecular arrangement in the lamellae that the formation of intermolecular hydrogen bonds, such as $-C-H^{\delta+\cdots\delta-}H-B-$, is the driving force in the lamella formation. This property leads to a peculiar monomolecular structure of the lamella in comparison to the common bilayer structure, encountered with phospholipids in cell walls, which originates from the hydrophobic effect. This monomolecular structure, reminiscent of the structure of clay sheets, also constitutes the wall of the vesicles formed in the diluted regime as it was highlighted previously.[1]

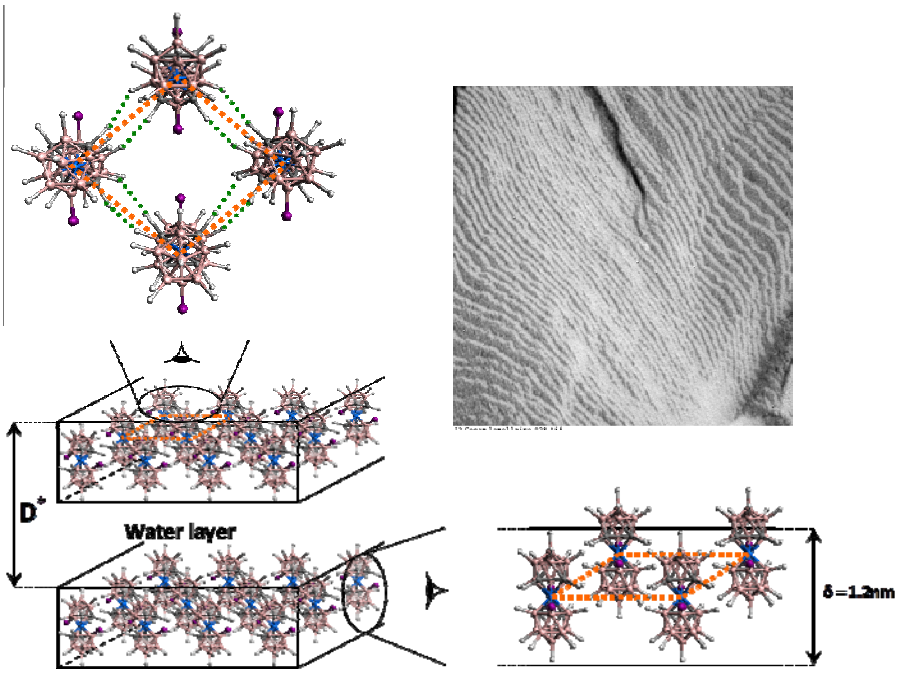

Fig. 1 Structure of the lyotropic lamellar phase formed by di-iodo-cobalta-bis-dicarbollide anion in water

Literature:

1. Bauduin, P; Prevost, S; Farras, P.; Teixidor, F.; Diat, O.; Zemb, T. 2011. A Theta-Shaped Amphiphilic Cobaltabisdicarbollide Anion: Transition From Monolayer Vesicles to Micelles. *Angwandte chemie International Edition* 50(23) 5298-5300.

C3Ms as Diffusional Nanoprobes: Design and Characterization

Nadia Bourouina[1]*, Martien A. Cohen Stuart[1] , Mieke Kleijn[1].

[1] – Laboratory Physical Chemistry and Colloids Science

* - nadia.bourouina@wur.nl

Functionalised Complex Coacervate Core micelle (C3M) consisting of a crosslinked core surrounded by a soluble shell were developed to be used as diffusional nanoprobes. The core crosslinked micelles were first formed by electrostatic interactions between poly(ethylene oxyde-methacrylic acid) (PEO-PMAA) and fluorescently labelled poly(allylamine hydrochloride) (PAH) and then the core was irreversible crosslinked through amide bonds. The resulting diffusional nanoprobe is 15 nm in radius and stable against factors that could influence its stability such as ionic strength and pH. The diffusion of the fluorescent micelles was measured in xanthan solution using Fluorescent Recovery After Photobleaching (FRAP), giving information about the structure of xanthan in solution. This result provides a promising example of the application of these fluorescent micelles.

Surface-mediated Fibril Formation of Modular Protein Polymers

Mieke Kleijn*, Arifur Rahim, Céline Charbonneau, and Martien Cohen Stuart

Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6,
6703 HB, Wageningen, The Netherlands
* - mieke.kleijn@wur.nl

We developed a new class of stimulus-responsive, biologically produced block polymers that can self-assemble into filamentous structures [1]. In this contribution we present experimental work on the surface-induced association behavior of 'silk-collagen' triblock copolymers. These have a structure CS^hS^hC where C stands for a hydrophilic collagen-based part of 198 amino-acids long, rich in glutamine, arginine and serine, and S for a silk-based part that consists of 24 octapeptide repeats GAGAGAGX, where the X position is taken by histidine (h). In bulk solution, at pH-values above the pKa of histidine (6.5), the silk block is uncharged and folds into compact so-called β-rolls, while the polymers self-assemble into filaments [2,3]. We show that the presence of a negatively charged silica surface modulates and accelerates the molecular assembly process. Within a narrow window of solution pH values *below* the pK_a of histidine, surface grown filamentous structures were found using atomic force microscopy (Figure 1). Fibrils start to form on the surface within a very short period of time implying that the surface provides nucleating sites for the growth. Fibril length, morphology and surface population were found to depend on solution pH, polymer concentration and ionic strength. We propose a mechanism for the surface-induced self-assembly process that may render insight to the fundamentals of fibril formation.

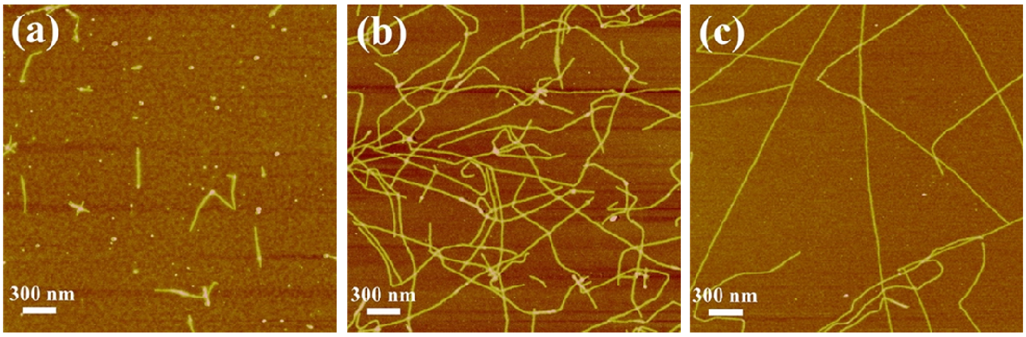

Fig. 1 Surface-grown protein polymer fibrils on silica at (a) pH 4, (b) pH 5 and (c) pH 6; ionic strength 2.5 mM.

Literature

1. Martens A.A, Portale G., Werten M.W.T., De Vries, R., Eggink G., Cohen Stuart M.A., De Wolf F.A. 2009. Triblock protein copolymers forming supramolecular nanotapes and pH-responsive gels. Macromolecules 42: 1002-1009.
2. Schor M., Martens A.A., De Wolf F.A., Cohen Stuart M.A., Bolhuis P.G. 2009. Prediction of solvent dependent β-roll formation of a self-assembling silk-like protein domain. Soft Matter 5: 2658-2665.
3. Beun L., Beaudoux X., Kleijn J.M., De Wolf F.A, Cohen Stuart M.A. Self-assembly of silk-collagen-like triblock copolymers resembles a supramolecular living polymerization. 2012. ACS Nano 6: 133-140.

Chitosan-DNA complexes: charge inversion and DNA condensation

Simona Sennato[1]*, Francesca Bomboi[1], Adalberto Bonincontro[1] and Federico Bordi[1],

Laura Chronopoulou[2] and Cleofe Palocci[2]

[1] *Department of Physics, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy*
[2] *Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy*
* - simona.sennato@roma1.infn.it

The design of biocompatible polyelectrolytes complexes (PECs) is a promising strategy for in vivo delivery of biological macromolecules, such as proteins and DNA. Particularly, the condensation of DNA by polycations (with the formation of the so called "polyplexes") received considerable attention for its potential in gene delivery applications, where the development of safe and effective non-viral vectors remains a central challenge [1]. Among polymeric polycations, chitosan has recently emerged as a suitable material for the preparation of non-viral gene delivery vectors [2]. There has been recently a significant research effort aimed at understanding the general aspects of the PEC formation and the influence of the polycation valence, degree of polymerization and polydispersity, theoretical phase diagrams for polyanion-polycation complexes have been calculated [3]. Despite the significant efforts, a comprehensive theory for the complex phenomenology has not been developed yet, probably due to the fact that most experimental studies focused on empirical attempts to design "optimal" carriers (in terms of some biological effect), paying scant attention to the systematic study of the complexation process and to the comparison with theory. In this study, we investigate the aggregation behavior of Chitosan-DNA complexes in different conditions, by considering Chitosan of different degree of polymerization, by a combined study using Dynamic Light Scattering, Electrophoresis, Atomic Force and Scanning Electron Microscopy. We compare the results with the existing models for the complexation of oppositely charged polyions and show that they represent a consistent "frame" for the different observations reported in the literature that previously appeared uncorrelated, and that they can hence be used as a guide to the rational design of new and more efficient polycation-based vectors, for an effective delivery of genetic material.

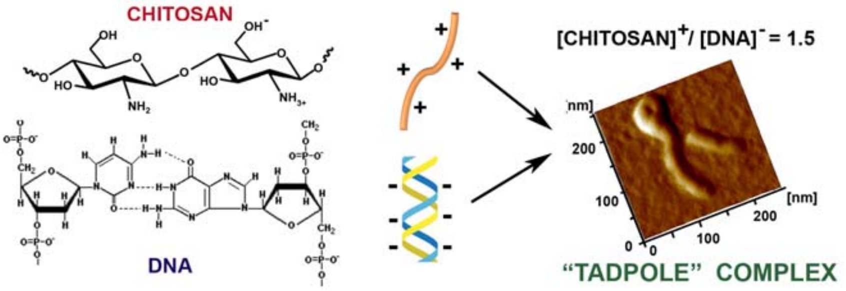

Fig. 1 AFM image of the "Tadpole" complex formed at Chitosan excess.

Literature:

1. C. L. Grigsby, K. W. Leong, 2010, J. R. Soc. Interface 7 S67-S82.
2. S. Mao, W. Sun, T. Kissel, 2010, A. Masotti, F. Bordi, G. Ortaggi, F. Marino, C. Palocci, 2008, Nanotechnology 19: 055302/1-055302/6.
3. N. N. Oskolkov, I. I. Potemkin, 2007, Macromolecules 40: 8423-8429.

Quiescent bilayers at the mica-water interface

Francesca Speranza [1], Robert K. Thomas [2] and Wuge H. Briscoe [1]*

[1] *School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK*
[2] *PTCL, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK*
* wuge.briscoe@bristol.ac.uk

Despite extensive studies with many experimental techniques, the morphology and structure of the self-assembled aggregates of quaternary alkyl ammonium bromides (C_nTABs) at the solid-liquid interface remains controversial.

Using a home-built liquid cell that employs the "bending mica" method, we have performed unprecedented synchrotron X-ray reflectometry (XRR) measurements to study the adsorption behaviour of a C_nTAB series (n = 10, 12, 14, 16 and 18) at the mica-water interface at different surfactant concentrations.[1] We find that our XRR data cannot be described by surface aggregates such as cylindrical and spherical structures reported by AFM studies. In addition we have observed that the bilayer thickness, surface coverage and the tilt angle all depend on the surfactant concentration and surfactant hydrocarbon chain length n, and that the bilayer thickness reaches a maximum value at approximately the critical micellisation concentration (~ 1 cmc) for all the C_nTABs investigated (*cf*. Fig. 1).

We propose that C_nTABs form disordered bilayer structures on mica at concentrations below cmc, whilst at ~ 1 cmc they form more densely packed bilayers with the tails possibly tilted at an angle θ_t ranging from ~ 40 – 60° with respect to the surface normal in order to satisfy the packing constraints due to the mica lattice charge, *i.e.* so that the cross-section area of the tilted chain would match that of the area of the lattice charge ($A_s \cong 46.8$ Å^2). As the surfactant concentration further increases, we find that the bilayer thickness decreases due to desorption of surfactant molecules as described by an *Evans-Wennerström's model*.

In light of our XRR results, we suggest that the surface aggregates observed by AFM could be induced by the interaction between the scanning probe and the surfactant layer, thus representing *transient* surface aggregation morphologies; whereas the C_nTAB bilayers we observe with XRR are intrinsic structures under *quiescent* conditions. The suggestion of such quiescent bilayers will have fundamental implications to processes such as lubrication, self-assembly under confinement, detergency and wetting, where the morphology and structure of surfactant layers at the solid-liquid interface is an important consideration.

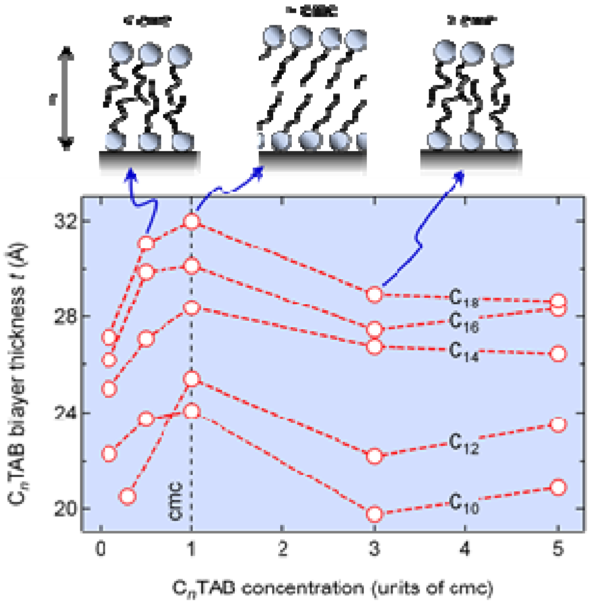

Fig. 1 Under *quiescent* conditions, C_nTAB surfactants form *disordered* or *tilted* bilayers with a maximum layer thickness at ~ 1 cmc.

Literature:

1. F. Speranza *et al.* (2013) *Soft Matter*, in press.

Acknowledgements:

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Study of closed-cage silsesquioxane in pure and mixed Langmuir monolayers

Katarzyna Dopierala1*, Robert Cedro1, Joanna Karasiewicz2,

Hieronim Maciejewski[2], Krystyna Prochaska[1]

[1] – *Poznan University of Technology, Institute of Chemical Technology and Engineering, Pl. Marii Sklodowskiej- Curie 2, 60-965 Poznan, Poland*
[2] – *Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*
* - katarzyna.dopierala@put.poznan.pl

Polyhedral oligomeric silsesquioxanes (POSS) have attracted considerable attention over the last years because of their unique hybrid properties. POSS compounds have found numerous applications in various fields ranging from medicine to chemistry. These three-dimensional molecules of nanometric sizes can be easily modified, thus featuring attractive properties as nanofillers, in sensor systems, fuel cells, in homo- and heterogeneous catalysis, in coating technology [1]. While numerous silsesquioxane-based applications are emerging, most of them are focused on materials synthesis and surprisingly very little is known about the interfacial properties of these materials. However understanding interfacial properties of POSS is required for their future applications for example as nanofillers, in electronics, in medical hybrid materials or in coating technology. While open cage-POSS can be regarded as a novel Langmuir monolayer model, closed cage silsesquioxanes have not been widely studied in this area. Therefore there are rationales for study of fully condensed silsesquioxanes in Langmuir monolayers. In this study we present the properties of tetrakis({1,1,2,2,3,3,4,4-octafluoropentyloxypropyl}dimethylsiloxy))tetrakis{2-trimethoxsysililoethyl} dimethylosiloxy)octasilsesquioxane (POSS 4:4) in pure and mixed Langmuir monolayers. The surface pressure-area isotherms, Brewster angle microscopy, surface potential were used to determine the interfacial properties of the silsesquioxane at the air/water interface . Moreover, the dilational viscoelasticity of the monolayers was investigated by oscillating barriers method.

Literature:

1. David B. Cordes, Paul D. Lickiss and Franck Rataboul, 2010, Recent Developments in the Chemistry of Cubic Polyhedral Oligosilsesquioxanes, Chem. Rev. 110, 2081-2173.

Acknowledgements:

The research was financially supported by Polish National Science Centre by grant No. UMO-2012/05/B/ST5/02200.

Controllable Self-Assembly and Functionalization of Hybrid Supramolecular Reverse Micelles As Building Units

Lixin Wu *

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, China
* - wulx@jlu.edu.cn

Polyoxometalates (POMs) are a family of nanosized metal-oxygen polyanion clusters with diverse composition and topology exhibiting interesting applications. To combine the functional features with their dispersivity, porosity, size controllability, and biocompatibility, POMs were tried to organize into various media and/or carriers. However, it is often difficult to incorporate POMs into organic materials in a well defined way. Since organic components bear excellent merits for self-organization in soft materials systems such as surface and solution, while inorganic components display stable functions, it is significant to combine them into one building unit through covalent and non-covalent approaches. Due to the intrinsic anionic feature, the counterions of POMs can be replaced by cationic organic amphiphiles through electrostatic interaction, generating organically-modified POMs. In most cases, the formed supramolecular complexes possess precise aggregation structure of reverse micelles, where the inner core of water is occupied by POMs. This kind of hybrid supramolecular reverse micelles exhibit fantastic self-assembled properties because of the structural uniformity, changeable morphology and amphiphilicity, which demonstrate an important and a simple route for tuning the organization of POMs in different chemical environments. By grafting photoactive groups such as azobenzene derivatives into inorganic and/or organic components, we can obtain photosensitive hybrid supramolecular complexes. With such a strategy, we successfully realized several interesting reversible transformations, such as between fibrous and spherical self-assembled structures,[1] assembly and disassembly through photo-irradiation.[2] In addition, we carried out a photocontrolled reversible phase transfer of hybrid supramolecular complexes from organic phase to aqueous solution toward an automatic separation of catalyst and recycles. We also apply the photochromism of POMs for chiral generation and extinction,[3] and the smart reversible transformation from helical to spherical assembled structures of achiral complexes. All these results indicate that the supramolecular reverse micelles represent a new type of soft amphiphiles with full properties but beyond functionalities of general amphiphiles.

Literature:

1. Yan Y., Wang H. B., Li B., Hou G. F., Yin Z. D., Wu L. X., Yam V. W. W., 2010 “Smart Self-Assemblies Based on a Surfactant-Encapsulated Photoresponsive Polyoxometalate Complex” Angew. Chem. Int. Ed., 49: 9233.
2. Yang Y., Yue L., Li H. L., Maher E., Li Y., Wang Y. Z., Wu L. X., Yam V. W.-W., 2012 “Photo-Responsive Self-Assembly of an Azobenzene-Ended Surfactant-Encapsulated Polyoxometalate Complex for Modulating Catalytic Reactions” Small, 8: 3105
3. Wang Y. Z., Li H. L, Wu C., Yang Y., Shi L., Wu L. X., 2013, “Chiral Heteropoly Blues and Controllable Switching of Achiral Polyoxometalate Clusters”, Angew. Chem. Int. Ed., 52: DOI: 10.1002/anie.201209497.

Acknowledgements: MOST973 (2013CB834503) and NSFC (21274053, 91227110, 21221063).

Determination of Layer-by-Layer Blend Film Formation and Drug Uptake Properties Using QCM-D Technique

Öznur Yolaçan and Hüseyin Deligöz*

Istanbul University, Engineering Faculty, Chemical Engineering Dept., 34320 Avcilar-Istanbul, TURKEY
* hdeligoz@istanbul.edu.tr

Quartz Crystal Microbalance (QCM) is commonly used to study sensor devices because of its high sensitivity, durability and linear response to the mass of the target materials. Characterization and drug uptake properties of lbl films by QCM-D were reported only scarcely [1-2]. In this study, it was aimed to determine the formation of layer-by-layer (lbl) blend film and their drug uptake properties in terms of different types of polyelectrolytes, blend composition, lbl deposition conditions. Here, the determination of blend film composition of lbl assembled multilayers by QCM-D and UV-vis was also reported as a novel approach. Furthermore, the adsorbed mass and thickness of lbl films were calculated using Sauerbrey equation. For this purpose, 10 bilayered polyelectrolyte blend films were prepared from highly and weakly charged polyelectrolytes. Polyvinylamine hydrochloride (PVA), polyallyamine hydrochloride (PAH) were used as cationic polyelectrolytes while polystyrene sulfonate sodium salt (PSS), polyvinyl sulfate potassium salt (PVS) or mixtures of PSS and PVS were applied as anionic polyelectrolytes in different ratios (25/75, 50/50 and 75/25). Ibuprofen-sodium salt (IBF-Na) was used as a model drug compound. A schematic representation of lbl blends multilayer formation is given in Fig.1. From the results, it was found out that pure PAH/PSS adsorbed higher on the gold crystal than that of PAH/PVS at pH 1.8. Similar results were observed with the system that PVA was used as a cationic polyelectrolyte. The adsorbed mass values in the blend lbl films were found to be in the range from 335 to 1752 ng while the drug uptake values for pure and blend films were between 390 and 1910 ng. Interestingly, the drug uptakes of lbl blend films were found to be higher than those of pure films. This may be attributed to a rougher surface and a more porous structure of blend films. In summary, QCM-D studies clearly showed that the lbl films can be succesfully fabricated via alternating deposition of polyelectrolytes and drug uptake properties can be finely tuned by choosing appropriate lbl deposition conditions.

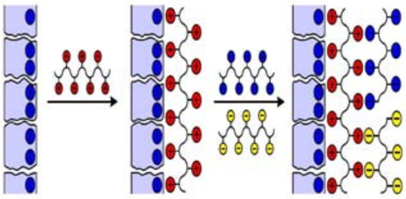


Fig. 1: A schematic representation of lbl blends multilayer formation.

Literature:

1. Yoshida K.; Hashide R.; Ishii, T.; Takahashi, S.; Sato, K.; Anzai, J-I. **2012,** Layer-by-Layer Films Composed of Poly(allylamine) and Insulin for pH-Triggered Release of Insulin. *Colloids Surf., B.*, *91*, 274-279.
2. Jang, Y.; Akgun, B.; Kim, H.; Satija, S.; Char, K. **2012,** Controlled Release from Model Blend Multilayer Films Containing Mixtures of Strong and Weak Polyelectrolytes. *Macromolecules*, *45*, 3542-3549.

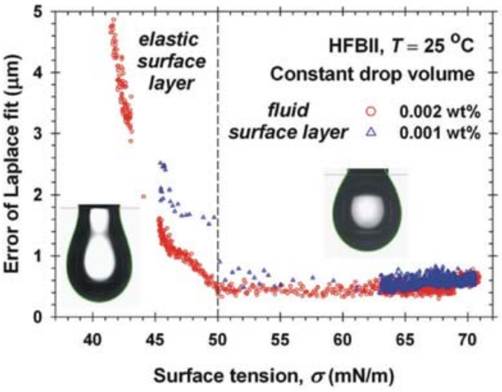
Acknowledgements: This work was supported by TUBITAK (Turkish Science and Research Council) under the contract number of 112M290.

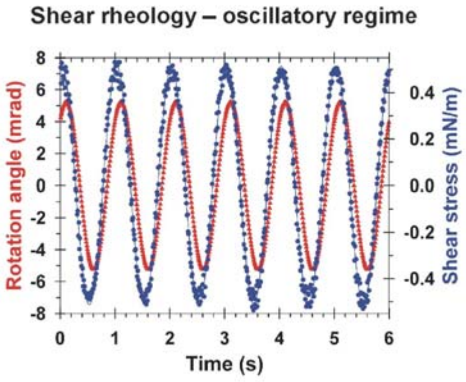
Surface Shear and Dilatational Rheology of Hydrophobin Adsorption Layers: Laws of Viscoelastic Behavior

Krassimir Danov[1]*, Peter Kralchevsky[1], Gergana Radulova[1], Simeon Stoyanov[2]

[1] – *Department of Chemical Engineering, Faculty of Chemistry & Pharmacy, Sofia University St. Kliment Ohridsky, Sofia, Bulgaria*
[2] – *Unilever Research & Development, 3133AT Vlaardingen, The Netherlands*
* - KD@LCPE.Uni-Sofia.BG

The hydrophobin (HFBII) is an amphiphilic protein that can irreversibly adsorb at the air/water interface. The formed protein monolayers can reach a state of two-dimensional elastic solid that exhibits a high mechanical strength. The pendant-drop method and Langmuir trough are applied to investigate the characteristic relaxation times and surface dilatational elasticity, E_{dil}, of HFBII adsorption layers [1]. The experimental data for the relaxation time suggest that the adsorption rate is determined by the balance of two opposing factors: (i) the barrier to detachment of protein molecules from bulk aggregates; (ii) the attraction of the detached molecules by the adsorption layer due to the hydrophobic surface force. At lower surface pressures all experiments give close values of E_{dil} that are increasing with the rise of surface pressure.





The surface shear rheology of viscoelastic HFBII adsorption layers is studied by means of a rotational rheometer in angle-ramp/relaxation and oscillatory regimes. In angle ramp regime, the experimental data comply with the Maxwell model of viscoelastic behavior. The surface shear elasticity, E_{sh}, and viscosity, η_{sh}, are determined as functions only of the shear rate from the fits of rheological data [2]. In oscillatory regime, the storage and loss moduli depend on the rate of shear strain in a quasi-linear regime. At large amplitudes the Lissajous plot is not an ellipse and the Fourier expansion of the measured torque contains two or more odd modes [2]. Our analysis of data in both angle-ramp and oscillatory regimes revealed that the rheological behavior of the system obeys a combined Maxwell-Herschel-Bulkley model. The quantities, E_{sh}, η_{sh}, and the frequency of the system's response $\nu_{\mathrm{sh}} = E_{\mathrm{sh}}/\eta_{\mathrm{sh}}$, are universal functions of the rate of strain. A complete agreement between the results obtained in the two different kinetic regimes has been achieved in a wide range of the shear rates [2].

Literature:

1. N.A. Alexandrov, K.G. Marinova, T.D. Gurkov, K.D. Danov, P.A. Kralchevsky, S.D. Stoyanov, T.B.J. Blijdenstein, L.N. Arnaudov, E.G. Pelan. A. Lips, Interfacial layers from the protein HFBII hydrophobin: dynamic surface tension, dilatational elasticity and relaxation times, J. Colloid Interface Sci. 376 (2012) 296–306.
2. K.D. Danov, G. Radulova, P. Kralchevsky, K. Golemanov, S. Stoyanov, Surface shear rheology of hydrophobin adsorption layers: laws of viscoelastic behavior with applications to long-term foam stability, Faraday Discuss 158 (2012) 195–221.

Effect of the Headgroup on the Thermal Behavior of Surfactants

Pierandrea Lo Nostro[1]*, Chiara Venturini[2], Niccolò Peruzzi[1], Barry W. Ninham[3], Piero Baglioni[1]

[1] – *Dept. Chemistry & CSGI, University of Florence, 50019 Sesto Fiorentino (Firenze), Italy*
[2] – *Nanosciences Group, CEMES UPR 8011 CNRS, 31055 Toulouse cedex 4, France*
[3] – *Research School of Physical Sciences & Eng., Australian Natl. Univ., Canberra, Australia*
* - PLN@csgi.unifi.it

The effect of the structural and chemical features of the heagroup on the thermal behavior of surfactants is studied through the analysis of the phase diagrams of binary mixtures of ascorbyl-alkanoates. These amphiphiles carry a polar head group of L-ascorbic or D-isoascorbic acid directly linked to a fatty acid chain (see Fig. 1, left). In particular we studied the binary mixtures composed of:

- L-ascorbyl-dodecanoate (L-ASC12) and D-isoascorbyl-dodecanoate (D-ASC12)
- L-ascorbyl-octanoate (L-ASC8) and L-ascorbyl-heaxadecanoate (L-ASC16).

The phase diagrams show the presence of two eutectics and a molecular compound in the first mixture,[1] while the second system produced two eutectics and a peritectic point (see Fig. 1, right).

In order to determine whether the different behavior is due to the chain length difference or to the headgroups, we acquired the phase diagram also for the octanoic acid + hexadecanoic acid system. The results, supported by DSC, FTIR, optical microscopy and WAXD data, indicate that the specific thermal behavior is mainly due to the peculiar structural and chemical properties of the headgroups, and in particular to the presence of intermolecular hydrogen bonding that involve the ascorbyl rings.

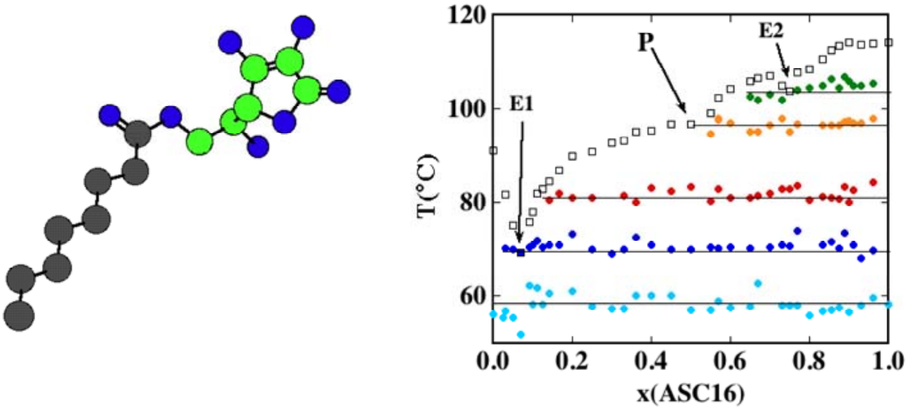


Fig. 1 Left: Structure of ascorbyl-octanoate. Right: Phase diagram of L-ASC8 + L-ASC16.

Literature:

1. Ambrosi M., Lo Nostro P., Fratini E., Giustini L., Ninham B.W., Baglioni P. 2009. Effect of Headgroup Chirality in Nanoassemblies. 2. Thermal Behavior of Vitamin C-Based Surfactants. J. Phys. Chem. B 113: 8324-8331.

Acknowledgements:

Partial financial support from CSGI (Florence) and Ministero dell’Istruzione, dell’Università e della Ricerca (MIUR, Rome) is greatly acknowledged.

Hofmeister effect on adsorption and micellization of ionic surfactants

Radomir I. Slavchov[1], Tonya Andreeva[2], Ivan Ivanov[3*]

[1] – *Sofia University, Dept. of Physical Chemistry*
[2] – *Bulgarian Academy of Sciences, Institute of Biophysics*
[3] – *Sofia University, Laboratory of Chemical Physics and Engineering*
* – ii@lcpe.uni-sofia.bg

The Hofmeister effect on the adsorption at liquid surfaces and the micellization of ionic surfactants is studied. Models are presented for the effect of the counterion on the adsorption parameters (water|gas or water|oil interface) – adsorption constant, actual area of an adsorbed molecule, second virial coefficient and Langmuir's spreading pressure of the liquid expanded monolayer [1-3]. The models are based on a quantity called *ion-specific adsorption energy* u_{i0}, which is related directly to the basic ion characteristics (crystallographic and hydrated ionic radii, polarizability, ionization potential), and is a measure of the intensity of the ion-surface dispersion and hydration interactions [1]. The value of u_{i0} is calculated for several counterions without using any free adjustable parameters. This thorough analysis revealed the dependence of the adsorption on the medium (nature and composition of the hydrophobic phase) and on the surfactant structure (hydrocarbon chain length, nature of the counterion). Extensive comparison of the theoretical results with tensiometric experimental data demonstrated the applicability of the theoretical model. The universality of the concept for ion-specific adsorption energy is further demonstrated by considering the role of the Hofmeister effect on critical micelle concentration [2]. The model was generalized to adsorption and micellization of ionic surfactants in the presence of mixture of counterions [2,3]. Comparison is made with the ion-specific effects observed with the surface properties of concentrated inorganic electrolyte solutions. This reveals the very different physical origin of the latter Hofmeister effects which are largely controlled by the ion-specific bulk solution properties [4]. Thus the specific value of the surface tension of solutions of various simple electrolytes seems related to the mean activity coefficients, and the specificity of $\Delta\chi$-potential is originating from the dielectric permittivity decrement in concentrated solutions [4].

Literature:

1. Ivanov, I.B., Marinova, K.G., Danov, K.D., Dimitrova, D., Ananthapadmanabhan, K.P., Lips, A. 2007. *Adv Colloid Interface Sci* **134-135**: 105–124.
2. Ivanov, I.B., Slavchov, R.I., Basheva, E.S., Sidzhakova, D., Karakashev, S.I. 2011. *Adv. Colloid Interface Sci* **168**: 93–104.
3. Slavchov, R. I., Karakashev, S.I., Ivanov, I.B. 2013. In: Surfactant Science and Technology: Retrospects and Prospects, Ed. L. Römsted, Taylor and Francis, LLC, in press.
4. Slavchov, R.I., Novev, J.K. 2012. *J Colloid Interface Sci* **387**: 234–243; Slavchov, R.I., Novev, J.K., Peshkova, T.V., Grozev, N.A. 2013. *J Colloid Interface Sci*, in press.

Acknowledgements:

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In-Plane Self-Assembly of 2D Colloids through Substrate-Induced Condensation of Langmuir Monolayers

Dmitry S. Turygin,[1] Denis I. Babenko,[1] Alexander A. Ezhov,[2] Vladimir K. Ivanov,[3] Vladimir V. Arslanov,[1] and Maria A. Kalinina*,[1]

[1]*Frumkin Institute of Physical Chemistry and Electrochemistry RAS*
[2]*Faculty of Physics, Lomonosov Moscow State University*
[3]*Kurnakov Institute of General and Inorganic Chemistry RAS*
* - kalinina@phyche.ac.ru

Langmuir monolayers have been widely employed for the ordering of nanoparticles in 2D colloidal crystals and patterned colloidal assemblies. However, the controlled fabrication of 2D open structures such as fractal and percolated 2D nanoparticle networks (NNTs) remains a challenging issue for this area of research.

We use substrate-mediated condensation of Langmuir monolayers on aqueous colloids to suggest a new, simple and inexpensive method which makes it possible to generate 2D nanoparticle networks as well as other colloidal morphologies over large areas.[1] In this method, the planar assemblies of nanoparticles are formed via cooperative process of colloid-induced “cooling” of the mixed monolayer of fatty surfactants followed by a formation of colloidal gel-like structures on a surface of hydrosol. We used catanionic mixtures of surfactants, for which the interactions between oppositely charged surfactants are much stronger than those between surfactants and solids. The adsorption of anion-stabilized nanoparticles on such monolayers increases the intermolecular interactions and leads to a rapid condensation of surfactant mixture. This process promotes an aggregation of adsorbed nanoparticles into 2D gel-like networks or other arrested phases within rigid organic phase, which acts as a chemically inert dispersion medium. The substrate-mediated self-assembly allows the formation of 2D open structures with widely varying compositions, which can comprise either individual or mixed colloids of different chemistry. The as-formed assemblies can be further transferred onto various planar solids via dip coating.

The same approach was used in formation of photosensitive hybrid system comprising conducting monolayer of polymerized amphiphilic diacetylenes and AuNPs. The mixing of cationic and anionic diacetylenes yielded defect-less, extended coverages of stable red form of the polymer upon UV-irradiation. The polymerization of the monolayer on the surface of gold hydrosol gave condensed, uniform and conducting polymeric film, arresting non-aggregated nanoparticles at the distances comparable to the size of AuNPs. Such hybrid 2D assemble also exhibited a resonance-enhanced absorption of visible light and an increase in conductivity upon light irradiation.

We believe that substrate-mediated self-assembly offers a new route for to generate 2D structures from various starting materials and it provides an opportunity for a deeper insight of the interfacial phenomena related to the metastability of the ultrathin films at the air/water interface.

Literature:

1. Babenko, D. I., Ezhov, A. A., Turygin, D. S., Ivanov, V. K., Arslanov, V. V., & Kalinina, M. A. (2011). *Langmuir*, *28*, 125-133.

New Superspreading Siloxane Surfactants for Firefighting

Shute Ye[1], Richard Meisenheimer[1], Kai Wirz[1], Ralf Hetzer[2], Dirk Blunk[1],*

[1] – *University of Cologne, Department of Chemistry, Greinstr.4, 50939 Cologne, Germany*
[2] – *Bundeswehr Research Institute for Protective Technologies and NBC Protection, 29633 Munster, Germany*
* - d.blunk@uni-koeln.de

Pool fires of fuels, organic solvents or meltable plastics are exceedingly dangerous and demanding for firefighters and due to the burning liquids involved such fires are a particular challenge for the fire defense. The most effective means for fighting such fires are special extinguishing foams, which spread on the surface of the burning apolar material, forming an aqueous film (aqueous film forming foams, AFFF).

Until today, without exception the currently available AFFF contain polyfluorinated surfactants (PFT), which are seen to be indispensable as film formers but which are also non-biodegradable (persistent), possibly accumulate in the ecosystem (bioaccumulative) and are suspected to have toxic effects. For these reasons, the application of perfluorooctane sulfonate (PFOS) in AFFF, which had been much used in the past, was prohibited.

But also the currently used substitute surfactants still contain fluorine and are not harmless. As a consequence, some AFFF applications led to remarkable contamination of the soil and groundwater and the local drinking water abstraction had to be partially suspended.

Our research aims to develop new eco-friendly and non-toxic high performance surfactants to substitute the fluorinated compounds in AFFF.

With respect to their physicochemical properties only siloxane amphiphiles could serve as possible substitutes for the above mentioned critical per- or polyfluorinated surfactants. However, in experiments it turned out that the commercially available surfactants of this type are unsuitable to serve as AFFF: their aqueous solutions did not form water films on the surface of fuels.

To overcome this situation we synthesized, characterized and tested over thirty new siloxane amphiphiles based on carbohydrate substituted siloxane derivatives. A number of these new compounds are very effective as film formers and proved their effectiveness in first extinguishing tests.

We will discuss the structures, synthesis and properties of the new superspreading amphiphiles.

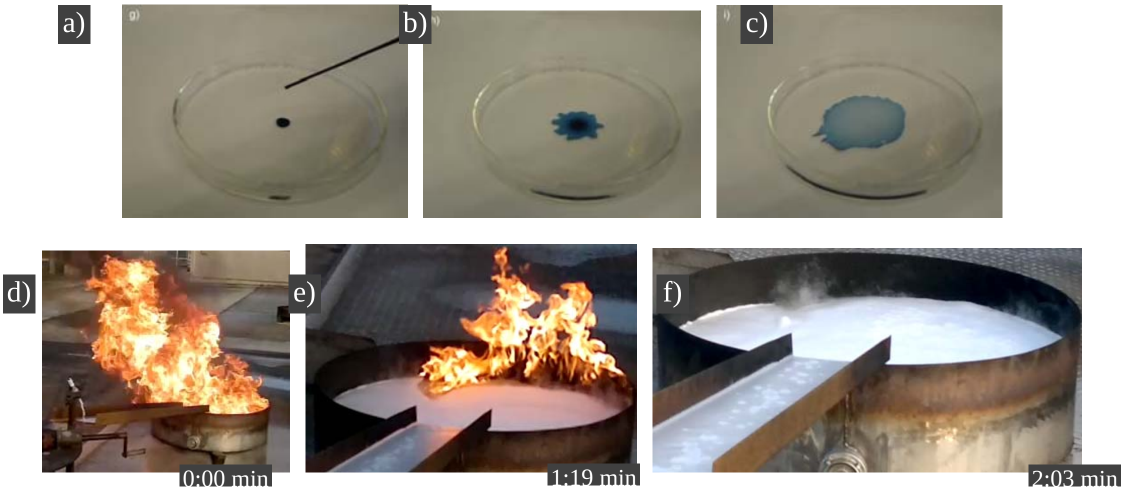

Figure 1:a) – c) Demonstration of the film formation of an aqueous solution containing one of the new siloxane surfactants as film forming component on cyclohexane as model fuel (AFFF solution colored for better visibility); d) – f) fire extinguishing test on jet fuel (JP-8) with the new AFFF.

Inverse micelles as charge carriers in nonpolar liquids: Characterization with current measurements

Filip Beunis [1,2]*, Filip Strubbe [1,2], Masoumeh Karvar [1,2], Oksana Drobchak [1,2], Toon Brans [1,2], Kristiaan Neyts [1,2]

[1] – *ELIS Department, Ghent University, Sint-Pietersnieuwstraat 41, B9000 Ghent, Belgium*
[2] – *Center for Nano and Biophotonics (NB-Photonics), Sint-Pietersnieuwstraat 41, B9000 Ghent, Belgium*
* - fbeunis@elis.ugent.be

Despite the increasing importance of charges in colloidal dispersions based on nonpolar liquids for practical applications and fundamental research, their origin, nature and behavior is not yet completely understood. The most widely (but not generally) accepted view is that in mixtures of a nonpolar liquid with surfactant, inverse micelles act as charge carriers. A lot of research is still needed to support this view, and to gain a fundamental understanding of the electrical properties of inverse micellar solutions. In this contribution, we discuss transient current measurements as a valuable technique for the characterization of charged inverse micelles in nonpolar liquids, and we illustrate how they can be used to study a large number of properties, such as the concentration of both neutral and charged inverse micelles, their mobility, size, aggregation number and valency, and their behavior and generation in the bulk and at surfaces.

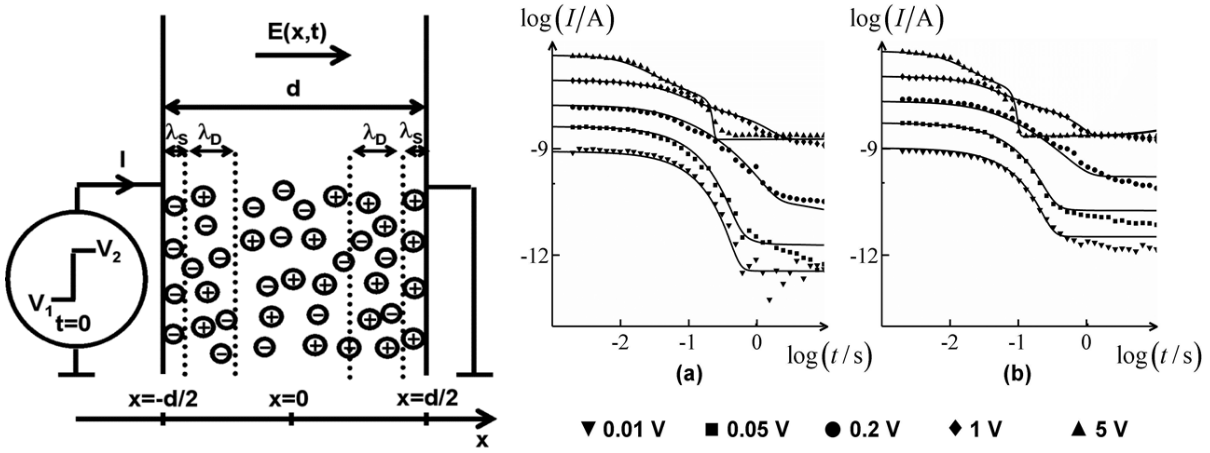

Fig. 1 Schematic overview of a transient current measurement on a layer of nonpolar liquid with surfactant, and some typical experimental results.

Literature:

1. Beunis Filip,Strubbe Filip, Karvar Masoumeh, Drobchak Okasana, Brans Toon, Neyts Kristiaan. 2013. Inverse micelles as charge carriers in nonpolar liquids: Characterization with current measurements. Current opinion in Colloid & Interface Science 18(2): pp. 129-136.

Charge Partition at the Solid-Gas Interface: the Role of Water Adsorption

Fernando Galembeck [1,2]*, Thiago A. L Burgo [1], Rubia F. Gouveia [1,2] and Juliana S. Bernardes [1,2]

[1] – *Institute of Chemistry, University of Campinas - Unicamp, P.O. Box 6154, Campinas SP, Brazil, 13083-970.*
[2] – *National Nanotechnology Laboratory at the National Center for Energy and Materials Research, Campinas SP, Brazil 13083-970.*
* - fernando.galembeck@lnnano.cnpem.br

Solid-liquid and liquid-liquid interfaces are usually charged, due to specific ion adsorption, differential ion solubility or surface group ionization. Electrostatic charging at gas-solid and gas-liquid interfaces is also often observed but reproducible experiments are rarely described in the literature and the intervening mechanisms are still being debated. Recent results from this laboratory (1,3) on the formation and stability of charges at interfaces involving gases shows that water vapour adsorption plays a major role in imparting and abating charges at interfaces. For instance, water adsorption on acidic surfaces contributes negative charge while on base surfaces it contributes positive charge, as shown in Figure 1. On the other hand, water adsorption largely decreases excess corona or tribocharges at interfaces, also due to ion partition.

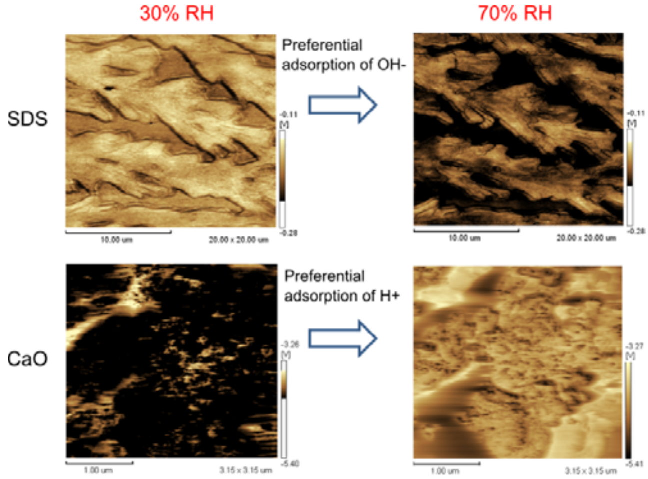

Fig. 1 Electric potential images of SDS (top) and partly hydrated CaO (bottom) exposed to low and high relative humidity.

Literature:

1. Gouveia, R. F. *et al* Acid-basic site detection and mapping on solid surfaces, by Kelvin force microscopy (KFM). *Anal. Chem* **2012**, *84*, 10191-10198.
2. Burgo, T. A. L. *et al* Macroscopic Charge Patterns Formed by Self-Arraying Ions on Polymer Surfaces. *Langmuir* **2012**, *28*, 7407-7416.
3. Bernardes, J.S. *et al* Electrostatic patterns on surfactant coatings change with ambient humidity. *J. Phys. Chem. C* **2010**, *114*, 19016-19023.

Acknowledgements:

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Binary Colloidal Alloys at Liquid Interfaces

Adam Law [1], D. Martin A. Buzza [2], Tommy S. Horozov [3]*

[1] – *Max-Planck-Institut für Intelligente Systeme, Heisenbergstrasse 3, 70569 Stuttgart, Germany*
[2] – *Department of Physics and Mathematics, Theory of Cond. Matter Group, University of Hull, Hull HU6 7RX, United Kingdom*
[3] – *Department of Chemistry, Surfactant and Colloid Group, University of Hull, Hull HU6 7RX, United Kingdom*
* - t.s.horozov@hull.ac.uk

We study the behaviour of monodisperse silica particles at oil-water interfaces by microscope observations. Particles of different sizes and/or hydrophobicity and their mixtures have been spread at the liquid interface to give one- or two-component particle monolayers. We have found that binary mixtures of large (3 µm diameter) and small (1 µm diameter) very hydrophobic particles form two-dimensional super lattices with different structure depending on the number fraction of small particles, *f* (Fig. 1a).[1] A rich variety of two-dimensional hexagonal super-lattices of large and small particles can be obtained in this system due to strong and long-range electrostatic repulsions through the non-polar oil phase. The structures obtained for the different compositions were in good agreement with zero temperature calculations and finite temperature computer simulations.

Binary monolayers of large very hydrophobic and large or small hydrophilic silica particles at an octane-water interface have shown interesting selective attraction between very hydrophobic and hydrophilic particles.[2] By tuning the composition and packing geometry of the mixed monolayer, we have found that a variety of two-dimensional hexagonal superlattices of mixed clusters are formed, stabilized by short-ranged electrostatic induced dipole interactions (Fig. 1b). The cluster structures obtained have been in excellent agreement with zero temperature calculations. Our results suggest that it should also be possible to obtain similar cluster structures for other types of binary monolayers ,e.g. metal-dielectric composites, with unique electromagnetic properties and potential applications in opto-electronics.

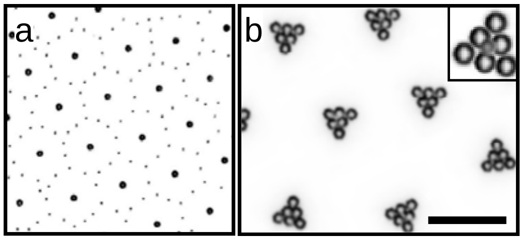

Fig. 1 Optical microscopy images of mixed silica particle monolayers at the octane-water interface. (a) A superlatice of large and small very hydrophobic particles at *f* ≈ 5/6. (b) A superlatice of mixed clusters of very hydrophobic (A) and hydrophilic (B) silica particles with composition AB_6 (see inset). The scale bar is 25 µm.

1. Law Adam D., Buzza D. Martin A., Horozov Tommy S. 2011. Two-Dimensional Colloidal Alloys. Phys. Rev. Lett. 106: 128302.
2. Law Adam D., Auriol Melodie, Smith Dean, Horozov Tommy S., Buzza D. Martin A. 2013. Self-Assembly of Two-Dimensional Colloidal Clusters by Tuning the Hydrophobicity, Composition, and Packing Geometry. Phys. Rev. Lett. 110: 138301.

Background-subtraction in electroacoustic studies of multi-component dispersions

Marek Kosmulski [1,2]*

[1] – *Lublin University of Technology, Lublin, Poland*
[2] – *Leibniz-Institut für Polymerforschung, Dresden, Germany*
* - mkosmuls@hektor.umcs.lublin.pl

The background-subtraction procedure makes this possible to extract the electroacoustic signals of particular components from the overall signal in multi-component dispersions. A few years ago the background-subtraction procedure was used to determine the ζ potentials of metal oxides at electrolyte concentrations >1 M [1]. At low concentrations, the contribution of the electrolyte to the overall signal is negligible, but at higher concentrations, the background-correction is necessary. More recently, the background-correction was used to analyze the electroacoustic signal of dispersions containing various types of particles. In titania-alumina dispersions (at various pH) the behavior of the ζ potential of alumina particles was unaffected by the presence of titania particles and vice versa. In silica-alumina and silica-titania dispersions at neutral pH, mutual interaction between the particles of both components was observed. The overall signal is probably due to aggregates containing both types of particles, rather than to independent particles of individual components.

Literature:

1. Kosmulski, M., Rosenholm, J.B., 1996, Electroacoustic Study of Adsorption of Ions on Anatase and Zirconia from Very Concentrated Electrolytes, *J. Phys. Chem.*, 100, 11681
2. Kosmulski, M., 2013, Electroacoustic Study of Dispersions Containing Two Types of Colloidal Particles. *J.Colloid Interf. Sci.*, in press.

Supercapacitors have an Asymmetric Electrode Potential and Charge due to Nonelectrostatic Electrolyte Interactions

Drew Parsons [1]*

[1] *Department of Applied Mathematics*
Research School of Physical Sciences and Engineering,
Australian National University,
Canberra, ACT 0200, Australia
* - Drew.Parsons@anu.edu.au

Electrostatic theories of electrolytes exemplified by the Poisson-Boltzmann model or the DLVO theory of colloidal interactions have been commonly employed to help understand the behaviour of colloids, supercapacitors or batteries. But in a purely electrostatic theory any distinction between ions of the same charge is lost. The measurement of real systems consistently reveals ion specific effects (also known as Hofmeister effects), particularly at salt concentrations exceeding 0.1M. In recent years we have built up a theoretical framework which aims to explain such ion specific effects. Our approach adds nonelectrostatic ion interactions such as ion dispersion forces alongside the usual electrostatic interactions of the ions. We have applied ab initio quantum chemical methods to build up a library of the relevant ion specific parameters, chiefly ion size and ion polarisability.

Using these techniques we have explored the impact that ion specificity may have on supercapacitors. Our model uses graphite electrodes at constant potential in 1.2M Li salt dissolved in propylene carbonate. For the counterion we used the common battery anions, PF_6^-, BF_4^- and ClO_4^- . We also investigated BrO_4^- and IO_4^- in order to form a regular Hofmeister series in the perhalate ions.

Ion specificity was found when a potential difference was applied between the two electrodes. In a pure electrostatic model a potential V will be split evenly with a surface potential of $+V/2$ found at one electrode, $-V/2$ at the other. When nonelectrostatic interactions of the ions with each electrode are included in the total free energy of the two-electrode system, minimisation of the total energy leads to an asymmetric distribution of the potential difference, with $\psi \neq V/2$ at the cathode, $\psi - V$ at the anode.

We found a corresponding asymmetry in the surface charge and the capacitance of each electrode. This asymmetry raises questions about the definition of capacitance of the two-electrode supercapacitor or battery.

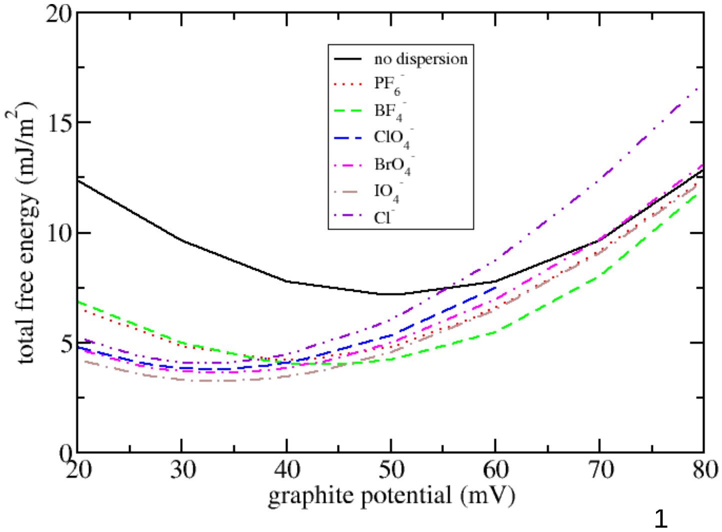

Fig. 1 Supercapacitor energy as a function of graphite electrode potential in 1.2M Li^+ salt with various counterions.

Measuring the electrophoretic retardation force of nonpolar colloids

Filip Strubbe, Filip Beunis, Toon Brans, Masoumeh Karvar, Wouter Woestenborghs, Kristiaan Neyts.

[1] – *Ghent University, Electronics and Information Systems, Sint-Pietersnieuwstraat 41, Ghent B-9000, Belgium and Center for Nano and Biophotonics (NB-Photonics), Ghent University*
* - filip.strubbe@elis.ugent.be

The electrophoretic retardation force originating from friction between a colloidal particle and charge carriers in the liquid is measured in a direct way [1]. The mobility of single, optically trapped particles is measured while depleting the charge carriers in the background electrolyte partially or completely with a small electric field (~0.01 V/µm). This situation is achieved in a nonpolar liquid where charged reverse micelles act as micellar ions. In such a way, by removing the charge carriers that form the diffuse part of the double layer, the ionic strength of the liquid around the trapped particle can be reduced continuously, essentially to zero. By measuring the particle mobility in the Hückel limit, in which the ionic strength is zero and the particle is propelled by the field only, the method allows direct measurement of the retardation force and the bare charge. The transition is measured from the equilibrium situation where the ionic strength is maximal to the Hückel limit where the ionic strength is zero, and the experimental results are compared to numerical calculations. By measuring the bare charge and retardation force, the method provides a direct way to experimentally verify the standard theory of electrophoretic retardation for nonpolar macro-ionic electrolytes.

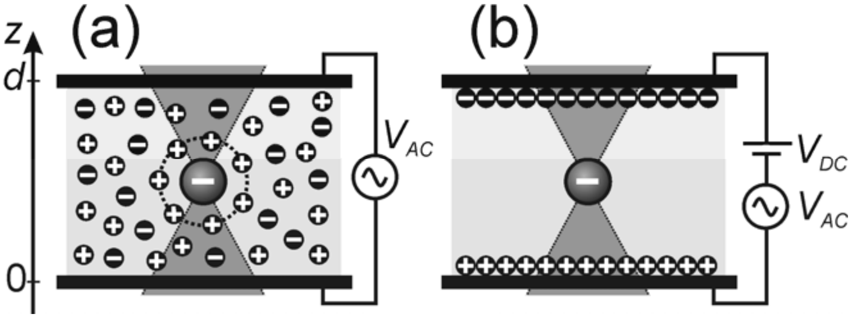

Fig. 1 (a) Schematic representation of a colloidal particle optically trapped at the mid-plane between two electrodes. The electrophoretic mobility is measured by applying an ac voltage V_{AC}. In (b) the positively and negatively charged reverse micelles are completely or partially separated depending on the magnitude of the additional dc voltage V_{DC}.

Literature:

1. Strubbe Filip, Beunis Filip, Brans Toon, Karvar Masoumeh, Woestenborghs Wouter, Neyts Kristiaan. 2013. Electrophoretic retardation of colloidal particles in nonpolar liquids. Physical Review X, 021001.

Acknowledgements: This research was supported by the Research Foundation—Flanders (FWO Vlaanderen), IWTVlaanderen, the IAP-VI project photon@be funded by BELSPO, the Belgian Science Policy program and the Hercules Foundation (Project No. AUGE/013).

Janus Particles in Confined Geometries: Density Functional Theory and Monte Carlo Simulations

Jaroslav Ilnytskyi[1], Andrzej Patrykiejew[2], Stefan Sokołowski[2]*

[1] – *Institute for Condensed Matter Physics, National Academy of Sciences of Ukraine,*
1 Svientsitskii Street, 79011 Lviv, Ukraine
[2] – *Department for the Modelling of Physico-Chemical Processes, MCS University, 20031*
Lublin, Poland
* - stefan.sokolowski@gmail.com

We propose a Density Functional Approach to calculate the structure, thermodynamic properties and phase transitions in the system of Janus particles at a single wall and confined in slit-like pores. The Janus molecules are modelled as spheres composed of a hydrophilic and hydrophobic part. Both lattice, as well as lattice-off models are considered. The results of theoretical predictions are compared with Monte Carlo data, as well as with the results of previous Density Functional calculations.[1,2] Moreover, in the case of lattice-off model we investigate how the solvation force between two plates changes with fluid chemical potential, temperature and the strength of the interparticle interactions. We also present a theory that describes Janus particles at planar walls modified by tethered chain molecules.[3] The pinned chains are treated as tangentially jointed spheres that can interact with fluid molecules via orientation-dependent forces. In this case we study the adsorption of the particles, focusing on the competition between the external field (due to the surface and due to attached chain molecules) and the interaction-induced ordering phenomena.

Literature:

1. Rosenthal Gerald, Klapp Sabine H. L., 2012. Micelle and Bilayer Formation of Amphiphilic Janus Particles in a Slit-Pore. International Journal of Molecular Sciences 13:9431-9446.
2. Rosenthal Gerald, Klapp Sabine H. L., 2011. Ordering of amphiphilic Janus particles at planar walls: A density functional study. The Journal of Chemical Physics 134:154707-1-11.
3. Borówko Małgorzata, Pőschel Thorsten, Sokołowski Stefan, Staszewski Tomasz, 2013.Janus Particles at Walls Modified with Tethered Chains. The Journal of Physical Chemistry B 117:1166–1175.

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Theoretical Analysis on the Orientational Characteristics and Rheological Properties of a Rod-like Hematite Particle Suspension in a Simple Shear Flow

Akira Satoh [1]*, Yasuhiro Sakuda [1]

[1] – *Faculty of System Science and Technology, Akita Prefecture University*
* - asatoh@akita-pu.ac.jp

We have theoretically investigated the particle orientational and rheological properties of a dilute suspension composed of spindle-like hematite particles. This spindle-like hematite particle has a characteristic feature that the particle is magnetized in a direction normal to the major particle axis [1]. We have derived the basic equation of the orientational distribution function by taking into account the spin rotational Brownian motion about the particle axis [2] and this basic equation has been solved numerically. For a very strong magnetic field applied in the shear flow direction, the particle inclines in the direction normal to the flow direction. Also, the particle is restricted in a plane normal to the shearing plane due to the spin Brownian motion. Although the negative viscosity was observed in the previous study [2], in the present case these orientational properties of the particle give rise to positive viscosity. The viscosity becomes large with increasing magnetic field strength. In the case of an external magnetic field applied in the direction of the angular velocity of a simple shear flow, the particle inclines toward a plane normal to the shearing plane, while the magnetic moment is restricted in the direction of the magnetic field. For a strong shear flow, the particle inclines in the shear flow direction and does not rotate around the magnetic moment. The viscosity due to magnetic properties does not occur under the situation of the present magnetic field direction.

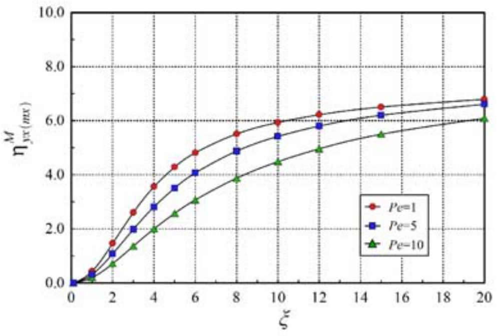


Fig. 1 Dependence of the viscosity on the magnetic field strength ξ for three cases of Peclet number (shear rate), *Pe*.

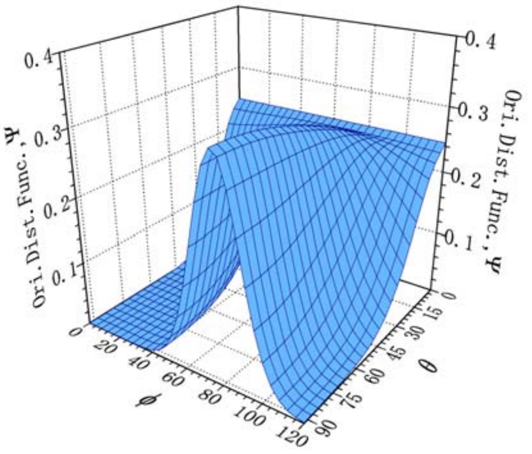


Fig. 2 Orientational distribution function for *Pe*=5 and ξ=20; the particle has a stronger tendency to incline in a direction normal to the shear flow direction with the magnetic moment aligning in the magnetic field direction.

Literature:

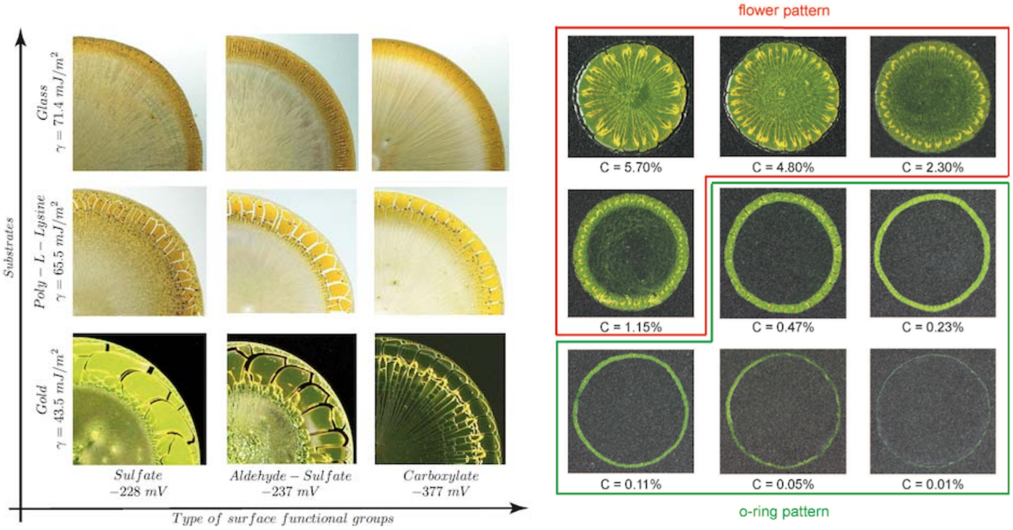
1. Sakuda, Y.[2], Aoshima, M. and Satoh, A.[1], 2012. Negative Magneto-Rheological Effect of a Dispersion Composed of Spindle-like Hematite Particles. Molecular Physics, 110: 1429.
2. Satoh, A.[1], 2013. Influence of the Spin Brownian Motion on the Negative Magneto-Rheological Effect in a Rod-like Hematite Particle Suspension. Molecular Physics, (to appear).

Driving mechanisms leading to the dry-out of nanofluids droplets

Carle Florian, Brutin David*

Aix Marseille University, IUSTI UMR 7343, 13013, Marseille, France
* - david.brutin@univ-amu.fr

The dry-out after the evaporation of a droplet of nanofluids is of great interest since it is the consequence of several mechanisms including convection, wetting, fracturation and delamination. We investigate the role of each contribution in the final pattern by changing: - the humidity to increase or decrease the evaporation rate, the concentration to change the type of pattern observed, the substrate chemical nature to analyze the interaction between the substrate and the nanoparticles, the surface function groupment at the nanoparticles surface to quantify the role of nanoparticles-nanoparticles interaction on the final dry-out.



Figs. 1 Droplets of 24 nm diameter of polystyrene dry-out – Left picture: different substrates and nanofluids surface functional charges – Right picture: Teflon substrate and different concentrations.

We will present a summary of the driving mechanism leading to the dry-out of nanofluid droplet using quantitative example recently published or submitted for publication [1,2].

1. Brutin D., 2013, Influence of relative humidity and nano-particle concentration on pattern formation and evaporation rate of pinned drying drops of nanofluids, Colloids and Surfaces A, Vol. 429, pp. 112-120.
2. Carle F., Brutin D., 2013, How surface functional groups influence fracturation innanofluid droplet dry-outs, Langmuir, submitted.

The short time dynamic signature of the liquid-crystal-glass transition in charged spherical colloidal suspension

P. Holmqvist*

[1]*Institute of Complex Systems (ICS-3),*
Forschungszentrum Jülich, D-52425 Jülich, Germany
* - p.holmqvist@fz-juelich.de

We present the short time dynamic transition of the liquid – crystal - glass transition. Applying dynamic light scattering (DLS) the short time dynamic function, D(q), has been determined from the intensity autocorrelation function, $g_2(q,t)$, at different concentrations in both the crystal and glass region. From D(q) the short time self diffusion, d_s, was determined as a function of concentration. We found that d_s speeds up in the crystal state but has very similar characteristics in the liquid and the glass region. The corresponding structure factor, S(q), will also be presented and we show similarity between the glass and the liquid. This investigation shows that the liquid – crystal and crystal-glass transitions can be identified in addition to the appearance or no appearance of Bragg peaks with the short time dynamics. However no sharp transition in the short time dynamics or S(q) can be found between the glass and the liquid.

Determination of the hydrodynamic friction matrix for various anisotropic particles

Daniela J. Kraft [1]*, Raphael Wittkowksi [2], Kazem V. Edmond[1], Borge ten Hagen[2], David Pine[1], Hartmut Löwen[2]

[1] – *Center for Soft Matter Research, New York University, USA*
[2] – *Heinrich Heine University Düsseldorf, Germany*
* - kraft@physics.leidenuniv.nl

The relationship between the shape of a colloidal particle and its Brownian motion can be captured by the hydrodynamic friction matrix. It fully describes the translational and rotational diffusion along the particle's main axes as well as the coupling between rotational and translational diffusion. We observed a wide variety of anisotropic colloidal particles with confocal microscopy and calculated the hydrodynamic friction matrix from the particle trajectories. We find that symmetries in the particle shape are reflected in the entries of the friction matrix. We compare our experimentally obtained results with numerical simulations and theoretical predictions.

1. Daniela J. Kraft, Raphael Wittkowski, Borge ten Hagen, Kazem V. Edmond, David J. Pine, Hartmut Löwen, Brownian motion and the hydrodynamic friction tensor for colloidal particles of arbitrary shape (submitted)

Fluorescence Correlation Spectroscopy of Repulsive Systems: Theory, Simulation and Experiments

Jingfa Yang, Ligang Feng, Jiang Zhao[1]*, Kaloian Koynov,[2]** Hans-Jürgen Butt[2]

[1] – *Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*
[2] – *Max-Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*
* - jzhao@iccas.ac.cn; ** - koynov@mpip-mainz.mpg.de

The dynamics and structures of soft matter system with multiple charges have been attracting intensive research attention for decades. One of the most uniqueness is the multiple modes in the fluctuation dynamics, which should be originated from the long-range electrostatic interaction. However, a clear picture of such a complex dynamics is unclear, especially on its correlation with the structures. In this research, a systematic investigation into this problem has been performed by dual-color fluorescence correlation spectroscopy (FCS), taking charged colloids as the model system. The research consists of development of theory, Brownian simulation and FCS experiments.

The theoretical basis of FCS for repulsive systems is further expanded and developed. The results of the theoretical analysis are further proved by Brownian simulation and most importantly, by the experimental observation. It is found that the collective correlation function can be divided into the self-part and the distinct-part. The former shows the self-diffusion of the objects while the latter describes the mutual interactions. Dual-color fluorescence cross-correlation spectroscopy provides the direct measurements, from which these two parts can be separated. The particle concentration and the mean squared displacement of single particles can be derived from the self-correlation function while the correlation volume between particles can be approximately estimated from the cross-correlation function. The Debye length of the solution and the surface charge number of particles can be fitted from the cross-correlation function in the case of charged colloids.

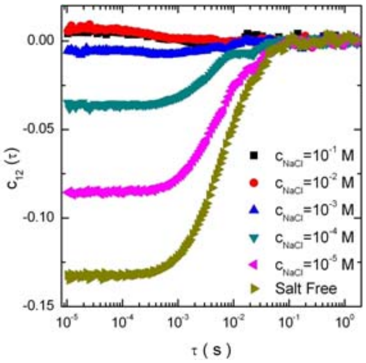


Fig. 1 The cross-correlation function of charged polystyrene colloids by dual-color fluorescence correlation spectroscopy.

References:

1. G. Nägele, Phys. Rep. 1996, 272, 215.
2. L. G. Feng. J. F. Yang, J. Zhao, K. Koynov, H.-J. Butt. 2013, J. Chem. Phys. submitted.

Acknowledgements:

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The effects of aggregation and protein corona on the cellular internalization of oxide nanoparticles

N. OuldMoussa, M. Safi, E. Seyrek, H. Conjeaud and J.-F. Berret*
Matiére et Sytemes Complexes, UMR 7057 CNRS Université Denis Diderot Paris-VII, Batiment Condorcet, 10 Rue Alice Domon et Léonie Duquet, 75205 Paris, France
* - jean-francois.berret@univ-paris-diderot.fr

Engineered nanoparticles are essential components in the development of nanotechnologies. For applications in nanomedicine, particles need to be functionalized to ensure a good dispersibility. In many cases however, functionalization is not sufficient. Particles dispersed in biological fluids become either coated by a corona of serum proteins or precipitate out of the solvent. In the present study, iron and cerium oxide particles of size 10 nm are put under scrutiny. These particles have important biological applicationsinmagnetic resonance imaging or regenerative medicine. As for living cells, murine fibroblasts, human lymphoblasts and macrophages are examined [1]. The interactions between oxide nanoparticles and cells are studied by electron microscopy (Figure 1) and flow cytometry. The previous studies were complemented by cytotoxicity assays.

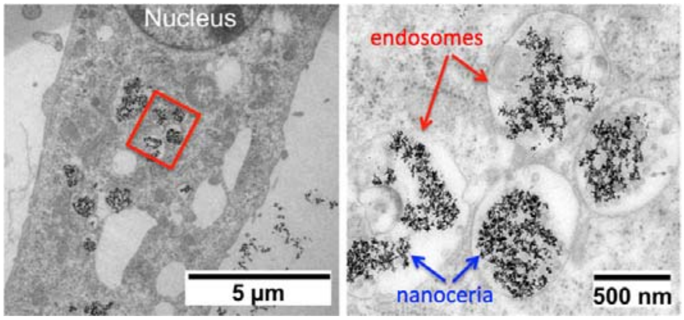

***Figure**1:.Transmission electron microscopy image of 10 nm nanoceria internalized by murine fibroblasts. The vesicles on the right-hand side are endosmomes*

We first show that by changing the coating of oxide particles from citrate ligands to small carboxylated or pegylated polymers, the colloidal stability of the dispersion is improved and the adsorption/internalization towards living cells is profoundly affected. As shown by time-resolved light scattering, citrate-coated particles in cell culture media are spontaneously covered by plasmic proteins and destabilize, whereas the polymer-coated particles exhibit an outstanding dispersibility and a structure devoid of protein corona. As a result of their precipitation, citrate-coated particles interact more strongly with cells. The present approach shows that the surface chemistry and coating of engineered particlesare the key parameters in the nanoparticle/cell interactions, and have moreover a strong impact on the toxicityand cell viability.

Literature:

[1] Galimard A, Safi M, Ould-Moussa N, Montero D, Conjeaud H, Berret JF.Thirty-femtogram detection of iron in mammalian cells. Small 2012;8:2036-2044.
[2] Safi M, Courtois J, Seigneuret M, Conjeaud H, Berret J-F.The effects of aggregation and protein corona on the cellular internalization of iron oxide nanoparticles. Biomaterials 2011;32:9353-9363

Total Internal Reflection Raman Spectroscopy of the Solid-Liquid Interface

Colin D. Bain [1]*

[1] - *Department of Chemistry, Durham University, U.K.*
* - c.d.bain@durham.ac.uk

Total internal reflection (TIR) Raman spectroscopy is a recent technique for studying the adsorption of surfactants, organic molecules, polymers, biological lipids and inorganic ions at solid-liquid interfaces.[1] The short penetration depth of the evanescent wave (typically ~100 nm) allows the discrimination of adsorbed species from those in the bulk. The combination of TIR Raman spectroscopy with chemometric analysis methods allows the acquisition of spectra in as little as one second even in multicomponent systems. A flow cell coupled to a continuous stirred tank allows the determination of complete adsorption isotherms in a few hours provided that the adsorption kinetics are sufficiently fast. If the substrate of interest is transparent, it can be used as incident medium for the pump laser light and molecules of interest adsorbed directly onto the substrate. More generally, thin films of other materials, such as cellulose or haematite, can be deposited on an optical prism and adsorption studied at the interface of the thin film with a liquid. This paper will describe the principles of TIR-Raman spectroscopy and the experimental set-up, discuss the strengths and weaknesses of the technique, and illustrate the application of TIR-Raman spectroscopy with recent examples from our laboratory.

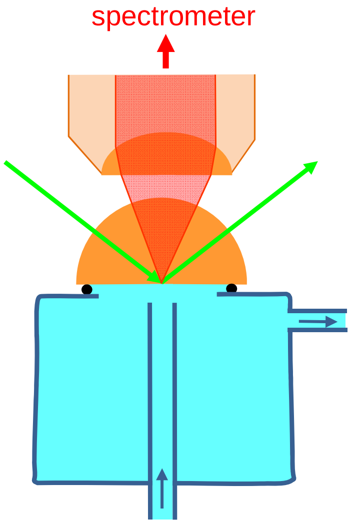

Fig. 1 Schematic illustration of a hydrodynamic flow cell for total internal reflection Raman spectroscopy.

Literature:

1. Woods, D. A., Bain, C. D., 2012 “Total Internal Reflection Raman Spectroscopy” *Analyst.* 137, 35.

On some experimentally established features of the osmotic kinetics and their interpretation

Emil Manev[1], Kiril Kolikov[2], Ivan Minkov[1], Boryan Radoev[1]

[1] *Sofia University "St. Kliment Ohridski", Sofia, Bulgaria*
[2] *University of Plovdiv,"Paisii Hilendarski", Plovdiv Bulgaria*
*** -** Radoev@chem.uni-sofia.bg

Osmosis, that is, the diffusion of solvent across a semipermeable membrane, has been a subject of investigation for more than a century. Although osmotic equilibrium is considered to be well understood from thermodynamic viewpoint and does not pose serious ambiguities, the dynamic aspects of the process frequently exhibit new and even surprising effects, which are difficult to explain within the frames of the traditional kinetic models. Such a non-trivial effect is the established in the present investigation maximum in the rate of solvent transferred through the membrane as a function of time, $q(t)$. This dependence invariably takes the shape of a curve originating at the zero, with gradually increasing values reaching eventually saturation; the plateau at $q(t\rightarrow\infty)$ reflects the equilibrium state. In our experimental investigation we obtained $q(t)$ dependences featuring S-shaped curves, passing through inflexion, equivalent to $d^2q/dt^2=0$. The experiments at varied concentrations confirmed the presence of maxima in the solvent transfer rates, whose heights increase with the solute concentration.

The attempt to interpret such maxima led us to the hypothesis for the occurrence of certain polarization in the vicinity of the membrane, similar e.g. to the concentration polarization at electrolysis. The influx of solvent results in local dilution of the solution in the near-membrane space which generates reverse diffusion flow from the interior, aiming to level the concentrations. An essential assumption here is that the driving osmotic pressure is proportional to the local difference of the concentrations on either side of the membrane. In its turn, the near-membrane concentration is equal initially to the mean concentration in the chamber space. Consequently, it decreases due to dilution, but eventually again reaches the mean concentration level at equilibrium. Such a passage through a minimum in local concentration we associate with the occurrence of the maximum in the rate of solvent influx.

Acknowledgment:

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Colloid Aggregation and Water Purification - using flocculents from Seeds of Moringa trees

Adrian R. Rennie [1]*, Maja S. Hellsing [1], Habbauka M. Kwaambwa [2], Bonang Nkoane [3], Fiona Selato [3]

[1] – *Uppsala University*
[2] – *Polytechnic of Namibia*
[3] – *University of Botswana*
* - Adrian.Rennie@physics.uu.se

Although flocculation has been studied for many years and the aggregate structures are understood as fractals, the different regimes of colloid aggregation are not always well-defined. Diffusion limited or reaction limited colloid aggregation of clusters is expected to give rise to mass fractals with characteristic exponents (dimensions) between 1.75 and 2.3. In order to develop alternative water purification technology we have been investigating flocculents from seeds of Moringa oleifera trees [1, 2]. Scattering experiments (reflection and small-angle scattering) with neutrons provide valuable information about how the protein binds to impurities and how flocculation occurs. New ultra-small angle neutron scattering experiments [3] have shown very dense clusters with dimensions between 2.4 and 2.95 when experiments are performed on concentrated dispersions. Interesting changes are observed with both concentration of particles (polystyrene latex) and flocculents. The increase in fractal dimension with concentration resembles some recently published simulations using Brownian dynamics [4]. The results suggest how the water purification process may be optimised and extended to larger scale purification plants.

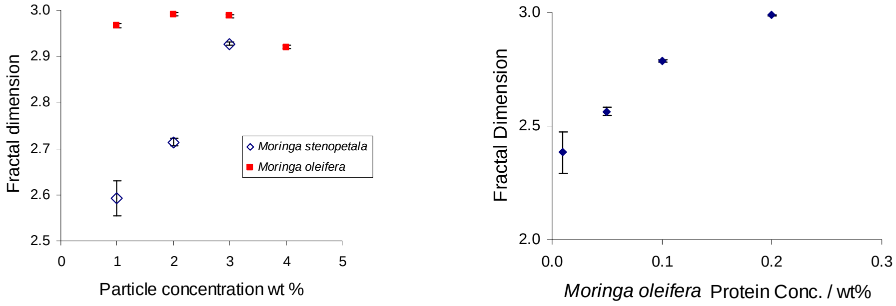


Fig. 1 Fractal dimensions of flocs obtained with (a) protein from two varietals of Moringa trees for various particle concentrations and (b) changes in fractal dimension with 3 wt% particles for different protein concentration.

Literature:

1. Kwaambwa, H. M., Hellsing, M. and Rennie, A. R. 2010, *Langmuir* **26**, 3902-3910.
2. Kwaambwa, H. M., and Rennie, A. R. 2012, *Biopolymers* **97**, 209-218.
3. Hellsing M. S. et al. - in preparation.
4. Lattuada M. (2012) *J. Phys. Chem.*, **116**, 120-129.

The Rheology of Shake Gels

Paul Luckham[1]*, Ann-Sophie Chevalier,[1,2], Maria del Mar Ramos Tejada,[1,3] & Francisco José Martínez Boza[1,4]

[1] –*Dept Chemical Engineering, Imperial College London, UK*
[2] – *Dept. Chimie, Universite de Paris Tech, Paris, France.*
[3]– *Dept. de Física, Universidad de Jaen, Linares, Spain*
[4]– *Dept de Ingeniería Química. Universidad de Huelva. 21071 Huelva, Spain*
* - p.luckham01@imperial.ac.uk

Polymer adsorption to particles to enhance colloid stability has been studied extensively for at least the last five decades due the role of polymers in stabilising particles against aggregation. It is also well known that under certain circumstances polymers can also induce the aggregation of particles either by simultaneously adsorbing on two particles, bridging flocculation, or due to the presence of non adsorbing polymer giving rise to depletion flocculation. Serendipitously we have discovered that certain formulations where we have particles in a relatively high molecular weight polymer solution are perfectly stable for many days, giving a low viscosity solution, but on shaking a gel is formed, some of which can have the consistency of silicone rubber (see the photo's below). On standing the gel relaxes back into the liquid state of the course of seconds to days, depending on the formulation. In searching the literature we found that Zebrowski *et al* [1] has reported similar observations for the synthetic clay Laponite- Polyetheyleneoxide-water system, however we have observed that this phenomenon is rather more general and similar systems can be formed in other inorganic oxide particulate systems, although to date we have not found another polymer which will form such a gel. (We note here that some aspects of this behavior has previously been observed by Cabane [2] and Otskube [3] and their colleagues.)

Initially attempts to monitor the formation of this gel under simple shear in a commercial rheometer were singularly unsuccessful, despite shearing at 1000s $^{-1}$.However, we have found that in a rheometer shear needs to be applied for a very long time, up to 2 hours before over the course of 20 seconds a solid like gel is formed. This has enabled us to characterize the rheological and the relaxation properties of these intriguing formulations, and to propose a mechanism for their formation based around a model for the shear thickening behaviour of hydrophobically modified polysaccharide solutions.

Figure 1 The formation of a shake gel, by simply shaking the formulation which then transforms from a viscous liquid to an elastic solid

References

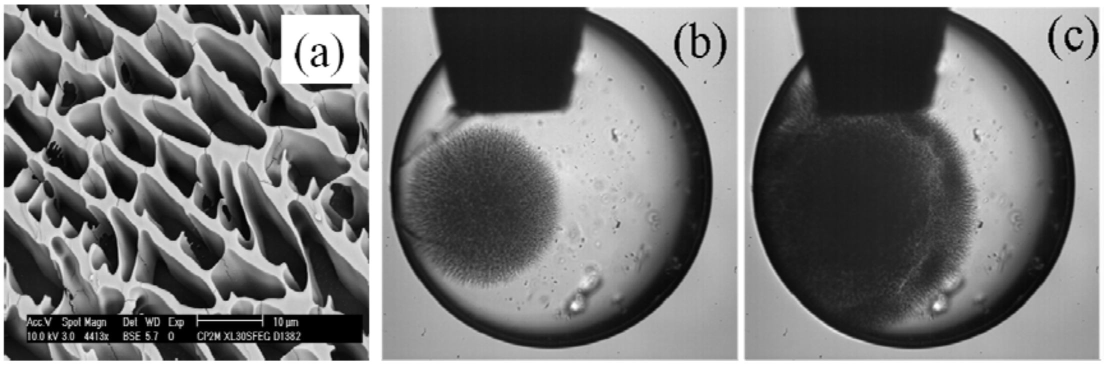
1. J. Zebrowski V. Prasada, W. Zhang, L.M. Walker and D.A. Weitz 2003. Shake-gels: shear-induced gelation of laponite-PEO mixtures, Colloids and Surfaces A: Physicochem. Eng. Aspects 213 189-197.
2. Cabane B., Wong K., Lindner P., and Lafuma F.. 1997, Shear induced gelation of colloidal dispersions, J. Rheology, , 41, 531-547
3. Otsubo, Y. and K. Watanabe, Rheological behaviour of silica suspensions during bridging flocculation induced by shear, J. Colloid Interface Sci. 133, 491–49

Microstructure formation in freezing nanofluid droplets

Renaud DENOYEL and Mickaël ANTONI*

Aix-Marseille Université, CNRS, MADIREL UMR 7246, 13397 Marseille cedex 20, France
* - m.antoni@univ-amu.fr

Nanofluids consist in suspensions of nanoparticles with specific interfacial properties that can be tuned by the addition of surface active molecules. When submitted to fast temperature changes, like for example quenching in slushed nitrogen, nanofluids can present important artifacts as illustrated in figure (a) [1,2]. In this work, the freezing kinetics of nanofluid droplets consisting in a suspension of 15 nm diameter silicon oxide nanoparticles is studied. When surfactant free, these nanoparticles are soluble in water up to 300 g/L. The droplets have few microliters volume and are kept at the end of a hydrophobic capillary tip immersed in a pure hexane continuous phase. This system is maintained in the field of view of an optical microscope and cooled down to -40°C. A high resolution image grabber and a temperature regulated device finally give a straightforward access to the solidification kinetics.



(a) Cryo-SEM image of a silicon oxide nanofluid after freezing in slushed nitrogen. The white pattern corresponds to nanoparticle microstructures. (b) and (c) freezing kinetics at two successive times at temperature T=-30°C. The black growing structure corresponds to propagating dendrites of frozen liquid. Time interval between the two images is 2.10^{-3} s and the field of view is 1 mm^2.

Depending on the silica nanoparticles concentrations and on the cooling rates (1 to 5°C/min), under cooled regimes up to 25°C can be achieved. Well known thermodynamical conditions are then reached for the formation of nucleation germs that will trigger the freezing of the complete droplets. Freezing starts either nearby the capillary tip or at the droplet interface (see figures (b) and (c)). A first regime then shows up. It is fast (few milliseconds) and displays rapidly growing dendrites that will fill out the droplet with a typical velocity that depends on the concentration of nanoparticles. This first regime is followed by a slow one (about one second) where the residual liquid between the dendrites progressively solidifies. It corresponds to the regime where the latent heat is evacuated from the inner part of the droplet to its periphery. When increasing the temperature back above 0°C, the droplets melt and flocculated silicon oxide microstructures can be evidenced.

References

[1] Limage, S., et al., Colloids and Surfaces A, 2009, 365, 154-161
[2] Mikula, R.J. and Munoz, V.A., Colloids and Surfaces A, 2000, 174, 23–36.

Poly(vinylamine) microgels: pH-responsive particles with high primary amine contents

Brian R. Saunders*

School of Materials, University of Manchester, Grosvenor Street, Manchester, M13 9PL, UK
* - brian.saunders@manchester.ac.uk

pH-Responsive microgels swell when the pH approaches the pK_a of the polybase or polyacid chains. We introduce a simple and scalable method for preparation of pH-responsive PVAM microgels[1]. First, non-aqueous dispersion polymerization was used to prepare new monodisperse water-swellable poly(*N*-vinylformamide-co-2-(*N*-vinylformamido)ethyl ether microgels (PNVF-xNVEE). Here, *x* is the mole% of the crosslinker (NVEE) used. Alkali-hydrolysis in water gave colloidally stable poly(vinylamine-co-bis(ethyl vinylamine) ether) (PVAM-xBEVAME) microgel dispersions. The hydrodynamic diameters and electrophoretic mobilities increased as the pH decreased (See Fig. 1).

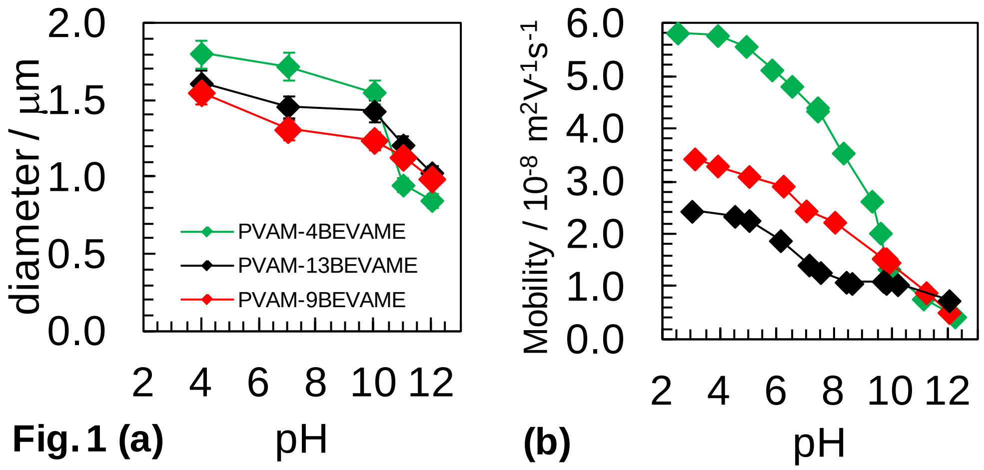


Fig. 1 Variation of (a) hydrodynamic diameter and (b) electrophoretic mobility with pH.

1. Thaiboonrod et al., Soft Matter, 9, 3920, 2013.

Fine-tuning the structure of stimuli-responsive polymer films by temperature and hydrostatic pressure

Matthias Reinhardt [1]*, Joachim Dzubiella [2], Marcus Trapp [3], Philipp Gutfreund [4], Martin Kreuzer [1], André H. Gröschel [5], Axel H. E. Müller [5], Matthias Ballauff [1,2], Roland Steitz [1]

[1] – *Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin*
[2] – *Department of Physics, Humboldt-University Berlin*
[3] – *Department of Physical Chemistry, Ruprecht-Karls-Universität Heidelberg*
[4] – *Institute Laue-Langevin*
[5] – *Macromolecular Chemistry II, University Bayreuth*
* - matthias.reinhardt@helmholtz-berlin.de

Planar multi stimuli responsive PDMAEMA brushes from diblock copolymer Langmuir layers with varied grafting density were prepared by Langmuir-Schäfer transfer. Utilizing neutron reflectometry, NR, the brushes were analyzed at the solid-liquid interface in the temperature range 20 to 60 °C for hydrostatic pressures from 1 to 1000 bar. A novel theoretical model of the brush density profile as a function of grafting density σ, temperature T and hydrostatic pressure p was used to fit the experimental NR data. Within that model, temperature and pressure effects are described independently. Increasing temperature caused a continuous decrease of polymer brush thickness (cf. Fig. 1). The reason for this response of the brush is a hydrophobic coil to globule transition of the polymer chains. When crossing the lower critical solution temperature (LCST) the brushes collapse into a high density polymer layer near the grafting plane and a low density Gaussian tail towards the liquid fronting phase. The new analytical model intrinsically includes the observed vertical phase separation and yields the correct position of the LCST in a thermodynamically consistent way, exclusively based on structure data. Hydrostatic pressure is found to act perfectly antagonistic to temperature. The hydrophobic collapse of the PDMAEMA brush that is caused by a temperature increase of ~10K is counterbalanced by a pressure increase of 1000 bar.

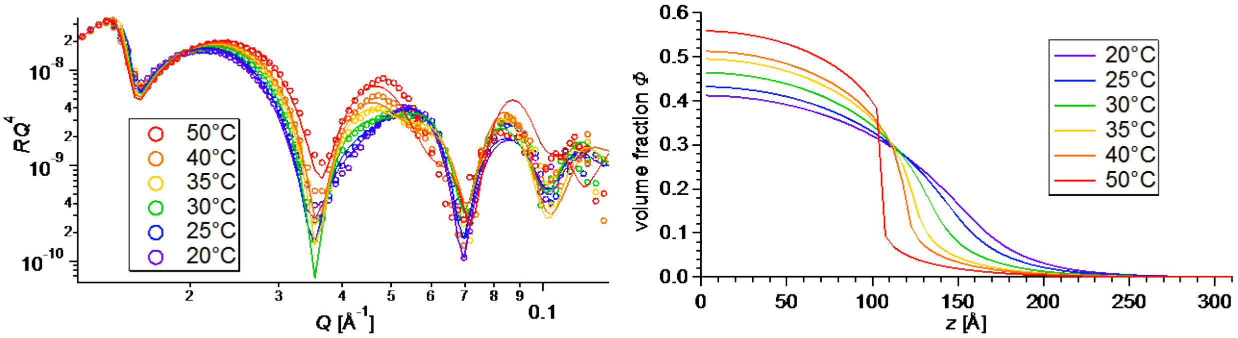


Fig. 1 Neutron reflectivity *R(Q)* from a PDMEAMA brush grafted to a dPS coated silicon support at a grafting density of σ = 0.22 nm^{-2} against D_2O liquid phase as a function of sample temperature (left panel). Solid lines are fits to the experimental data according to the brush volume fraction profiles from the analytical model (right panel).

Time-limitable Hydrogels Controlled by Peptide Self-assembly

Nobuyuki Higashi [1]*, Yuji Nikaido [1], and Tomoyuki Koga [1]

[1] *Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering,*
Doshisha University, Kyotanabe, Kyoto 610-0321, Japan
* - nhigashi@mail.doshisha.ac.jp

Hydrogels are networks of polymer chains with a large amount of water. Their water-swollen structures offer excellent biocompatibility and flexibility similar to natural tissue necessary to apply as biomaterials. Recent dramatic developments of this research field have enabled the construction of a wide variety of hydrogels with unique properties such as stimuli-responsive hydrogels and hydrogels with high mechanical property. However, there is no report about the hydrogels acted only for a limited period without any external-stimuli. We report herein for the first time a new class of intelligent hydrogel fabricated by self-assembling three-armed peptides ($\mathbf{1}_n$) that undergoes gel-to-sol transition in response to time under a physical condition. The peptides consist of short collagen-mimetic chains (Gly-Pro-Hyp triplet repeat, n = 5 or 6) linking a central lysine-template through flexible spacer as shown in Fig. 1a. These peptides were prepared by means of solid-phase synthesis with Fmoc chemistry and characterized by ^{1}H-NMR and MALDI-TOFMS. Analyses of the conformation and self-assembling properties of the peptides in aqueous solutions were performed by using circular dichroism (CD) spectroscopy, vapour pressure osmometry and fluorescent resonance ernergy transfer experiment. With CD study, the peptides $\mathbf{1}_n$ in dilute solutions are found to take triple helices at lower temperature (4 °C) and exhibit transition from helix to random coil with elevating temperature. The transition temperature T_m depends strongly upon the peptide sequence and the chain length (n). With condensing the solutions up to 6 wt%, formation of triple helix structure intermolecularly triggers formation of metastable self-assembled fibrillar network, which leads to gelation in water at 4 °C. Interestingly, we found out that these hydrogels transformed spontaneously to sols after a prescribed period under a constant physical condition. Spontaneous transfer from the self-assembling form to thermodynamically favored dimeric form, which occurs without a loss of triple helix structure, causes dissolution of the gel (Fig. 1b). Furthermore, lifetime of such hydrogel can be controlled by manipulating the stability of the triple helix based on amino acid sequence. These time-limitable hydrogels using metastable assemblies offer novel design principle for functional soft-materials, and also have potential in biological applications.

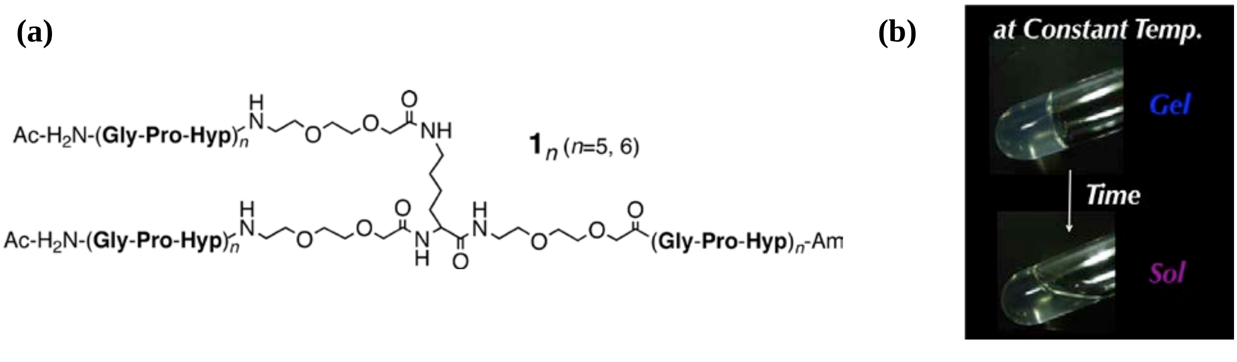


Fig. 1 (a) Molecular structures of collagen-mimetic peptides. (b) Time-dependence of $\mathbf{1}_6$-hydrogel (6 wt%) at a constant temperature of 4 °C.

Hydrogels with nanoparticle cross-linkers for magnetic sensing of chemical changes

Susanne van Berkum[1], Albert P. Philipse[1] and Ben H. Erné[1*]

[1] – *Van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute for Nanomaterials Science, Utrecht University*
* - B.H.Erne@uu.nl

To detect chemical changes in aqueous media using a magnetic sensor, we develop hydrogels with embedded magnetic nanoparticles. Our gels are currently based on poly-acrylic acid, so that they can be made to swell or to shrink at constant temperature via a change in pH. Homogeneous ferro-hydrogels are prepared under chemical conditions where aggregation of the magnetic nanoparticles is minimized and they act as cross-linkers in the polymer network. The frequency-dependent magnetic properties of the ferro-hydrogels are strongly dependent on the type of magnetic nanoparticles used, which affects the rapidity of Néel relaxation of the magnetic dipole inside the nanocrystals. With magnetite nanoparticles of a few nanometers, the magnetic relaxation at 50 kHz is almost as strong as when the particles are in colloidal dispersion in a liquid. Magnetite particles of 20 nm or cobalt ferrite particles lead to ferrogels with magnetic remanence, whose permanent magnetic field can be detected with a Hall sensor. The presentation will include aspects of chemical preparation, rotational arrest of the nanoparticles, time-dependent swelling and shrinking, and the detection of magnetic fields from ferro-hydrogels.

The role of vesicles in the gelling of dilute aqueous mixtures containing surfactant and fatty alcohol

F. Grewe [1]*, F. Polzer [2], G. Goerigk [3], S. Eriksson [4], D. Topgaard [4], C. Schmidt [1]

[1] – *Department Chemie, Universität Paderborn, Germany*
[2] – *Institut für Physik, Humboldt-Universität zu Berlin, Germany*
[3] – *Helmholtz-Zentrum Berlin, Germany*
[4] – *Physical Chemistry, Lund University, Sweden*
* - ertelf@mail.uni-paderborn.de

Aqueous mixtures containing surfactant and alcohol can self-assemble into a wide variety of liquid crystalline structures [1,2]. They often have gel-like properties and are applied in pharmaceutical, cosmetical, personal care, laundry, and food products [1-3]. The gel-like character may persist at high dilution, even at water concentrations higher than 90 wt %.

The focus of our research lies on the investigation of the structure of the model system consisting of cetyl alcohol (CA), sodium dodecyl sulfate (SDS) and water [1]. A series of samples with a constant amount of water of 97 wt. % and a varying ratio of SDS to CA with a total mass of 3 wt. % was investigated. As for many colloidal systems, the processing parameters like temperature and shear rate have a large influence on the structure of the emulsion, which is not in thermodynamic equilibrium. Therefore, reproducible conditions for sample preparation must be chosen. The range of concentrations where gels are formed was identified and the structure of the gel-forming emulsions was investigated using a variety of different techniques, including rheology, electron microscopy, scattering techniques, NMR spectroscopy and diffusometry. By means of transmission electron microscopy and very small angle neutron scattering the gels were found to consist of uni- and multilamellar vesicles. Since the gels contain high amounts of the fatty alcohol, which has a small head group, lamellar structures were expected. The formation of vesicles is due to the shear applied during the mixing procedure [4,5]. Since the alkyl chains of CA are rigid at room temperature the vesicles are very stable. We propose that the gel property of the system is caused by the jamming of the vesicles, which prevents the system from flowing. A change of the surfactant parameter or the distance between bilayers may break the gel.

Literature:

1. R. J. Goetz and M. S. El-Aasser, 1990. Dilute phase behavior of cetyl alcohol, sodium lauryl sulfate, and water. Langmuir 6: 132-136.
2. T. S. Awad, E. S. Johnson, A. Bureiko and U. Olsson, 2011. Colloidal structure and physical properties of gel networks containing anionic surfactant and fatty alcohol mixture. Journal of Disperion Science and Technology 32: 807-815.
3. L. L. Schramm, E. N. Stasuik and D. G. Marangoni, 2003. Surfactants and their applications. Annual Reports Section C 99: 3-48.
4. O. Diat, D. Roux and F. Nallet, 1993. Effect of shear on a lyotropic lamellar phase. Journal de physique II 3: 1427-1452.
5. M. Bergmeier, H. Hoffmann and C. Thunig, 1997. Preparation and properties of ionically charged lamellar phases that are produced without shearing. Journal of Physical Chemistry B 101: 5767-5771.

"Sideways" Nanotechnology - Enzymatic Production of Colloidal Hierarchical Materials

Ben J. Boyd [1]*, Stephanie Phan[1], Wye-Khay Fong [1], Adrian Hawley[2]

[1] – *Drug Delivery, Disposition and Dynamics, Monash Institute of Pharmaceutical Sciences, Monash University (Parkville Campus), VIC, Australia*
[2] – *SAXS/WAXS beamline, Australian Synchrotron, Clayton, VIC, Australia*
* - ben.boyd@monash.edu

Enzymatic production of nanostructures is utilized widely by nature to transform biological materials and promote self assembly, but is often ignored as an alternative to bottom up or top down assembly of nanomaterials. As one example, during the digestion of lipids in the gastrointestinal tract a variety of self-assembled structures may be formed transiently that eventually and inevitably result in micelle formation.

In this study, inspired by lipid digestion, the generation of stable hierarchically structured nanostructured particles with internal bicontinuous cubic structure from emulsions is triggered via enzymatic lipolysis of a short chain triglyceride additive to the main structure forming lipid. Structural aspects were elucidated using real time synchrotron small angle x-ray scattering, dynamic light scattering and cryoTEM (below). The concept of mixing enzymatically labile and inert lipid substrates has not previously been harnessed for the deliberate selection of such self assembly structures. Through design of specific mixtures that transit from unstructured emulsions to highly structured dispersed liquid crystalline particles, new low energy methods to generate particles such as cubosomes and hexosomes are achieved. This new route to stabilised internally structured particles holds promise across the pharmaceutical, agricultural and food technology fields.

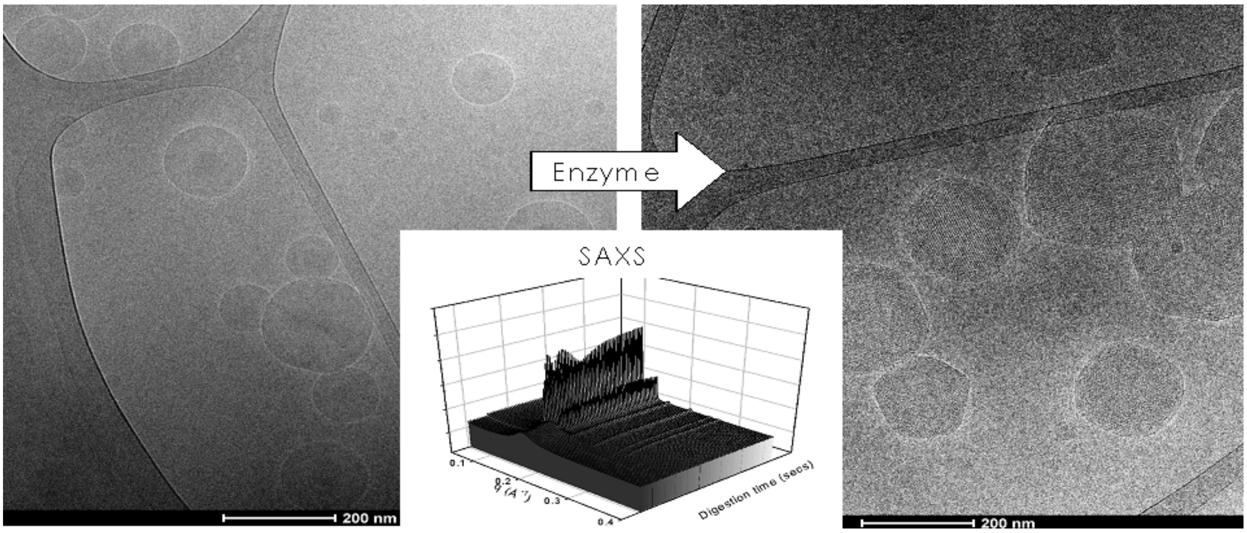


Fig. 1 Transformation from emulsion to hierarchically structured cubosomes using enzymatic trigger

Influence of Polymer Weight and Barrier Layers on Interdiffusion in Polyelectrolyte Multilayers

Peter Nestler[1], Malte Paßvogel[1], Olaf Soltwedel[2], Ralf Köhler[3] and Christiane A. Helm[1*]

[1]*Institut für Physik, Greifswald University, D-17487 Greifswald, Germany*
[2] *Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany*
[3]*Stranski-Laboratorium and Helmholtz Zentrum Berlin für Materialien und Energie GmbH,*
Hahn-Meitner-Platz 1, 14109 Berlin, Germany
* - helm@uni-greifswald.de

Polyelectrolyte multilayers are made from poly(diallyldimethylammonium) (PDADMA), poly(styrenesulfonate) (PSS), and deuterated PSS-d.[1] Each film consists of a protonated and a deuterated block. The films are annealed in 1 M NaCl and investigated with neutron reflectivity. During annealing the internal interface between both blocks broadens due to interdiffusion.

The PSS interdiffusion constant depends non-monotonically on the PDADMA molecular weight, a maximum is observed at 45 kDa, in contrast to polymer theory. The experiments suggest that PSS and PDADMA move as a complex. If one polycation layer in the film centre is branched poly(ethyleneimine) (PEI), then PEI serves as a diffusion barrier. Consistent with polymer theory, the diffusion constant through the barrier decreases monotonically with PDADMA molecular weight.

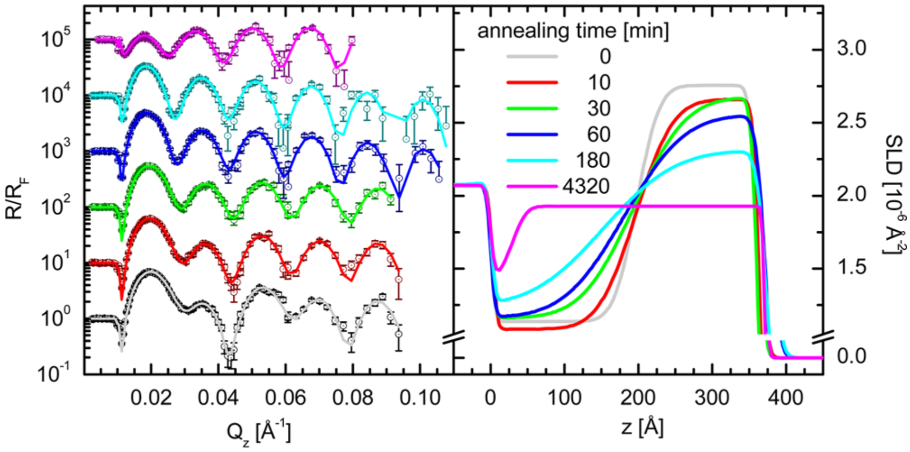


Fig. 1 Normalized neutron reflectivity curves (left) and corresponding SLD profiles (right) of a $(PEI/PSS)_1(PDADMA/PSS)_8/(PDADMA/PSS\text{-}d)_5$ film, measured at 0% rh (preparation conditions: $M_{w,PDADMAC}$ = 35 kDa, 0.1 M NaCl, T = 20 °C). After preparation, the PEMs are immersed for the time indicated into 1 M NaCl solution at 20 °C and dried. For clarity, the reflectivity curves are shifted relative to each other by 1 order of magnitude.

Literature:

1. O. Soltwedel, P. Nestler, H.G. Neumann, R. Köhler, C.A. Helm; Macromolecules **45** (2012) 7995

Electro-optics of polyelectrolyte multilayers on colloidal particles

Viktoria Milkova *, Kamelia Kamburova, Tsetska Radeva

Institute of Physical Chemistry, Bulgarian Academy of Sciences
* - vmilkova@ipc.bas.bg

Polyelectrolyte multilayer films made by self-assembly of oppositely charged polymers onto submicron particles are promising systems for applications in fields as biomaterial coatings, drug delivery systems, electrocatalysis, electrochemistry [1]. The structure, stability and electrical properties of the multilayer films are crucial for all the envisaged applications.

We demonstrate the advantages of electro-optics for *in situ* investigation of multilayer films on non-spherical colloidal particles. The electro-optical signal is related to the electrical moment orientation mechanism, which in turn reflects the electrical double layer features of the particles through their electrical polarizability. The electro-optical signal contains also information on the shape and size of the particles, which makes this technique useful for controlling the stability of colloidal systems during preparation of the multilayer films as well as for determination of the film thickness.

We present results for films made from synthetic and bio-polymers on particles of different shape: ellipsoids (β-FeOOH), rods (α-Fe_2O_3) and discs (indomethacin) [2,3]. Multilayer films are found to grow linearly or exponentially in dependence on the charge density ratio of the polymers. In contrast to electrophoretic mobility, the electrical polarizability of the particles coated by multilayer films increases with the number of deposited layers, in agreement with the film thickness increase. Our results also showed that the electrical parameters of the last adsorbed polymer dominate the behavior of the whole film. We will discus potential applications of the encapsulated colloidal particles for controlled drug release and corrosion protection of steel.

References

1. Decher G 1997 Fuzzy nanoassemblies: toward layered polymeric multicomposites *Science* **247** 1232-1237.

2. Radeva Ts, Milkova V, Petkanchin I 2004 Dynamics of counterions in polyelectrolyte multilayers studied by electro-optics *Colloids Surf. A: Physicochem. Eng. Aspects* **240** 27-34.

3. Radeva Ts, Kamburova K 2007 Polypeptide multilayer films on colloidal particles: An in situ electro-optical study *J. Colloid Interface Sci.* **308** 309-317.

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Oppositely Charged Polyelectrolyte/Surfactant Mixtures: Structural Origin of Changes in Viscosity

Ingo Hoffman[1,2]*, Bela Farago[2], Michael Gradzielski[1]

[1] – *TU Berlin Institut für Chemie*
Stranski-Laboratorium für Physikalische und Theoretische Chemie
Straße des 17. Juni 124, Sekr. TC 7, D-10623 Berlin
[2] – *Institut Laue Langevin*
6, rue Jules Horowitz
F-38042 Grenoble Cedex 9
* - hoffmann@ill.fr

Systems composed of oppositely charged polyelectrolytes (PE) and surfactants show rich self-aggregation behavior that varies over a large size range and have many applications e.g. in cosmetics, detergency and drug delivery [1]. Mixtures of the cationic polyelectrolyte JR 400 with anionic surfactants in the semi-dilute regime with a slight excess of polymer charges form highly viscous network structures, with their viscosity increasing by 3-4 orders of magnitude as compared with the pure polymer solution, while mixtures with excess surfactant charges form solutions with viscosities even below those of the polymer solution [2,3].

With the help of neutron scattering, namely small-angle neutron scattering (SANS) and neuton spin-echo (NSE), we have been able to track the structural origins at the meso scale responsible for the remarkable changes in the macroscopic behavior of these solutions. As neutrons allow for an easy variation of the contrast simply by changing the isotopic composition, it is possible to study the individual components of the sample, thereby gaining insights difficult to acquire with other methods. While SANS observes the structure of solutions, NSE monitors the dynamics on a time scale of nano seconds and allows to investigate the behavior of the PE in the aggregates. It is observed that mixed rod-like aggregates are formed in the PE excess part of the phase diagram. However, these aggregates are still existent if an excess of surfactant is added and the origin of the change in macroscopic behavior is more subtle.

In summary, we studied the mesoscopic structure and dynamics of oppositely charged PE/surfactant complexes with both an excess of surfactant and PE. Using different contrasts, we gained an understanding of the role of the individual components and the structural changes at the mesoscale responsible for the changes in macroscopic viscosity.

Literature:

1. L. Chiappisi, I. Hoffmann, M. Gradzielski, 2013. Soft Matter, 9: 3896-3909
2. I. Hoffmann, P. Heunemann, S. Prévost, R. Schweins, N.J. Wagner and M. Gradzielski, 2011. Langmuir 27: 4386–4396
3. I.Hoffmann, S. Prévost, M. Medebach, S. Rogers, N. J. Wagner, M. Gradzielski, 2011. Tenside, Surfactants, Deterg 48: 488-494

Aging Dynamics and Phase Behaviour of a Charged Colloidal Clay

Roberta Angelini [1]*, Barbara Ruzicka [1], Emanuela Zaccarelli [2], Giancarlo Ruocco[1,3]

[1] – *CNR-IPCF and Physics Department Sapienza University of Rome, I-00185 Italy*
[2] – *CNR-ISC and Physics Department Sapienza University of Rome, I-00185 Italy*
[3] – *Istituto Italiano di Tecnologie, Center for Life Nano Science, Sapienza, Rome, Italy*
* - roberta.angelini@roma1.infn.it

The continuous interest in studying dynamics of colloidal systems has over the last decade led to a broadening of our knowledge on dynamical arrest and the glass transition. Many experiments performed on colloidal glasses and gels as well as theoretical and numerical simulation results aim at understanding the nature of the aging phenomena that are typical for systems with time evolving dynamics. Among these, colloidal clays, have recently emerged as complex fluid systems characterized by a peculiar aging dynamics. Here we investigate dilute suspensions of Laponite, an industrial synthetic clay made of nanometre-sized discotic platelets with inhomogeneous charge distribution and directional interactions. The anisotropy of the face-rim charge interactions, combined with the discotic shape of Laponite, produces a very rich phase diagram encompassing fluid, gel, glassy states [1,2] on varying colloidal volume fraction at fixed ionic strength. At low concentrations (C_W<2.0 %) the system ages very slowly up to a final non-ergodic state. Extending the observation time to timescales significantly longer than those previously studied, although samples seem to be arrested on the second timescale, a significant evolution takes place on the year timescale. Samples undergo an extremely slow, but clear, phase-separation process into clay-rich and clay-poor phases. The phase separation terminates at a finite but very low clay concentration (C_W=1.0 %), above which the samples remain in a homogeneous arrested state (equilibrium gel (1.0%<C_W<2.0 %). The observed features are strikingly similar to those predicted in simple models of patchy particles, suggesting that Laponite forms an (arrested) empty liquid at very low concentrations. These new phenomenology has been observed by direct visual inspection and by Small Angle X-ray measurements and it has been confirmed by extensive numerical simulations with a primitive model of patchy Laponite discs [3]. At high concentrations (2.0%≤C_W≤3.0 %) the system ages faster up to a final Wigner glassy state [4]. Here we show a very recent unexpected dichotomic aging behaviour observed through X-Ray Photon Correlation Spectroscopy and Dynamic Light Scattering for spontaneously aged and rejuvenated samples [5]

Literature:

1. B. Ruzicka *et al.* (2011). A fresh look at the Laponite phase diagram, *Soft Matter* **7**: 1268.
2. H. Tanaka *et al.* (2005). Kinetics of ergodic-to-nonergodic transitions in charged colloidal suspensions: Aging and gelation, *Phys. Rev. E* **71**: 021402.
3. B. Ruzicka *et al.* (2011). Observation of empty liquids and equilibrium gels in a colloidal clay, *Nature Materials* **10**: 56.
4. B. Ruzicka *et al.* (2010). Competing interactions in arrested states of colloidal clays, *Phys Rev.Lett.* ***104:*** 085701.
5. R. Angelini *et al.* (2013). Submitted to *Phys Rev.Lett.*

Internal dynamics in ionic microgels in solution and in the adsorbed state

Stefan Wellert[1]*, Marcel Richter[1], Olaf Holderer[2], Regine von Klitzing[1]

[1] *Stranski Laboratory, Technical University Berlin, Str. d. 17.Juni 124, 10623 Berlin, Germany*
[2] *Jülich Centre for Neutron Science JCNS-FRMII, Lichtenbergstr. 1, 85747 Garching, Germany*
* s.wellert@tu-berlin.de

The physical properties of stimuli-responsive microgels still attract great interest in basic research and lead to a lively discussion of potential technical applications. A prominent example are systems, which undergo a temperature induced phase transition reflected in a discontinuous shrinking with increasing sample temperature. Microgel particles can be easily organized as ultra-thin films at solid surfaces, e.g. silicon single crystal surfaces. This leads to changes in the swelling behavior and shifts of the LCST with respect to the bulk phase. These findings raise the question how the interactions with the solid surface affect the internal structure and dynamics of the microgel particles. In a series of surface sensitive scattering experiments we addressed this question.

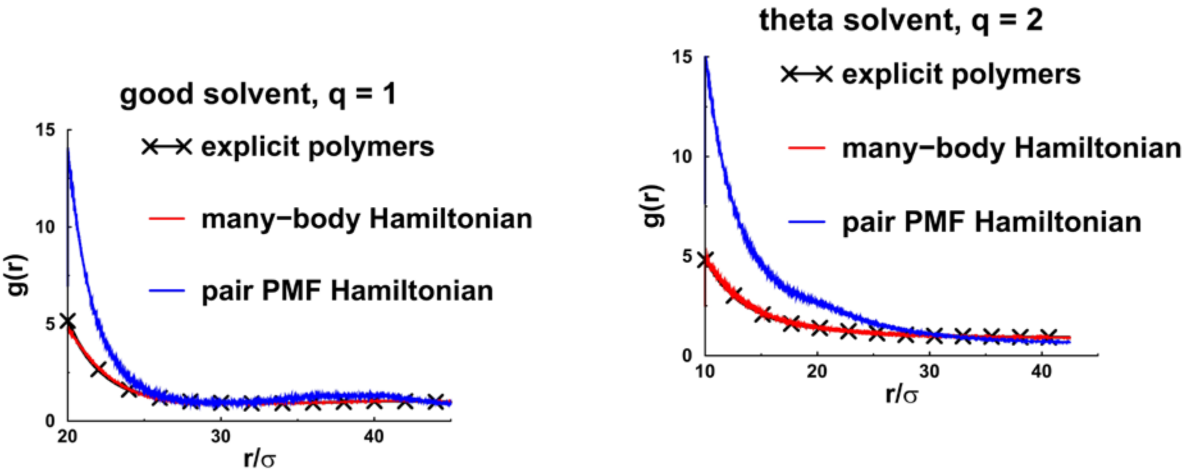
Here, we focus on neutron spin echo spectroscopy (NSE) experiments in transmission and reflection geometry. Up to now, only few publications report NSE experiments on the internal dynamics in microgels. NSE provides access to the dynamics in the ns to ms time range on nanoscopic length scales. In particular, we studied the internal dynamics in ionic microgels in the bulk phase and in thin films adsorbed onto silicon surfaces. The internal dynamics in bulk phase samples was studied at different concentrations and degrees of protonation. Results of these measurements are compared to previously published work on neutral microgels and to our results on the internal dynamics in microgels in close-packed films adsorbed at silicon surfaces. Thin films of adsorbed microgels were studied for the first time by NSE under grazing incidence (GINSES) which uses evanescently scattered neutrons and therefore probes the near-surface dynamics in the adsorbed microgel films.

A many-body theory for colloid+polymer dispersions

Jan Forsman*

Lund University, Box 12, 221 00 Lund, Sweden
* - jan.forsman@teokem.lu.se

We utilize an effective potential theory, averaging over polymer configurations, so as to derive a many-body Hamiltonian between particles, in a colloid+polymer dispersion. Our theory utilizes a generalization of the Edwards-deGennes treatment of continuous chains. A recent extension is "good solvent" cases, wherein the polymer are modelled as hard-sphere chains. "Excess" many-body interactions are handled by an expansion apporach, whereas the pair contribution enters via an explicit separate calculation. Scaling theory is adopted to ensure correct responses to changes of chain length and concentration. The many-body Hamiltonian can be utilized in Monte Carlo simulations, wherein only the particles are treated explicitly. These simulations are no more costly than corresponding ones for systems with pairwise interactions. Our treatment thus allows predictions, not only of phase diagrams, but also of structure, permitting direct comparisons with experimental SAXS/SANS data. Comparisons with computationally expensive simulations wherein the polymers are included explicitly, have shown that the theory is remarkably accurate. Examples are provided in the Figure below.



Colloid-colloid radial distribution functions, in colloid-polymer mixtures. Simulations using the many-body Hamiltonian (red) with implicit polymers,are compared with exact results from simulations where polymers are explicit (crosses). With longer chains, the latter simulations become unmanageable, while the former remain fast (minutes). The blue curves, displaying an exaggerated attraction, result if only the *pair* contribution to the Hamiltonian is included (implicit chains). Many-body effects are obviously important in these systems. Left graph: ideal chains (601-mers), and q=2. Right graph: hard-sphere monomer chains (176-mers), and q=1. Here, q is the ratio between the polymer radius of gyration, and the colloids radius.

Bulk and Interfacial Microreology

Francisco Ortega[1]*, Laura J. Bonales[1], Armando Maestro[1] , Nuria Mancebo[1], Fernando Martínez-Pedrero[1], José E. Fernandez-Rubio[1], Raquel Chuliá[1], Alma J. Mendoza[1], Ramón G. Rubio[1]

[1]Departamento de Química Física I, Universidad Complutense de Madrid, Ciudad Universitaria s/n Madrid, Spain
* - *fortega@quim.ucm.es*

Micro and nanoreology [1,2] encompass a family of methods that uses micro- and nanoparticles as mechanical probes of the rheological behavior of soft materials. Microrheology presents several advantages over conventional mechanical rheology: smaller size samples (~µL), use in heterogeneous samples (i.e. simultaneous measurement of several environments), use in situ (e.g. cells), high throughput screening capability and very small perturbation applied (in passive microrheology the thermal energy $\sim K_B T$). The fact that the applied stress is very small is of great importance when dealing with interfacial systems which are very fragile soft materials.

We will discuss the experimental techniques [1,2] and the different procedures [1,3] used to extract the complex shear modulus from the microrheological experiments. In this discussion we will present results from two different 3D systems, agarose gel solutions and pluronic solutions, and several monolayers (quasi-2D systems) of surfactants and polymers.

Literature:

1. Waigh, T.A., **2005.** *Rep. Prog. Phys.***,** 68:685.
2. Mason, T. G.; Weitz, D.A., **1995.** *Phys. Rev. Lett.*, 74:1250
3. Mason, T.G., **2000.** *Rheol. Acta*, 39:371.

Acknowledgements: This work has been supported by MINECO under grant FIS2012-38231-C02-01, by COST Action CM1101 and by ESA under grants FASES and PASTA.

Chain Exchange Dynamics in n-Alkane–PEO Soft Colloidal Model Systems

Lutz Willner[1]*, Thomas Zinn[1], Matthias Amann[1], Jörg Stellbrink[1], Aurel Radulescu[1], Marie-Soussai Appavou[1], Dieter Richter[1], Reidar Lund[2], Peter Lindner[3]

[1] *Jülich Centre for Neutron Science (JCNS) & Institute for Complex Systems (ICS),*
Forschungszentrum Jülich GmbH, 52425 Jülich, Germany.
[2] *Dept. of Chemistry, University of Oslo*
Postboks 1033 Blindern, 0315 Oslo, Norway.
[3] *Institute-Laue-Langevin (ILL), Grenoble, France.*
* - l.willner@fz-juelich.de

Block copolymers spontaneously self-organize into polymeric micelles when dispersed in a selective solvent. Micellar growth is primarily driven by the incompatibility of the insoluble block with the solvent and counterbalanced by unfavorable configurations of the chains in core and corona of the micelles. An important prerequisite to reach and to attain equilibrium in micellar solutions is a continuous exchange of constituting chains between different micellar entities. In recent years time –resolved small angle neutron scattering (TR-SANS) turned out to be a very successful method to investigate chain exchange kinetics of block copolymer micelles. The TR-SANS technique relies on a specific labeling scheme, the so-called kinetic zero average contrast (KZAC) technique, where deuterated and proteated micelles are mixed in a solvent that is contrast matched with the average of the oppositely labeled h and d polymers. This technique has led to an understanding of fundamental kinetic processes as described in more detail in a recent review [1].

In this contribution we will present kinetic results on n-alkyl-PEO polymers (C_nH_{2n+1}-O-PEOx) in aqueous solution. The n-alkyl-PEOs can be considered as hybrids between low-molecular weight surfactants and block copolymers. We have studied kinetics varying the n-alkyl length (n=18, 21, 24, 27, 28, 30), the molecular weight of PEO, (x=5, 10, 20, 40 kg/mol at constant n=27) and temperature. In all cases we observed a first order kinetic process which is characterized by a single exponential relaxation function, $R(t) \sim \exp(t/\tau)$. It was found that the time scale for chain exchange extremely depends on the alkyl chain length, n, and temperature T, while increasing the PEO chain length reveals only a moderate slowing down of the rate. Time temperature superposition reveals an Arrhenius type behavior where the characteristic times show a linear dependence for 1/T. Activation energies were deduced from Arrhenius plots. They depend linearly on n with an increment of $\Delta E_a \sim 10$ kJ/mol and reaches values of about 180 kJ/mol for n=30. In this contribution detailed experimental results will be presented and discussed in terms of the Halperin & Alexander scaling theory. Activation energies will be compared to values obtained by rheology on transient networks formed by similar telechelic PEOs.

Literature:

[1] R. Lund, L.Willner, D. Richter Adv. Polym. Sci. 2013 in press.
[2] A. Halperin, S. Alexander, Macromolecules 22, 2403 (1989).

Osmotic pressure of polyacrylate salts solutions: simulations and experiments

Joaquim Li [1]*, Marie Skepö [1], Magnus Ullner [1], Bo Jönsson [1]

[1] – *Division of Theoretical Chemistry, Department of Chemistry, Lund University*
* - joaquim.li@teokem.lu.se

Polyacrylate salts are widely used in daily life as well as in industrial processes. We use their adsorption properties and their swelling properties in diapers, concrete, cosmetics, and paper. A key parameter controlling the behaviour of all these systems is the osmotic pressure. The osmotic pressure will be linked to the aggregation and conformational extension of the polyacrylates, to their degree of ionisation and therefore will tell us a great deal about the molecular behaviour of the polymeric chains and their counterions. Here we present our progress in the measurements of the osmotic pressure of polyacrylate salts. We tried to improve the accuracy of the osmotic stress technique and used it for the measurement of the osmotic pressure of polyacrylates of varying length, at different pH and in the presence of different salts. We compare these measurements with coarse-grained Monte Carlo simulations of polyacrylate chains in the cell model. We find good agreement between simulations and experiments and discuss the significance and limitations of this agreement.

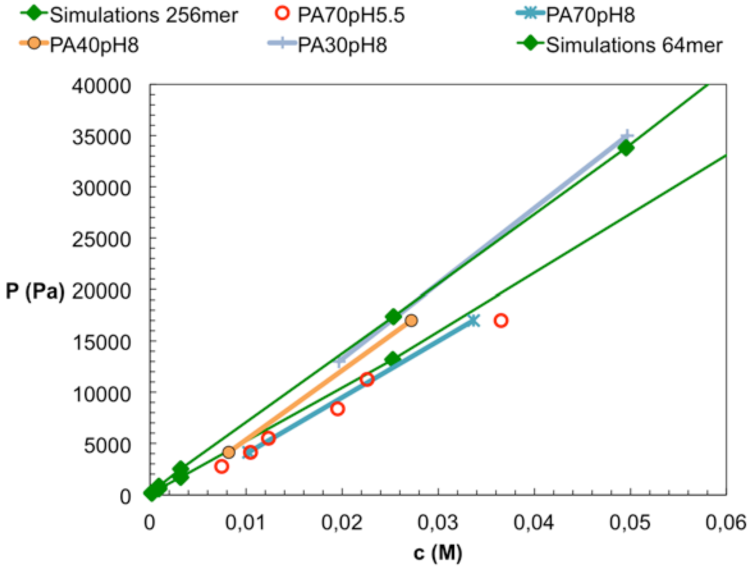


Fig. 1 Comparison between the simulated osmotic pressure and the experimental osmotic pressure of different sodium polyacrylate samples. The sizes of the polymers in the simulations are 256 and 64 monomers. The sizes of the polymers in the experiments are ~800, ~400 and ~80 monomers. For the longest polymer, the pH has been varied between 5.5 and 8.

Designing peptide-based biomaterials: structure and related properties

Laura Chronopoulou [1]*, Simona Sennato [2], Federico Bordi [2], Andrea Barbetta [1], Mariella Dentini [1], Anna Rita Togna [3], Giuseppina Ines Togna [3], Cleofe Palocci [1]

[1] – *Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2] – *Department of Physics and CNR-IPCF, Sapienza University of Rome, Rome, Italy*
[3]– *Department of Physiology and Pharmacology Vittorio Ersparmer, Sapienza University of Rome, Italy*
* - laura.chronopoulou@uniroma1.it

Recently, scientific as well as technological interest in the synthesis of novel peptide-based hydrogel materials have grown dramatically. Applications of such materials mostly concern the biomedical field with examples covering diverse sectors such as drug delivery, tissue engineering and production of scaffolds for cell growth, thanks to their biocompatibility and biodegradability.

In this framework, we successfully explored the possibility of using microbial lipases to catalyze the synthesis in water of self-assembling peptides such as Fmoc-Phe_3, that afforded self-supporting hydrogels able to promote microglial cells proliferation and NGF production (1). Our interest was then drawn by the possibility of using unconventional peptides, such as D-peptides, to enhance hydrogel *in vivo* stability. D, L and mixed D,L peptides formed β-sheet-based molecular structures, as evidenced by circular dichroism. Atomic Force Microscopy investigation on hydrogels deposited on mica support evidenced a complex self-assembled network formed by nanofibers, whose structural details depend on the chirality of the peptide. The hydrogelators show the ability to form helical nanofibers within the hydrogels, and the chirality of the hydrogelators apparently dictates the handedness of the nanofibers.

Thus, this new class of D-form self-assembling peptides has proven to be very versatile in fabricating novel supramolecular architectures and may have a wide range of applications in nanobiotechnology.

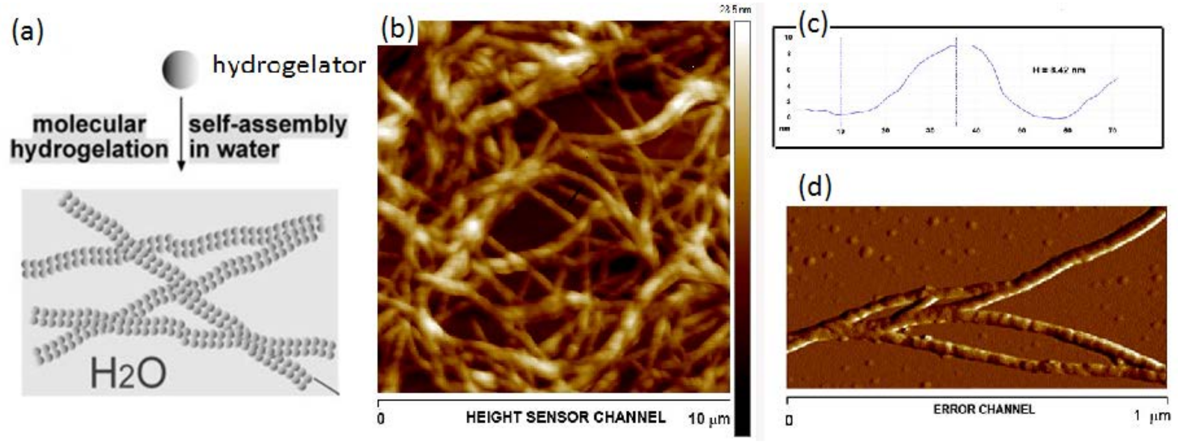


Fig. 1 Molecular hydrogelation (a), AFM image of Fmoc-D-Phe_3 (b), with height profile of a single fiber (c) and a detail showing the handedness of some nanofibers (d).

Literature:

1. L. Chronopoulou, A.R. Togna, G. Guarguaglini, G. Masci, F. Bordi, F. Giammaruco, G.I. Togna, C. Palocci 2012. Soft Matter 8: 5784-5790.

Molecular Modeling of Ion Atmosphere of Colloidal Systems

Hitoshi Washizu [12]*, Tomoyuki Kinjo [12], Hiroaki Yoshida[12]

[1] – *Toyota Central R&D Labs., Inc., 41-1 Yokomichi, Nagakute, Aichi 477-0140, Japan*
[2] – *Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8520, Japan*
* - h@washizu.org

Theoretical understanding of colloidal systems is extremely difficult even if a simple model is used for a macroion. This is because the internal motion of the macroion, the concentrations of small mobile ions, the long-range coulomb potential, and the solvent velocity are coupled with each other through essentially nonlinear equations. Coarse-grained simulations are useful tools to analyze the mechanism dynamics of colloidal systems. The importance of the system may due to the nonuniformity of the small ion distribution interacting with each other over the wide space of the solution. On the other hand, if the motion of solvent molecules is neglected, the effect of solvent flow that may play a large role cannot be incorporated. Also the important effect of solvent hydration cannot be discussed. A simulation involving coupling the dynamics of a vast ion atmosphere, the effect of local solvation around each of the ions, and macroscopic friction should be constructed to overcome the difficulty. Multiphysical course-grained simulators for molecular scale to meso-scale dynamics are under construction.

First, the Monte Carlo Brownian Dynamics method[1] is used to simulate the nature of polyelectrolyte brushes. The polyions are grafted to the surface at an equal pitch. Long-range Coulomb interactions are coarse-grained by the modified Particle-Particle Particle-Cell method. For a flexible polyion model, a bond and bond angle degree of freedom is adopted. Charge densities of the polyions are an essential topic concerning the friction of a polyelectrolyte brush. In order to understand the charge density effect, the linear charge density parameter of the polyion is set to 0.0 to 2.0 in order to discuss the Manning's counterion condensation theory. The effect of added salts has been observed as the shrinkage of the brush heights.

In order to discuss the friction behaviours in these systems, improvements in the simulator are then needed to include the effect of the solvent. First, the solvent model is made to include the solvation effect of polymers and counter-, and co-ions. In the framework of dissipative particle dynamics, polarizability of a set of solvent molecules is described as oscillators. The solvent flow is then included by calculating the Brownian particles by Langevin dynamics and the solvent flows by the Lattice Boltzmann method. In this method, the dynamics of a huge amount of small ions are enabled by treating each Brownian particle as a point described by a Stokes-source. These methods essentially treat ions as particles. In order to treat macroscopic phenomena, a multiphysical simulator based on continuum equations of ion distribution, solvent flow, and electric fields is created. Distributions of small ions are treated by Nernst-Planck equations to treat transitional and non-bulk ion distribution.

Literature:

1. H. Washizu, K. Kikuchi, 2006, J. Phys. Chem. B, 110 (6), 2855-2861.

Acknowledgements:

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Contact Line Dynamics During Rapid De-Wetting Of Dilute Polymer Solutions On Hydrophobic Surfaces

Davide Biolé [1], Volfango Bertola [1]*

[1] – *University of Liverpool, School of Engineering, Liverpool, UK*
* - Volfango.Bertola@liverpool.ac.uk

The wetting dynamics of dilute polymer solutions on hydrophobic surfaces is remarkably different from the case of simple liquids. The comparison between experiments carried out with pure water and dilute polymer solutions reveals a deep difference in the behaviour of the moving contact line during the receding phase, in the amplitude of the contact angle, as well as in the intrinsic time of the phenomenon. Recent experiments relate this behaviour to the stretching of polymer molecules caused by the receding movement of the contact line [1,2]. The present work aims to get a deeper insight of this phenomenon through systematic experiments aiming at the investigation of the independent effects of the relevant parameters (polymer concentration, Weber number, surface energy of the substrate) on the morphologies of the contact line and of the contact angle during the receding phase. In comparison with pure water, the contact line of dilute polymer solutions is pinned at several points on the impacting surface; thus, the effect of the polymer is to slow down the receding phase after drop impact, also modifying the morphology of the contact line. The results of this experimental work allow a quantitative estimation of the dissipative force opposed to the contact line displacement, shedding more light on our understanding of the wetting dynamics of dilute polymer solutions.

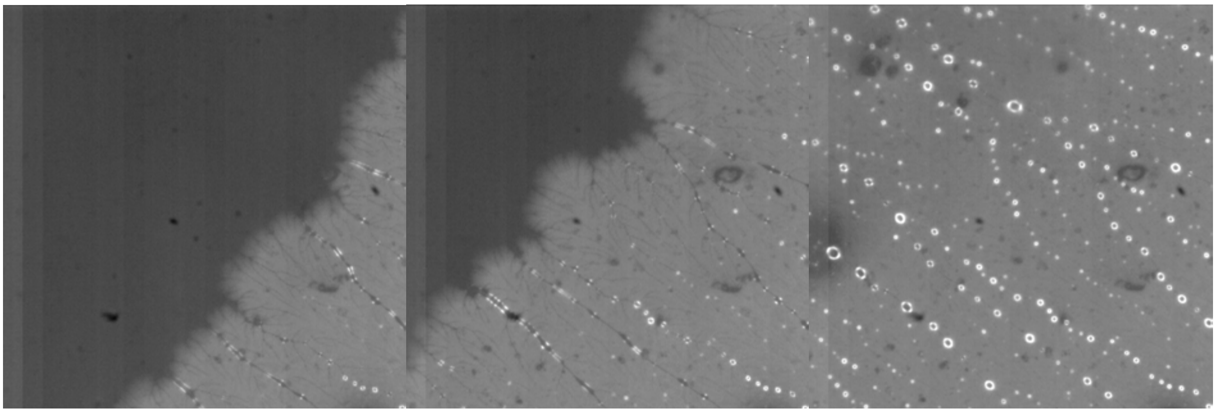

Fig. 1 Formation of liquid filaments and dendrites during the receding contact line motion.

Literature:

1. Smith, M.I., Bertola, V., 2010. Effect of polymer additives on the wetting of impacting droplets. Physical Review Letters 104: 154502.
2. Bertola, V., 2013. Dynamic wetting of dilute polymer solutions: the case of impacting droplets. Advances in Colloids and Interfaces 193-194: 1-11.

Acknowledgements:

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Reorganization of Nanosized Lipid Assemblies Spread at Model Membrane Interfaces

Ivan Panaiotov[1*], Tzetanka Ivanova[1], Patrick Saulnier[2]

[1]*Biophysical Chemistry Laboratory, Faculty of Chemistry and Pharmacy, University of Sofia, Sofia, Bulgaria*
[2]*INSERM U1066 MINT* « Micro et nanomédecines biomimétiques »*, 49033Angers, France*

* - ipanaiotov@chem.uni-sofia.bg

The number of potential applications of nano-particles, vesicles and capsules in drug research and nanomedicine is rapidly increasing with the developed technologies to tune and control their bulk and mainly surface properties. For a better understanding of nanoparticle behavior at the membrane interfaces an "*in vitro*" study of the mechanisms of small unilamellar vesicles (SUVs) and lipid nanocapsules (LNCs) loss of mechanical stability and reorganization on various membrane systems seems indispensable. A particular attention has to be paid to the SUVs and LNCs structural destabilization due to the enzymatic action and appearance of lipolytic products.

By using the simplest convenient monolayer model the mechanisms of destabilization and reorganization of various classical or modified SUVs and LNCs spread on pure air-water (A/W) interface and on the preformed monolayers of DPPC, Curosurf (model of the alveolar surface) and mucus (model of the epithelial surface) were studied.

SUVs spread at A/W interface undergo an interfacial destabilization of closed spherical vesicles and formation of a surface film of partly open vesicles studied by measuring the evolution with time (t) of the surface pressure (p) and surface potential (DV). In the presence of phospholipase PLA_2 the appearance of lipolytic products destabilizes additionally the vesicles and transformation is accelerated.

LNCs spread at A/W interface undergo a destabilization and disaggregation leading to the formation of a triglyceride (TG) monolayer. The kinetic of the process was followed by measuring the surface pressure (p) at constant area (A), $p(t)_A$, and change of the surface area (DA) at constant surface pressure, (p), $DA(t)_p$. The interpretation of $p(t)_{A=const}$ and $DA(t)_{p=const}$ data allows us to determine the rate k_1 of the LNCs interfacial destabilization, the degree (d_{TG}) and the effectiveness (e_{TG}) of inclusion of TG molecules into the model membrane monolayer. The obtained results about the LNCs mechanical stability viewed at phenomenological level by k_1 and e_{TG} show that the LNCs destabilization depends strongly on the nature of the used model membrane monolayers in accordance with the usual ideas about the role of electrostatic interaction "particle-monolayer" as well as about the role of the length of PEG protecting the LNCs from external medium. When the enzyme PLA_2 is present in the LNCs dispersion an additional loss of their mechanical stability and additional spreading of released TG molecules was observed.

A relationship between SUVs and LNCs stability and enzyme activity was theoretically established and experimentally confirmed.

Understanding the Interactions of Antimicrobial Amphiphilic Molecules with Bacterial and Human Cell Membranes from Molecular Dynamics Simulations

Daniel W. Cheong[1]*, Jernej Zidar[1], Geraldine S. Lim[1], Marco Klähn[2]

[1] – *Institute of High Performance Computing, Agency for Science, Technology and Research, Singapore*
[2] – *Institute of Chemical and Engineering Sciences, Agency for Science, Technology and Research, Singapore*
* - dcheong@ihpc.a-star.edu.sg

It has been demonstrated that certain amphiphilic molecules, such as polymers and ionic liquids, can exhibit highly effective antimicrobial properties. The antimicrobial activity is closely related to the structure and composition of the molecules. Therefore, it is important to understand the detailed mechanisms through which some of these novel antimicrobial molecules interact and disrupt different cell surfaces, in order to enable the intelligent design of molecules with improved antimicrobial properties.

In this work, we investigate two classes of molecules with known antimicrobial properties: polycarbonate polymers and ionic liquids. Molecular dynamics simulations have been performed to investigate the interactions between these molecules and bacterial and mammalian cell membranes, and to understand the selective adsorption and penetration to the bacterial cell membranes. Different structures of the polymers and ionic liquids were also considered to elucidate the effect of molecular structure on the antimicrobial properties. Through this work, wehope to gain some insight into the mechanism of the antimicrobial activity of the polymers and ionic liquids, and establish guidelinesto design new and improved antimicrobial molecules.

Novel Nanomaterials with Antimicrobial Activity and Their Application in Biomedical Field

Polina Prokopovich[1,2,]*, Stefano Perni[1].

[1] – *School of Pharmacy and Pharmaceutical Science, Cardiff University, Cardiff, UK*
[2]– *School of Engineering, Cardiff University, Cardiff, UK*
* - prokopovichp@cf.a.c.uk

The development of novel antimicrobial agents not based on antibiotics molecules is an urgent need as the rise of resistant strains is reducing the efficacy of the traditional therapies against infections. Metal nanoparticles, mainly silver, are used to prevent infections due to their lethal activity against bacteria without promoting insurgence of resistance and without causing any cytotoxic effect. Catheters, wound dressing, creams and bone cement are examples or medical devices where silver nanoparticles have been integrated to achieve antimicrobial activity. Copper nanoparticles have been used as antimicrobial agents and as stimulants of bone growth.

Although metal nanoparticles have been synthesised by a variety of physical and chemical routes, it is the reduction of metal salts that has become the standard route for their synthesis due to the flexibility of the particles produced and its reproducibility. Nanoparticles can also be stabilized using chelating substances such as: citrates, and oleic acid and glutamic acid or prepared with a capping agent that allows binding of other compounds to the nanoparticles such glutathione or tiopronin.

The activity of nanoparticles is regulated by their physico-chemical, surface and geometrical characteristics, for examples size, shape, charge, hydrophobicity and composition affect the interaction of nanoparticles with fluids components, the adhesion to the cells and the transport through the cell membranes. It is also accepted that different cells respond differently to the same nanomaterial. Nanoparticles of very different geometrical (size and shape) characteristics can be obtained controlling the synthetic conditions tuning the nanoparticles to the required application.

Many of the current synthetic routes employ chemical reagents or physical agents that are expensive and harmful; the increasing interest in using low energy processes and safe chemicals (so called “green chemistry”) has originated novel synthetic methods for the preparation of metal nanoparticles. Plant extracts along with fungi or bacterial filtrate have been used for this synthesis, but the faster growth rate of bacteria makes their use more industrially appealing.

Conformation Change and Amyloid Formation of Protein at Liquid-Liquid Interfaces

Hitoshi Watarai[1,2]*, Kimika Matsuura[1] and Shiori Watanabe[1]

[1] – *Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043 Japan*
[2] – *Institute for NanoScience Design, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531 Japan*
* - watarai@chem.sci.osaka-u.ac.jp

Conformational change of proteins in biological systems affects significantly on their enzymatic activity and solubility. Biological micro-environment is mainly composed of heterogeneous media like an oil-water system. Therefore, the study of conformational change of proteins at liquid-liquid interfaces should give valuable insight in the state of protein in real bio-colloidal systems. In the present study, the conformation changes of insulin and poly-L-lysine (PLL) were investigated in liquid-liquid systems by means of our original technique of the centrifugal liquid membrane (CLM) method combined with circular dichroism (CD) spectrometry.[1] Insulin formed amyloid fibril under acidic condition or at higher temperature (Fig. 1). However, there was no evidence to prove the formation of amyloid at the liquid-liquid interface. In the present study, a 2 mL/2 mL of organic phase-water system including insulin was stirred with a magnetic stirrer at 960 rpm under the temperature of 38 °C. Then, the amyloid formation was observed by the intercalation of fluorescent dye, thioflavine T (ThT). Fluorescence and Raman microscope measurements showed that toluene is an effective solvent for the formation of insulin amyloid, which is formed at the interface. The CD spectra of insulin in the dodecane-water system, kept standing overnight at 40 °C, were measured by CLM method. The peak at 209 nm of α-helix form decreased and the broad negative band at ca. 220 nm appeared (Fig.2). It clearly showed that the α-helix form of insulin was converted to the β-sheet form very slowly in dodecane-water system at 40 °C. The interfacial tension measurement confirmed the high interfacial activity of insulin in oil-water systems. The chiral interaction between poly-L-lysine (PLL) and bilirubin (BR) at the heptane-water interface was investigated by the CLM method. The pH dependence of the vis-absorption and CD spectra of BR indicated that BR could recognize the helical structure of α-helix of PLL. At the heptane-water interface, the fraction of α-helix of PLL was more decreased in higher pH than that in the aqueous phase. The observed interfacial tension showed the high interfacial adsorptivity of PLL and the interfacial aggregation of PLL. It was concluded that a favorable conversion of α-helix form to β-sheet form was carried out at the liquid-liquid interface, due to the higher stability of β-sheet form at the interface.

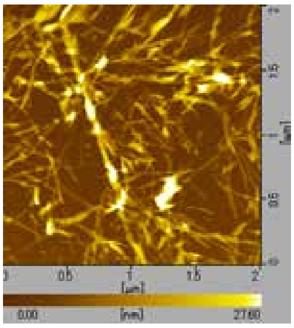

Fig. 1 AFM image of insulin amyloid fibril with 7 nm diameter

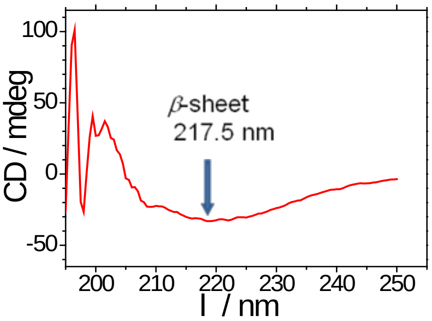

Fig. 2 CLM-CD spectra of insulin in dodecane-water interface

Literature:

1. Wada, Sayaka; Fujiwara, Kazuhiko; Monjushiro, Hideaki; Watarai, Hitoshi, 2004. Measurement of circular dichroism spectra of liquid/liquid interface by centrifugal liquid membrane method. Anal. Sci. 20: 1489-1491.

Nonlamellar Lipid Liquid Crystalline Model Surfaces for Biofunctional Studies

Maria Wadsäter[1]*, Justas Barauskas[2,3], Tommy Nylander[1] and Fredrik Tiberg[1,3].

[1] – *Department of Physical Chemistry, University of Lund,*
[2] – *Biomedical Science, Faculty of Health and Society, Malmö University*
[3] – *Camurus AB*
* - Maria.Wadsater@fkem1.lu.se

Lyotropic nonlamellar lipid liquid crystalline (LC) bulk phases show promise as functional nanostructured materials of potential use as controlled release matrices e.g. of pharmaceuticals. For instance, the reversed cubic micellar (I_2) phase has been proposed to be able to serve as an in vivo drug reservoirs[1] and LC nanoparticles as injectable drug carriers.[2] Furthermore, the I_2 phase of soy phosphatidylcholine (SPC) and glycerol dioleate (GDO) has been demonstrated to have excellent mucoadhesive film properties.

In this work we report on the controllable formation and characterization of thin nonlamellar LC SPC/GDO films on solid support. Such films can be useful as model surfaces with tuneable properties for routine studies of a range of relevant properties of lipid nonlamellar LC phases for drug delivery applications. For instance, their adhesion to biological surfaces, interaction with biomolecules and degradation at various simulated physiological conditions can be investigated.

Lipid LC films of controllable thickness were formed by spin-coating of a non-aqueous SPC/GDO formulation on solid support. Upon hydration, a LC films were formed, as verified by spectroscopic ellipsometry, non-contact mode atomic force microscopy and synchrotron small angle X-ray diffraction (SAXD), which provided information on the thickness, topography and LC phase structure of the hydrated lipid film, respectively (Fig. 1).

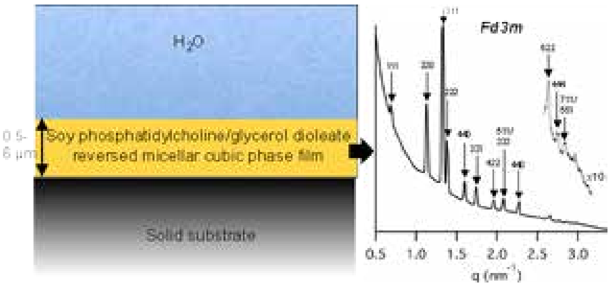

Fig. 1 The hydrated 35/65 wt%/wt% SPC/GDO film on solid support has a reverse cubic micellar phase at 25 °C, as measured by SAXD.

Literature:

1. Thuresson, K.; Tiberg, F.; Johansson, M.; Harwigsson, I.; Johnsson, M.; Joabsson, F., EP1768650: Liquid depot formulations, 2005.

2. Leesajakul, W.; Nakano, M.; Taniguchi, A.; Handa, T., 2004, Interaction of cubosomes with plasma components resulting in the destabilization of cubosomes in plasma, Colloids and Surfaces B: Biointerfaces, 34, 253–258.

Acknowledgements:

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Enhanced Chemical and Colloidal Stability of Carboxylated Magnetite Nanoparticles Designed for Biomedical Use

Etelka Tombácz*, Ildikó Y. Tóth, Erzsébet Illés, Dániel Nesztor, Márta Szekeres

Department of Physical Chemistry and Materials Science, University of Szeged, Hungary
*tombacz@chem.u-szeged.hu

Magnetic nanoparticles (MNPs) have been applied efficiently in a number of various biomedical applications such as MRI contrasting, targeted drug delivery and hyperthermia. Appropriate aqueous dispersions of MNPs need to be prepared. The colloidal stability of magnetic fluids under physiological conditions is of crucial importance. Biomedical applications require the MNPs to be non-toxic, chemically stable, uniform in size, and well-dispersed in aqueous media.

A series of organic acids such as small molecular complexant (citric acid - CA), synthetic (poly(acrylic acid) - PAA, poly(acrylic acid-co-maleic acid) - PAM) and natural (chondroitin-sulfate A - CSA) macromolecules was chosen systematically to coat the synthetic MNPs in order to enhance their chemical and colloidal stability. Adsorption isotherms were measured and bond formation on °Fe-OH sites was detected by ATR-FTIR measurements. The pH-dependent charge state of MNPs was characterized by electrophoretic mobility and their aggregation by dynamic light scattering. The salt tolerance was measured in coagulation kinetic measurements. Desorption of stabilizing shell and iron-dissolution was determined in selected products. The carboxylated MNPs were tested in cell proliferation experiments.

The chemical interactions between the °Fe-OH sites and the adsorbed carboxylic groups are specific, and so their bond strengths differ significantly from each other and their stabilizing efficiency changes definitely due to the different structure and thickness of the coating layer on the MNPs. Exceeding adsorption saturation, the nanoparticles are stabilized in a way of combined steric and electrostatic effects. Well-stabilized magnetic fluids (MFs) were prepared by using these organic acids. The PAA, PAM and CHA coated MNPs fulfilled the stability criteria of physiological condition regarding the pH and salt concentration [1]; however, the CA coating does not provide suitable resistance against salt. In addition, Fe(III)-CA complexation can promote the dissolution of magnetite nanocrystals in aqueous medium, which do cause problems in vivo. Our products have been tested in MRI as contrast agents and in cell experiments in vitro [2]. The interaction of some of these carboxylated MFs with human plasma has been also studied [3] within the framework of ESF network program Epitopmap.

Literature:

1. Tóth Y. Ildikó, Illés Erzsébet, Bauer A. Rita, Nesztor Dániel, Zupkó István, Szekeres Márta, Tombácz Etelka, 2012. Designed polyelectrolyte shell on magnetite nanocore for dilution-resistant biocompatible magnetic fluids, Langmuir, 28 (48), 16638-16646.
2. Jedlovszky-Hajdu Angéla, Tombacz Etelka, Banyai István, Babos Magor, Palko András, 2012. Carboxylated magnetic nanoparticles as MRI contrast agents: Relaxation measurements at different field strengths, JMMM, 324, 3173-3180.
3. Jedlovszky-Hajdú Angéla, Baldelli Bombelli Francesca, Monopoli P. Marco, Tombácz Etelka, Dawson A. Kenneth, 2012. Surface Coatings Shape the Protein Corona of SPIONs with Relevance to Their Application in Vivo. Langmuir 28, 14983-14991.

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Protein Coated Gold Nanoparticles: Towards Biological Interfaces on Nanomaterials

Munish Chanana[1]*, Luis Liz-Marzán[2], Wolfgang Parak[3] and Andreas Fery[1]

[1] – *Department of Physical Chemistry II, University of Bayreuth, Bayreuth, Germany*
[2] – *CIC biomaGUNE, Paseo de Miramón 182, 20009 Donostia - San Sebastián, Spain*
[3] – *Department of Physics, Univeristy of Marburg, Marburg, Germany*
* - munish.chanana@uni-bayreuth.de

Stimuli-responsive nanoparticles (NPs) are highly interesting for their potential applications as sensors due to their keen sensitivity towards environmental changes and thus, pronounced response. A plethora of stimuli-responsive nano-systems based on plasmonic nanoparticles have been developed, which are sensitive towards environmental temperature, pH and light. However, the modern trend for stimuli-responsive systems is moving towards multi-responsive systems, where the sensitivity towards various environmental factors is condensed on one single device. Hence, many strategies have been developed to combine such responsive properties on a single system, in order to obtain multi-responsive materials. One of the major fields is based on polymer-particle hybrid systems, where the particle is capped with multifunctional polymers, consisting of block copolymers or mixed polymers. However, nature has developed multi-functional polymers since the evolution of life, such as DNA/RNA, polysaccharides and proteins. Proteins are natural copolymers of polar, nonpolar, and ionic (anionic and cationic) monomers (in total 21 aminoacids) and are highly sensitive to temperature, pH, ionic strength, solvent, chiralty and metal ions. Hence, protein coated nanoparticles provide access to a multi-functional and multi-responsive hybrid materials with controlled properties and bio-functions. In this work, we present protein capped metal nanoparticles, which are extremely sensitive to pH, temperature and heavy metals, exhibiting a pronounced optical response, which can be monitored even by naked eye. Moreover, such NPs are extremely stable, mimicking somehow nature´s concept of colloids and interfaces and consequently also highly biocompatible. Hence, such NPs exhibit remarkable physicochemical properties in biological fluids inside and outside living cells.[1-3]

Literature:

1. Chanana, M., M.A. Correa-Duarte, and L.M. Liz-Marzán, *Insulin-Coated Gold Nanoparticles: A Plasmonic Device for Studying Metal–Protein Interactions.* Small, 2011. 7(18): p. 2650-2660.
2. Chanana, M., et al., *Physicochemical Properties of Protein-Coated Gold Nanoparticles in Biological Fluids and Cells before and after Proteolytic Digestion.* Angewandte Chemie International Edition, 2013. 52(15): p. 4179-4183.
3. Strozyk, M.S., et al., *Protein/Polymer-Based Dual-Responsive Gold Nanoparticles with pH-Dependent Thermal Sensitivity.* Advanced Functional Materials, 2012. 22(7): p. 1436–1444.

A Microfluidic Platform for Synthesis of Controlled Release Nanoparticles for Targeted Cancer Therapy

Jiang Xu [1, 2]*, Annie Colin [1], Frank Gu [2].

[1] – *UMR 5258, Lab of Future, Rhodia-CNRS-University of Bordeaux 1, France*
[2] – *Department of Chemical Engineering, University of Waterloo, Canada*
* - Jiang.xu-exterieur@solvay.com

Biocompatible polymeric nanoparticles (PLGA, PLA and PEG, etc.) are considered to be promising drug delivery carriers because they are capable of performing functions like biodegradability, long-term sustainable release, modifiable surface properties and so on. However, parameters of these NPs such as density of targeting receptors, drug loading efficiency, surface charge potential, size, hydrophilicity, etc. must be optimized before optimized in order to minimize the side effects.

We propose to fabricate a microfluidic chip on glass wafers with SU-8 resin, which provides a platform for both producing homogenous NPs and screening them for further optimization. With our simple yet robust design, synthesis of NPs can be achieved in a highly controlled nanoprecipitation step using precursor reagents from a single batch, thus minimizing variability and enhancing reproducibility. Compared to traditional bulk synthesis method, NPs from microfluidic devices have both smaller size and narrow distribution[1]. Given the strong surface tension between water and DCM (Dichloromethane) in the polymeric solution, the droplets could theoretically encapsulate all the drugs (DOX) inside. By manipulating small volume of fluids (~10 ul/h), characteristics of NPs: size, the amount of drug loading and surface properties could be tuned precisely, without consuming excessive expensive reagents. Currently, the relationship of w/o volume velocity ratio and size of droplets is being investigated in the initial stage. A particular attention will be paid to NPs surface modification and drug loading efficiency. Hopefully, we will perform vitro and vivo tests to optimize NP carriers for effective therapy of prostate cancer.

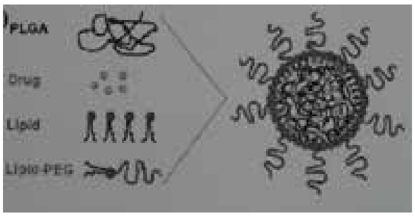

Fig. 1 The structure of Nanoparticle

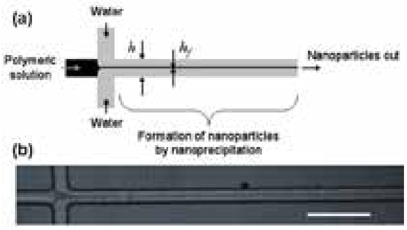

Fig. 2 (a) On-chip synthesis of NPs (b) Micrograph of the device in operation. Scale bar 100 nm**.**

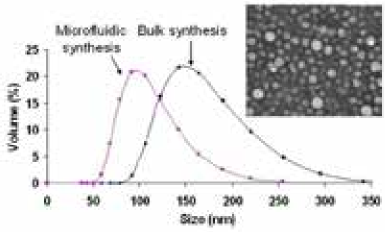

Fig. 3 TEM image of NPs synthesized on chip (inset).

Literature:

1. Rohit Karnik,Frank Gu, Pamela Basto, Christopher Cann- izzaro, Lindsey Dean, William Kyei-Manu, Robert Langer. 2008. Microfluidic Platform for Controlled Synthesis of Polymeric Nanoparticles. Nano Letters: 2906-2912

Acknowledgements:

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"Fit-for-Function" Design of Lyotropic Liquid Crystalline Matrices for On-Demand Drug Delivery

Wye-Khay Fong[1]*, Tracey L. Hanley[2] and Ben J. Boyd[1]

[1] – *Drug Delivery, Disposition and Dynamics, Monash Institute of Pharmaceutical Sciences*
[2] – *Australian Nuclear Science and Technology Organisation*
* - wye.fong@monash.edu

Self-assembled lipid based mesophases have been well studied to broaden the understanding of the interaction of these colloids in biological settings and their exploitation in applications such as drug delivery, food science, biosensing and protein crystallisation[1, 2]. In order to create matrices appropriate for their intended function, a resolution of the relationship between structure, composition and function must be achieved.

Many amphiphilic lipids self-assemble into liquid crystalline mesophases in aqueous environments. Of particular interest are the complex inverse phases the bicontinuous cubic (V_2) and inverse hexagonal phases (H_2). These thermodynamically stable phases are of interest due to their defined controlled release capabilities[3, 4]. As the mesophase formed is sensitive to environmental factors and composition, the assembly of the amphiphiles can be tuned on the molecular level to form different mesophases and drug delivery rate on demand[5].

We have demonstrated the ability to manipulate bulk and dispersed liquid crystalline material via the application of external stimuli, namely temperature[5], near-infrared (NIR)[6] and UV irradiation[7]. These systems were based on lipids which demonstrated a reversible V_2 to H_2 transition upon stimulation, that is, from a fast to a slow releasing mesophase, contradictory to what would be ideal for pulsatile release matrices. Consequently, this presented research focusses on the formulation of available lipids, shown in **Fig 1**, which undergo more ideal phase transitions e.g. from lamellar (L_α) to V_2 at biologically accessible temperatures, and are discussed according to the ability of an additive to influence the self-assembly of the matrix. Systems that transitioned from L_α to V_2 were investigated for their utility as photothermal matrices. It is anticipated that these optically addressable nanostructures will translate into on-demand systems for drug delivery or as biosensor substrates.

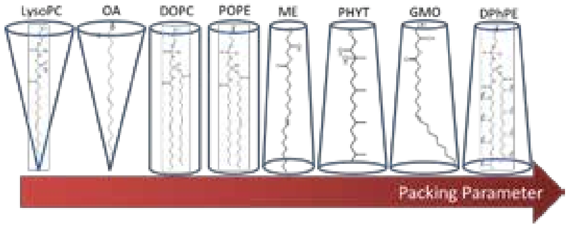

Fig 1. The increasing critical packing parameters of the lipids used in this study as shown by the increasing wedge shapes drawn around the molecular structures.

References:

1. Drummond, C. J.; Fong, C. *Curr Opin Colloid Interface Sci* **1999,** 4, (6), 449-456.
2. Cherezov, V.; Clogston, J.; Misquitta, Y.; Abdel-Gawad, W.; Caffrey, M. *Biophys J* **2002,** 83, (6), 3393-3407.
3. Phan, S.; Fong, W.-K.; Kirby, N.; Hanley, T.; Boyd, B. J. *Int J Pharm* **2011,** 421, (1), 176-182.
4. Lee, K. W. Y.; Nguyen, T.-H.; Hanley, T.; Boyd, B. J. *Int J Pharm* **2009,** 365, (1-2), 190-199.
5. Fong, W.-K.; Hanley, T.; Boyd, B. J. *J Contr Release* **2009,** 135, (3), 218-226.
6. Fong, W.-K.; Hanley, T. L.; Thierry, B.; Kirby, N.; Waddington, L. J.; Boyd, B. J. *Langmuir* **2012,** 28, (40), 14450-14460.
7. Fong, W.-K.; Malic, N.; Evans, R.; Hawley, A.; Boyd, B.; Hanley, T. *Biointerphases* **2012,** 7, (1), 1-5.

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Colloidal Properties of Spider Silk Protein Particles: Direct Force Measurements and Electrophoretic Mobility

Nicolas Helfricht,[1] Maria Klug,[1] Andreas Mark, [1] Claudia Blüm,[2]
Thomas Scheibel,[2] Georg Papastavrou*,[1].

[1] – [1]*Physical Chemistry II, University of Bayreuth, Bayreuth, Germany*
[2] – *Biomaterials, University of Bayreuth, Bayreuth, Germany*
* - georg.papastavrou@uni-bayreuth.de

Spider silk protein fibers have outstanding mechanical and biomedical properties. Recombinant spider silk proteins on the basis of the major ampullate spidroins of the dragline silk of the European garden spider *Araneus diadematus* can assemble into a huge variety of different morphologies such as films, hydrogels and particles. In addition, good biocompatibility and weak immune response have been reported for these proteins. Thus, spider silk materials are interesting for medical applications like wound dressings, implant coatings, and drug delivery.Surface properties (e.g. charge, chemistry and adhesion properties) are crucial parameters for these applications. The properties of spider silk proteins on the molecular level have been studied intensively in the past years. However, the properties of particles formed from spider silk proteins have been examined to a smaller degree.

Here, we report the characterization of recombinant spider silk protein particles by combination of AFM and electrophoretic mobility as used previously for colloidal particles. The protein particles have been prepared by salting-out.The colloidal probe technique was used to determine the interaction force profiles. The setup is schematically shown in **Fig. 1**. Diffuse layer potentials were obtained by fits to Poisson-Boltzmann equation. In addition, steric interaction forces can be observed. These direct force measurements have been compared to the electrophoretic mobility of the same spider silk protein particles. Our results are of importance to understand the stability of spider silk protein particle suspensions and their adsorption to solid interfaces.

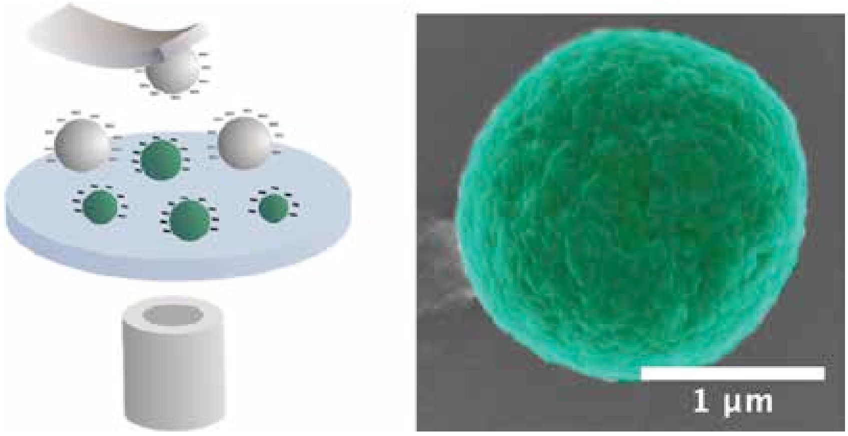

Fig. 1 Direct force measurements by colloidal probe and SEM-image of spider silk particle

How Do We Place Liposome as a Model Membrane?

Yuji Yamashita[1]*, Hiroyasu Ohtaka[1]*,Haruka Kuwahara[2], Kenichi Aburai[2], Shiroh Futaki[3],
and Kazutami Sakamoto[1,2]

[1]*Faculty of Pharmacy, Chiba Institute of Science*
[2]*Faculty of Science and Technology, Tokyo University of Science*
[3]*Institute of Chemical Research, Kyoto University*
* yyamashita@cis.ac.jp

LUV (Large, Unilamellar Vesicles) is composed of self-assembled phospholipids as an enclosed bi-layer with diameter ranging c.a. 100 nm or larger. LUV is often used as a model to investigate structures and functions of bio-membrane and further as a vehicle for drug delivery. On the contrary, sizes of cells in nature are usually larger than 10 micron, and GUV (Giant Unilamellar Vecilces) is often used as a modelmembrne. The objective of this study is to compare the physico-chemical properties of LUV and GUV to investigate the relevance of LUV utilization as a model of bio-membrane.

Bio-membrane has single bi-layer structure separating interior cytosol from exterior environment and preventing free transport of material through membrane to protect living cell. Whereas it is well known that a group of short peptides called Protein Transduction Domain (PTD) is able to spontaneously penetrate through bio-membrane, although the mechanism remains to be explored.[1]Previously we have proven that membrane penetration of PTD is dependent on the membrane curvature.[2] PTD changes membrane curvature toward positive (from L$_{\alpha}$ phase to V$_1$ then to H$_1$ phase) for phospholipid/water/PTD system, and furthermore the amount of internalized PTD increased by changing membrane curvature of erythrocyte toward positive by means of osmotic pressure modulation (Figure 1).On the basis of these results, we speculated that the phantom penetration of PTD through the cell membrane could be derived from the temporal curvature change.

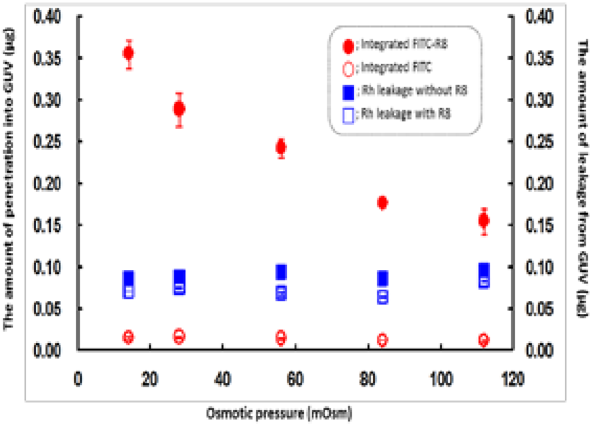

Fig. 1 Effect of osmotic pressure on the penetration of FITC-R8 (as PTD) at 37 ºC. The amount of the penetrated FITC-R8 was quantified 10 min. after adding FITC-R8. (n=5)

In the recent study, we have found the translocation of PTD into cytosol decreased when vesicle become smaller. The result indicates the contribution of lower mobility of lipid molecule at small vesicle causing PTD facing resistance to penetrate. Thus, the curvature energy would play an important role toward the temporal structural change.Physiological meaning of such vesicle size will be further discussed at the presentation.

1. T. Takeuchi, M.K0suge, A. Tadokoro, Y. Sugiura, M. Nishi, M. Kawata, N. Sakai, S. Matile, S. Futaki, “Direct and Rapid Cytosolic Delivery Using Cell-Penetrating Peptides Mediated by Pyrenebutyrate”ACS Chem. Biol. 1(5), 299-303 (2006).
2. K. Sakamoto, K. Aburai, T. Morishita, K. Sakai,H. Sakai, M. Abe, I. Nakase, S. Futaki,“Bioinspired Mechanism for the Translocation of Peptide through the Cell Membrane”Chem. Lett. 41, 1078-1080 (2012).

New Antibacterial Surfaces: Biomimetic Black-silicon with Dragonfly Wing Nanostructures

Russell J Crawford*[1], Jafar Hasan[1], Hayden K Webb[1], Gediminas Gervinskas[2,3], Saulius Juodkazis[2,3], Vi Khanh Truong[1], David E Mainwaring[1], Xiaofei Duan[4], Robert N Lamb[4], Vladimir Baulin[5,6], Gregory S Watson[7], Jolanta A Watson[7], Russell J Crawford*[1], Elena P Ivanova[1*]

[1]Faculty of Life and Social Sciences, and [2]Faculty of Engineering and Industrial Sciences, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia
[3]Melbourne Centre for Nanofabrication, 151 Wellington Road, Clayton, VIC 3168, Australia
[4]School of Chemistry, University of Melbourne, Parkville, Victoria 3010, Australia
[5]ICREA, 23 Passeig Lluis Companys, 08010 Barcelona, Spain
[6]Departament d'Enginyeria Quimica, Universitat Rovira i Virgili 26 Avenue dels Paisos Catalans, 43007 Tarragona, Spain
[7]School of Pharmacy & Molecular Sciences, James Cook University, Townsville, Queensland, 4811, Australia
* - rcrawford@swin.edu.au

Cicada wings were recently reported as the first example of a novel class of antibacterial surfaces, which are selectively lethal to Gram-negative bacterial cells. The bactericidal effect was found to be a function of the wing surface physical nanoarchitecture. Surfaces such as these insect wings represent an exciting opportunity for the development of a wide range of antibacterial biomaterials for industrial and biomedical applications. Here, we assessed the bactericidal potential of *Diplacodes bipunctata* dragonfly wings and black silicon, a nano-structurally similar surface fabricated using a simple and fast reactive-ion etching technique compatible with large-scale production.

We conclusively demonstrate that both the dragonfly wings and the black silicon surfaces are lethal for the bacterial cell types studied, despite their differences in surface chemistry and wettability. Insect wings and black silicon surfaces were lethal to the Gram-negative *Pseudomonas aeruginosa,* Gram-positive *Staphylococcus aureus* and *Bacillus subtilis* bacterial cells. Both surfaces were also effective against *B. subtilis* spores, which are highly resistant to most forms of sterilisation. The bactericidal efficiencies of both the wing and silicon surfaces were very similar in most cases, with each square centimetre killing in excess of 100000 cells per minute in the case of *S. aureus*, however the black silicon was almost twice as effective as dragonfly wings at killing *Pseudomonas aeruginosa* cells; inactivating > 70000 cells cm^{-2} min^{-1}. Our results demonstrated that (i) *D. bipunctata* wings are highly effective bactericidal surfaces, (ii) a simple ion etching technique can be used to produce antibacterial nanomaterials from silicon wafers based on dragonfly wing structures and (iii) these bio-inspired black silicon surfaces have enhanced activity relative to their natural counterparts.

1. Song Ha T. Nguyen, Hayden K. Webb, Jafar Hasan, Mark J. Tobin, Russell J. Crawford, Elena P. Ivanova. 2013. Dual Role of Outer Epicuticular Lipids in Determining the Wettability of Dragonfly Wings. Colloids and Surfaces B: Biointerfaces. 106: 126 – 134.
2. Sergey Pogodin, Jafar Hasan, Vladimir A. Baulin, Hayden K. Webb, Vi Khanh K. Truong, The Hong Phong Nguyen, Veselyn Boshkovikj, Christopher J. Fluke, Gregory S. Watson, Jolanta A. Watson, Russell J. Crawford, Elena P. Ivanova. 2013. Biophysical Model of Bacterial Cell Interactions with Nano-Patterned Cicada Wing Surfaces. Biophysical Journal. 104: 835 – 840.

New Synthetic Routes to Thiolated Mucoadhesive Nanoparticles

Vitaliy Khutoryanskiy*

Reading School of Pharmacy, University of Reading, Whiteknights, Reading, United Kingdom
* - v.khutoryanskiy@reading.ac.uk

Mucoadhesion, defined as the ability of materials to stick and retain on mucosal surfaces in human body, has become a very attractive approach for designing improved delivery systems for oromucosal, nasal, ocular, vaginal and intravesical drug administration.[1] Polymeric thiomers, typically synthesised by conjugation of water-soluble polymers with thiol-bearing moieties, have been found to exhibit excellent mucoadhesive properties.[2] This communication will report the use of new synthetic routes for the development of thiolated nanomaterials:

1. **Self-condensation of 3-mercaptopropyltrimethoxysilane (MPTS)**

Self-condensation of MPTS in aprotic solvents (e.g. dimethylsulfoxide, dimethylformamide and acetonitrile), initiated by small quantities of NaOH, results in formation of sub-100 nm nanoparticles with thiolated surfaces. These nanoparticles could be easily functionalised via PEGylation and fluorescent labelling[3,4]. The thiolated nanoparticles were found to adhere and retain on ocular surfaces, but this ability was lost after their PEGylation.[3]

2. **Thiol-ene click chemistry using the reagents with non-stoichiometric ratios**

A range of 251 – 554 nm nanoparticles have been synthesised from pentaerythritol tetrakis(3-mercaptopropionate) (PEMP) and pentaerythritol tetraacrylate (PETA) using thiol-ene click chemistry. Different PEMP/PETA ratios dissolved in dimethylformamide were used to form nanoparticles with excess of reactive groups (thiols or acrylates) on their surface. Using Raman spectroscopy and nuclear magnetic resonance spectroscopy (NMR) it was demonstrated that excess of PETA leads to nanoparticles with free acrylate groups on their surface, whereas the nanoparticles with thiolated surfaces could be synthesised using the feed mixtures with excess of PEMP. The thiolated nanoparticles were fluorescently labelled and were found to adhere to mucosal lining of porcine urinary bladder.

The applications of thiolated nanoparticles in drug delivery will be further discussed.

Literature:

1. Khutoryanskiy V.V., 2011. Advances in mucoadhesion and mucoadhesive polymers. Macromol. Biosci. 11, 748-764.
2. Bernkop-Schnurch A., 2005. Thiomers: A new generation of mucoadhesive polymers. Adv. Drug Delivery Reviews 57, 1569–1582.
3. Irmukhametova G.S., Mun G.A., Khutoryanskiy V.V., 2011. Thiolated mucoadhesive and PEGylated non-mucoadhesive organosilica nanoparticles from 3-mercaptopropyltrimethoxysilane. Langmuir 27, 9551-9556.
4. Irmukhametova G.S., Fraser B., Keddie J.L., Mun G.A., Khutoryanskiy V.V., 2012. Hydrogen-Bonding-Driven Self-Assembly of PEGylated Organosilica Nanoparticles with Poly(acrylic acid) in Aqueous Solutions and in Layer-by-Layer Deposition at Solid Surfaces, Langmuir, 28, 299-306.
5. Storha A., Mun E.A., Khutoryanskiy V.V., 2013. Synthesis of thiolated and acrylated nanoparticles using thiol-ene click chemistry: towards applications in drug delivery. Submitted.

Responsive Hyaluronic Acid Nanogels with Controlled Structure for Drug Delivery

Léa Messager[1], Naira Portecop[1], Véronique Lapeyre[1], Rachel Auzély[2], Bogdan Catargi[3], Valérie Ravaine[1*]
[1] – *Institut des Sciences Moléculaires, University Bordeaux 1, France*
[2] – *Centre de Recherche sur les Macromolécules végétales, Grenoble, France*
[3] – *CBMN, Université Bordeaux 2, France*
* - vravaine@enscbp.fr

Nanogels are an attractive class of delivery systems. These soft particles, made of highly swollen polymer network, can physically entrap a drug and release it at a rate depending on its diffusion though the network. Therefore, any change in the swelling ratio can trigger the release kinetics. In this work, thanks to the rational preparation of monodisperse and stable emulsions, we develop new nanogels made of hyaluronic acid with a controlled structure, which can swell or shrink in response to pH or glucose. These biocompatible and degradable matrices can encapsulate a drug and release it according to these stimuli.

Hyaluronic acid (HA) is a linear polysaccharide with acknowledged biocompatibility. HA is functionalized with polymerizable methacrylate functions to be processed as network[1] and with phenylboronic acid, a ligand of glucose, to introduce the glucose sensitivity. To get nanogels, this linear water-soluble polymer is confined in aqueous nanoreactors for further cross-linking. Water-in-oil nanoemulsions is chosen as template. Attention is paid to formulate stable and monodispersed nanoemulsions, which yield well-defined nanogels. Cross-linking is achieved via photopolymerization which allows a fine control of the polymerization conversion rate. As a consequence, their swelling properties is modulated[2] in different environments. We show that non-functional HA nanogels can be used as pH-responsive delivery systems for insulin (Fig. 1). Moreover, phenylboronate-functional nanogels exhibit glucose-responsiveness, which opens the route for the closed-loop release of insulin. Biocompatibility and enzymatic degradability is confirmed, thus proving their interest for *in vivo* use.

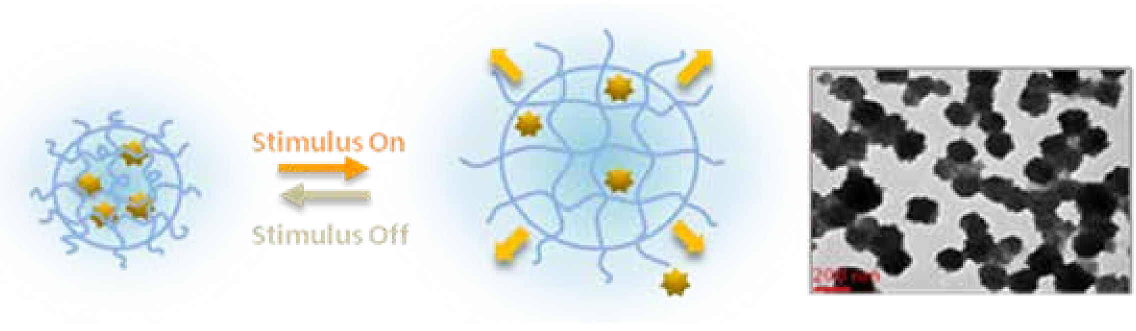

Fig. 1 a) Stimulus-triggered drug release; b) TEM image of HA-based nanogels.

Literature:

1. Hachet E.; Van Den Berghe H.; Bayma E.; Block M.; Auzély-Velty R. 2012, *Biomacromolecules*, **13**(6), p. 1818-1827
2. Messager, L., Portecop N., Lapeyre V., Hachet E., Pignot-Paintrand I., Catargi B., Auzély R., Ravaine V., 2013, *J. Mater. Chem. B*, DOI:10.1039/C3TB20300J.

Interfacial Rheology of Bacterial Biofilms

Patrick A. Rühs[1]*, Lukas Böni[1], Lukas Böcker[1], Gerald G. Fuller[2], R. Fredrik Inglis[3], Peter Fischer[1]

[1] – *Institute of Food, Nutrition and Health, ETH Zürich, Switzerland*
[2] – *Department of Chemical Engineering, Stanford, USA*
[3] – *Department of Environmental Sciences, ETH Zürich and Department of Environmental Microbiology, EAWAG, Switzerland*
* - patrick.ruehs@hest.ethz.ch

Biofilms are highly complex biological assemblies composed of bacterial cells embedded in an extracellular polymeric matrix. Biofilms are ubiquitous in any aqueous media and can cause severe environmental and health problems. Therefore it is intriguing to understand the influencing factors on formation and destruction of biofilms [1]. In this contribution, we study the transient structural development of air-water bacterial biofilms by interfacial rheology [2].

Model bacteria capable of forming biofilms at the water-air interface were chosen such as *Eschericha coli*, *Bacillus subtilis*, and *Pseudomonas fluorescens*. To measure the interfacial rheology of water-air biofilms, the subphase-exchange interfacial rheological setup is used to study the effects of external influences (e.g. pH changes, ionic strength changes, addition of surfactants) on the biofilm without destroying the interface [3]. To support the observed structural changes, the surface tension was measured over time with a pendant drop tensiometer.

All three bacteria showed a characteristic viscoelastic growth profile of their biofilm depending on growth media and temperature. Through the observation of the transient elastic moduli, we were able to observe the complex bacterial biofilm lifecycle. After biofilm formation, the film was stressed by external factors through the addition of a surfactant (Tween 20) and by lowering the pH with hydrochloric acid. The addition of Tween 20 to *Pseudomonas fluorescens* biofilms led to an immediate loss of elasticity with a subsequent recovery, whereas for *Bacillus subtilis* no visible effect was observed. For *Bacillus subtilis* the interfacial rheological data additionally unveiled the production of a surfactant-based spread aid rationalizing the limited response to the added Tween 20. The pH decrease from pH 7 to 4 revealed a strong dependency of pH on the elastic biofilm properties, as a complete loss of elasticity was observed at low pH.

Interfacial rheology proved to be a valuable tool for studying biofilms as the influence of temperature, media type, bacterial strain, pH and surfactant concentration could be observed successfully during biofilm formation.

Literature:

[1] Hall-Stoodley, L., Costerton, J. W., Stoodley, P., Bacterial biofilms: from the natural environment to infectious diseases, Nature Review Microbiology, 2004, 2, 95–108.

[2] Wu, C., Lim, J. Y., Fuller, G. G., Cegelski, L., Quantitative Analysis of Amyloid-Integrated Biofilms Formed by Uropathogenic Escherichia coli at the Air-Liquid Interface, Biophysical Journal, 2012, 103, 464-471.

[3] Rühs, P. A., Scheuble, N., Windhab, E. J., Mezzenga, R., Fischer, P., Simultaneous Control of pH and Ionic Strength during Interfacial Rheology of β-Lactoglobulin Fibrils Adsorbed at Liquid/Liquid Interfaces, Langmuir, 2012, 28, 12536–12543

Assembling of Graphene Oxide in an Isolated Dissolving Microdroplet

Xuehua Zhang [1]*, Haijun Yang[1,2], Yuting Song[1,3]
[1] *Department of Chemical and Biomolecular Engineering, University of Melbourne, Parkville, VIC 3010, Australia*
[2] *Research institute of Micro/Nano Science and Technology, Shanghai JiaoTong University, Shanghai 200240, China*
[3] *Beijing Key Laboratory of Ionic Liquids Clean Processes, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China*
* xuehuaz@unimelb.edu.au

Controlling of the morphology and assembly of graphene oxide (GO) is important in the structure design of carbon materials using GO sheets as building blocks. In this work, we have studied GO assembling driven by the dissolution of a microdroplet immersed in a surrounding liquid phase. The as assembled GO structures were highly crumpled with exotic morphology, which we refer to as GO snowballs (**Fig.1**). The detailed structure of GO snowballs was closely related to the dissolution dynamics of the droplet, which could be adjusted by the composition of the surrounding liquid. We have also studied the effects of salts and obtained two kinds of structures. One was a GO snowball with small salt crystals inserted between sheets, which formed with a low initial concentration of insoluble salt in the GO dispersion. The other was a hybrid nanostructure containing NaCl or KCl crystals on a GO snowball, which formed with a high initial salt concentration in the suspension. In addition, we report the novel nanodent-decorated GO snowballs formed by templating the spontaneously formed microdroplets through spontaneous emulsification (ouzo effects). Such highly crumpled snowball structures may find applications in super-capacitors or catalyst support.

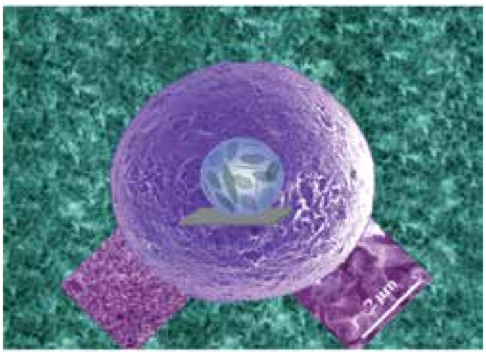

Fig. 1 SEM images with different resolutions of the structure of a GO snowball assembled in a dissolving microdroplet.

Literature:

1. Yuting Song,Haijun Yang,Yufei Wang, Shimou Chen, Dan Li, Suojiang Zhang, Xuehua Zhang. 2013. Controlling the assembly of graphene oxide by an electrolyte-assisted approach. *Nanoscale* (Accepted on 30-April-2013)
2. Haijun Yang,Yufei Wang,Yuting Song, Ling Qiu,Suojiang Zhang,Dan Li , Xuehua Zhang. 2012, Assembling of graphene oxide in an isolated dissolving droplet. *Soft Matter*, 8, 11249.

Acknowledgements:

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Thin Liquid Films as a Model of Alveolar Surface and Method for Interfacial Characterization of Therapeutic Surfactant Preparation

Roumen Todorov *, Dotchi Exerowa

Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria
* - rtodorov@ipc.bas.bg

Thin liquid film is introduced as an adequate model system for studying the structure, stability, molecular interactions and lateral mobility in the surfactant layer on the alveolar surface. Microscopic foam films studied by means of the microinterferometric technique enable introducing new parameters and measuring new dependences in order to characterize the structures at alveolar surface and their stability. The conditions for film formation are close to the physiological in order to “serve” the in vivo situation. The very sensitive parameters related to formation and stability of black foam films led to characterize therapeutic surfactants used in clinical practice.

Encapsulation and Protection of Vitamin A Palmitate with β-cyclodextrins in a Solvent-free Aqueous Solution

Neus Vilanova [1*], Conxita Solans [1*]

Institute for Advanced Chemistry of Catalonia, Consejo Superior de Investigaciones Científicas (IQAC-CSIC) and CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Barcelona, Spain

* neus.vilanova@iqac.csic.es, conxita.solans@iqac.csic.es

Fat-soluble vitamins have an important nutritional role in humans, and numerous health alterations are produced if their intake is not sufficient. For this reason, the preparation of vitamin supplements or the enrichment of conventional foods with vitamins is an interesting strategy to overcome its deficiency. However, their incorporation is not straightforward due to their poor water solubility and high instability under UV light, high temperatures or in the presence of oxygen. Hence, there is a need for the development of new technologies for the fortification of food with fat-soluble vitamins. In this context, we have used β-cyclodextrins as encapsulating agents to protect Vitamin A palmitate against its degradation to be used for food applications. Cyclodextrins have been extensively used in various applications due to their cyclic structure with a dual nature: a hydrophilic exterior with a hydrophobic cavity. Such interesting structure allows them to form inclusion complexes, where hydrophobic molecules can be hosted within the cavity [1]. However, in most of the cases organic solvents are used to disolve the hydrophobic guest and facilitate the complexation process, which is not desired if the complex is envisioned for food applications. In the present work, complexes of Vitamin A palmitate with β-cyclodextrin were successfully prepared in an aqueous solution with no need of cosolvents. The obtained inclusion complex was characterized by IR and UV-Vis measurements. Moreover, the stability of both the free and the encapsulated vitamin under extreme environmental conditions was also studied by TGA, DSC and using a UV lamp. The obtained results revealed that β-cyclodextrins were helpful protecting Vitamin A palmitate against UV light, high temperatures or in the presence of oxygen. Therefore, the obtained complexes could be incorporated in water-based food such as beverages or milk among others. Moreover, as the inclusion complex presents an amphiphilic structure their use as surface active agent is also envisaged.

Literature:

1. T. Loftsson, M. E., Brewster. 2012. Cyclodextrins as functional excipients: Methods to enhance complexation efficiency. *J. Pharm. Sci.* 101 (9): 3019-3032

Acknowledgements:

The authors gratefully acknowledge the Ministerio de Economia y Competitividad (grant CTQ2011-29336-C03- 01/PPQ) and Generalitat de Catalunya (grant 2009 SGR-961) for the financial support.

Nanoprecipitation of Polymers in a Bad Solvent

J.G.J.L. Lebouille [1], R. Stepanyan [2], J.J.M. Slot [2,3], M.A. Cohen Stuart [4] , R. Tuinier [1,5]*,

[1] *DSM ChemTech, Advanced Chemical Engineering Solutions (ACES), PO Box 18, 6160 MD Geleen, the Netherlands*
[2] *DSM Ahead, P. Box 18, 6160 MD Geleen, the Netherlands*
[3] *Department of Mathematics and Computer Science, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, the Netherlands.*
[4] *Laboratory for Physical Chemistry and Colloid Science, Wageningen University, Drijenplein 6, 6307 HB Wageningen, the Netherlands*
[5] *Van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, the Netherlands*
* - remco.tuinier@dsm.com

The functionality of polymeric nanoparticles (NPs) for biomedical drug delivery applications strongly depends on their size. The preparation of such particles can be performed by nanoprecipitation [1] of polymers or (block)copolymers into a bad solvent. In the presence of a stabilizing surfactant the size is governed by kinetics. We describe the diffusion-limited coalescence [2] process using a simple von Smoluchowski theory [3] for the size of NPs formed. Two relevant time scales, a mixing and a coalescence time, are identified and their ratio is shown to determine the final NP diameter. The size is found to scale in a universal manner and is predominantly sensitive to the mixing time and the polymer concentration if the surfactant concentration is sufficiently high. Theoretical predictions are in good agreement with experimental data [4].

References:

1. Molpecerec J., Guzman M., Aberturas M.R., Chacon M. and Kawashima Y., 1996. Application of Central Composite Designs to the Preparation of Polycaprolactone Nanoparticles by Solvent Displacement. J. Controlled Rel., 85, 206-213.
2. ben-Avraham D., 1998. Complete Exact Solution of Diffusion-Limited Coalescence, A+A -> A. Phys. Rev. Lett., 81, 4756-4759.
3. von Smoluchowski M., 1917. Attempt for a mathematical theory for kinetic coagulation of colloid solutions. Z. Phys. Chem., Abt. A 92, 129-168.
4. Stepanyan R., Lebouille J.G.J.L., Slot J.J.M., Tuinier R. and Cohen Stuart M.A., 2012. Controlled nanoparticle formation by diffusion limited coalescence. Phys. Rev. Lett., 109, 138301.

Formation and Characterization of Polyelectrolyte Multilayer Biolubricants

Tracey Ho [1], Benjamin Thierry [1], Kristen Bremmell [2], David A. Beattie [1]*

[1] – *Ian Wark Research Institute, University of South Australia, Mawson Lakes, Adelaide, SA 5095, Australia*
[2] – *School of Pharmacy and Medical Science, University of South Australia, Adelaide, SA 5000, Australia*
* - David.Beattie@unisa.edu.au

A drive towards creating biologically relevant functional surface coatings has led to the emergence of polysaccharide-based polyelectrolyte multilayers (PEM) for applications in biomaterials. These polysaccharide-based PEM surface coatings are formed easily through the Layer-by-Layer (LbL) assembly technique. In this study, we focus on the formation and properties of polysaccharide-based PEM consisting of alternating layers of polyanionic fucoidan and polycationic chitosan. Whereas chitosan is a well-studied component of polysaccharide PEMs, fucoidan, a sulfated polysaccharide extracted from seaweed, is relatively little studied in PEM formation. The formation of the fucoidan/chitosan PEM were investigated by zeta potential measurements, X-ray photoelectron spectroscopy (XPS), quartz crystal microbalance with dissipation monitoring (QCM-D), spectroscopic ellipsometry, and Attenuated Total Reflection (ATR) FTIR.

The zeta potential measurements revealed a periodic charge reversal of the PEM upon adsorption of each polyelectrolyte layer until the desired number of layers was obtained. Using QCM-D it was possible to follow the adsorption during the PEM build-up and elucidate the viscoelastic properties of the PEM using a Voigt model. An increase in both viscosity and shear modulus of the films was observed during buildup. Thickness measurements using spectroscopic ellipsometry showed that the thickness of the PEM increased supra-linearly upon the addition of each bilayer.

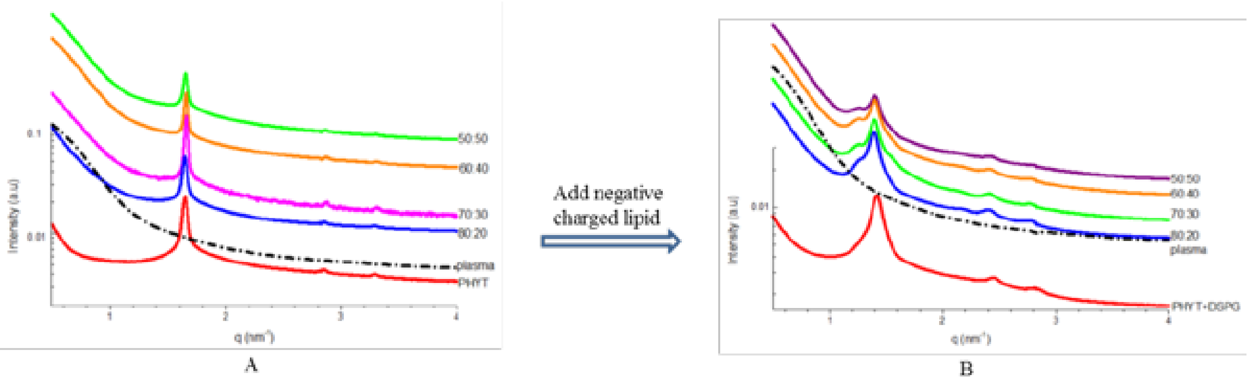
In addition to the characterization of PEM formation, the performance of the PEM as lubricants between two solid surfaces has been studied with colloid probe atomic force microscopy. These force measurements have been supplemented by in situ synchrotron FTIR spectroscopy of the PEM from within a solid-solid contact.

Direct Contact of Cisplatin-Loaded *Cubosomes*and *Hexosomes* with Human Plasma: SAXS Study

Intan Diana Mat Azmi[1]*, Christa Nilsson [1], Stefan Stürup [1],Jesper Østergaard [1],Bente Gammelgaard[1], SeyedMoeinMoghimi[2], ArtoUrtti[3], Anan Yaghmur[1].

[1] *Department of Pharmacy, Faculty of Health and Medical Sciences, University of Copenhagen, Universitetsparken 2, DK-2100 Copenhagen, Denmark*
[2] *Centre for Pharmaceutical Nanotechnology and Nanotoxicology, University of Copenhagen, Denmark*
[3] *Centre for Drug Research, University of Helsinki, Helsinki, Finland*
* - intan.azmi@sund.ku.dk

The experiments were designed to mimic the direct exposureof self-assembled cisplatinnanocarriersbased on *cubosomes* and *hexosomes* to biological environment after IV administration. They were performed under physiological conditions to fully understand the dynamic behavior of these liquid crystalline particles. The structural events occurring particularly within 17 hours after this direct contact with human plasma were investigated using small angle X-ray scattering (SAXS). The internal nanostructures of the lipidic aqueous dispersions after mixing with different concentrations of plasmaat different time intervals were investigated. In particular, the effect of different lipid compositions on the internal nanostructures of cisplatin-free and cisplatin-loaded *cubosomes* and *hexosomes* was evaluated. The investigated dispersions were either neutral or negatively charged. Theybased therefore on phytantriol (PHYT), PHYT/vitamin Emixture, or a binary mixture of PHYT with the negatively charged lipid 1,2-distearoyl-sn-glycero-3-phosphoglycerol (DSPG). The obtained SAXS patterns show a strong interaction of the neutral PHYT-based formulation with human plasma. It triggered the structural transition of the internal biphasic nanostructure (a bicontinuous cubic phase of the symmetry *Pn*3*m* co-existing with inverted type hexagonal (H_2) phase) to completely neat H_2 phase (*hexosomes*) after 17 hr of incubation in human plasma. In addition, the results revealed an interesting different behavior of*hexosomes* based on the neutral lipids (8 wt % of PHYT of total dispersion concentration)than that based on the binary phytantriol/DSPG mixture with a weight ratio of 90/10. The neutral cisplatin-free and cisplatin-loaded *hexosomal* formulations based on PHYT/vitamin E mixture with a constant weight ratio of 90/10were stable within the investigated time of the experiment (incubation up to 17 hours in human plasma without any change in the internal H_2 phase). Clearly, there is no indication on the interaction of the dispersions with plasma components that could affect the internal nanostructure. However, the internal H_2 nanostructure of *hexosomes* in the presence of DSPG is affected upon direct contact with human plasma. An additional peak is observed at lower *q* value in the obtained SAXS patterns after 10 min of incubation. It indicates most likely the formation of traces of new swollen H_2 phase coexisting with the initial H_2 phase. The findingsreveal that the effect of human plasma on the internal structures of these nanostructured dispersions is strongly affected by the lipid composition. The presence of the negatively charged lipid DSPG is most likely shows a binding effect to plasma components, thus induces a slightly change on the internal nanostructure of *hexosomes* upon direct contact with human plasma.



A B

Fig. 1 SAXS scattering patterns of panel A: neutral dispersion based on PHYT and panel B: negatively charged aqueous dispersion based on the binary PHYT/DSPG mixture before and after mixing at different volume ratios of the investigated dispersion to human plasmaat 37°C.

Optical Tweezing Electrophoresis for Enzyme Concentration Monitoring

Toon Brans [1,2]*, Caspar Schreuer [1,2], Chetna Sharma[1,2], Filip Strubbe [1,2], Filip Beunis [1,2], Kristiaan Neyts [1,2]

[1] – *Dept. of Electronics and Information Systems, Ghent University, Belgium*
[2] – *Center of Nano and Bio Photonics (NB-Photonics), Ghent University, Belgium*
* - toon.brans@elis.ugent.be

We use optical tweezing electrophoresis to determine the electrokinetic mobility of an individual particle in a colloidal suspension (Fig. 1). The particle is held by optical tweezers to counter diffusion by Brownian motion, allowing a fast and sensitive detection of its position over a long time with the aid of a quadrant detector. The particle is then subjected to an AC electric field, and its position is registered. From the amplitude of its oscillatory movements, the particle mobility can be derived.

The sensitivity of this method has been demonstrated by mobility measurements in both polar [1,2] and non-polar [3] media. We use optical tweezing electrophoresis to investigate the binding between a biotinylated particle and avidin. Since the latter has a highly positive zeta potential at pH 7, the electrophoretic mobility of the particle increases when it undergoes a binding with avidin molecules. Hence, the particle mobility is directly related to the number of avidin molecules bound to it. This property is used to determine the concentration of avidin in a buffer solution.

By employing specifically designed microfluidic devices, the signal-to-noise ratio of the mobility measurements can be increased and dynamic monitoring of the concentration can be demonstrated. This allows for more sensitive experiments to which the rate of the binding process can be linked.

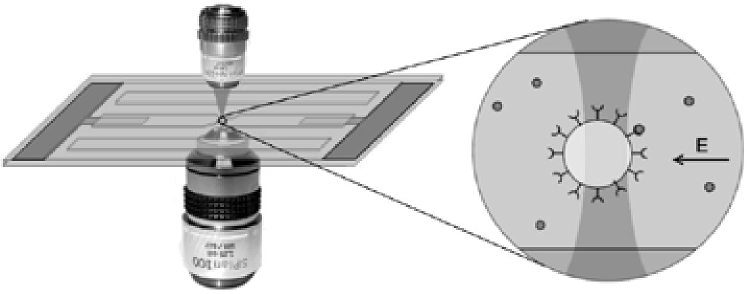


Fig. 1 Representation of the optical tweezing electrophoresis setup to determine the electrokinetic mobility of individual particles. The oscillation amplitude of a functionalized particle in an AC-field is monitored, while it is held by optical tweezers.

Literature:

1. R. Galneder, V. Kahl, A. Arbuzova, M. Rebecchi, J.O. Rädler and S. McLaughlin. 2001. Biophysical Journal 80(5):2298-2309.
2. J.A. van Heiningen and R.J. Hill. 2011. Macromolecules 44:8245-8260
3. F. Beunis, F. Strubbe, K. Neyts and D. Petrov. 2012. Physical Review Letters 108:016101

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Plasmonic Supra-Colloidal Structures: From Assembly Principles to Applications

Andreas Fery [1]*, Nicolas Pazos-Perez [1], Mareen B. Müller [1], Moritz Tebbe [1], Christoph Hanske [1], Matthias Karg [2], Alexander Wittemann [3], Ramon Alvarez-Puebla [4], Luis Liz-Marzan [5]

[1] *– University Bayreuth, Physical Chemistry II,Universitätsstr. 30, 95447 Bayreuth, Germany*
[2] *– University Bayreuth, Physical Chemistry I,Universitätsstr. 30, 95447 Bayreuth, Germany*
[3] *– University Konstanz, Department of Chemistry, Colloid Chemistry group, Universitätsstr. 10, 78457 Konstanz, Germany*
[4] *– Universitat Rovira i Virgili Tarragona, Department of Electronic Engineering & Center for Chemical Technology of Catalonia, Avda. Pasos Catalans, 2643007 Tarragona, Spain*
[5] *– CIC Biomagune, Biofunctional Nanomaterials Unit, Paseo de Miramón 182, 20009 Donostia - San Sebastián, Spain*
* - andreas.fery@uni-bayreuth.de

Plasmonic nanoparticles provide excellent means for controlling electromagnetic near-fields at optical frequencies, which has lead to a broad range of applications in various surface enhanced spectroscopy techniques in the past years. They as well hold great potential as building blocks for optical metamaterials.

While much research is dedicated to understanding nanoparticle synthesis and optimization for these tasks, understanding formation of supra-colloidal assemblies and unravelling their structure-property relations is still in its infancy. We discuss different assembly routes for the formation of well-defined supra-colloidal structures like linear assemblies [1], nanoparticle-clusters [2] and 3-dimensional ordered systems [3]. It turns out, that interfacial templating effects are a powerful tool for controlling particle order with nanoscale precision. We discuss the underlying physic-chemical effects and perspectives upscaling to macroscopic areas as well as perspectives for applications in Surface Enhanced Raman Spectroscopy.

Literature:

1. Pazos-Perez, N.; Ni, W.; Schweikart, A.; Alvarez-Puebla, R.; Fery, A.; Liz-Marzan, L., Highly uniform SERS substrates formed by wrinkle-confined drying of gold colloids. *Chemical Science* **2010,** *1* (2), 174-178.

2. Pazos-Perez, N.; Wagner, C. S.; Romo-Herrera, J. M.; Liz-Marzan, L. M.; Garcia de Abajo, F. J.; Wittemann, A.; Fery, A.; Alvarez-Puebla, R. A., Organized Plasmonic Clusters with High Coordination Number and Extraordinary Enhancement in Surface-Enhanced Raman Scattering (SERS). *Angew. Chem. Int. Ed.* **2012,** *51* (51), 12688–12693.

3. Alba, M.; Pazos-Perez, N.; Vaz, B.; Formentin, P.; Tebbe, M.; Correa-Duarte, M. A.; Granero, P.; Ferré-Borrull, J.; Alvarez, R.; Pallares, J.; Fery, A.; de Lera, A. R.; Marsal, L. F.; Alvarez-Puebla, R. A., Macroscaled plasmonic substrates for highly sensitive SERS. *accepted in Angew. Chem. Int. Ed., DOI: 10.1002/anie.201302285.*

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Liquid-Crystalline Organic-Inorganic Hybrid Dendrimer: Photoluminescence Behavior of Self-Organized CdS Nano-Core

Masaki Matsubara,[1] Kiyoshi Kanie,[1,*] Jun Yabuki,[1] Masafumi Nakaya,[1] Goran Ungar,[2,3] and Atsushi Muramatsu[1]

[1] – *Institute of Multidisciplinary Research for Advanced Material, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan,* [2] – *Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, U.K.,* [3] – *School of Chemical and Bio-logical Engineering, Seoul National University, Seoul 151-744, Korea*
* - kanie@tagen.tohoku.ac.jp

Semiconductor quantum dots (QDs) have attracted a great deal of attention in material science, because of their size-dependent and tuneable emission properties. In addition, periodic arrangement of QDs has many possibilities in application for novel nano-electronic device. Liquid-crystalline (LC) organic-inorganic hybrid dendrimer has been reported with use of spherical gold nanoparticles (NPs) as an internal core through modification by LC dendron self-organized in simple cubic structure.[1] Thus, we focused our attention on the introduction of such self-organization ability into QDs. Here, if monodispersed CdS NPs are used as the internal core, 3D-aligned QDs with dendritic corona would be obtained as applicable to future functional devices. Initially, CO_2H-modified CdS NPs **C1-C3** were prepared as the internal core of the dendrimer. Also, 2nd generation dendron **G2** with an amino-group at the apex was synthesized (Figure 1). Modification of **C1-C3** by **G2** was carried out by amidation reaction. Average particle size of **C1**, **C2**, and **C3** were calculated as 3.9, 3.9, and 3.8 nm, respectively from Figure 2a, b, c. Figure 2d shows a TEM image of **G2** modified **C1** (**G2**/**C1**). The interparticle distance of **G2**/**C1** expanded into ca. 9 nm after modification with **G2**. The numbers of **G2** molecules per one particle for **G2**/**C1**, **G2**/**C2**, and **G2**/**C3** were assigned as 69, 54, and 47 molecules, respectively, from TG analysis. SAXS and DSC measurements showed that **G2**/**C1** exhibited thermotropic LC phases in wide range of temperatures. At 150 °C, **G2**/**C1** formed cubic LC phase which could be assigned as a simple cubic structure. On the other hand, such self-organized LC structure was not found for **G2**/**C2** and **G2**/**C3**. **G2**/**C1** showed photoluminescence (PL) excited by UV irradiation at 365 nm. A significant decrease in the emission intensity was observed with increase in temperature. At 150 °C, where **G2**/**C1** self-organized in cubic LC structure, PL was almost quenched. Only **C1** showed no significant quenching of the emission. Such PL quenching would be derived from the periodic structure of **G2**/**C1**. The detailed analysis on PL quenching is now in progress.

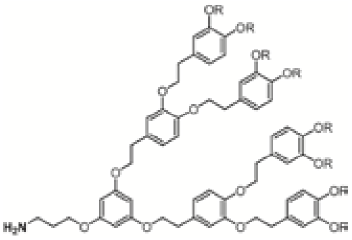


Figure 1. Structure of dendron **G2.** R = $C_{12}H_{25}$-.

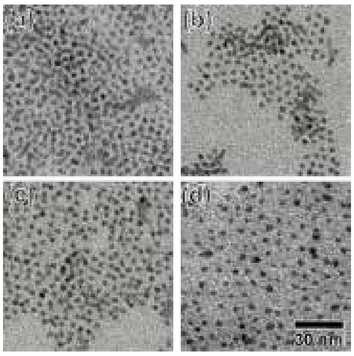


Figure 2. TEM images of (a) **C1**; (b) **C2**; (c) **C3**; (d) **G2**/**C1**. The scale bar in (d) is common for all images.

Reference:

1. K. Kanie, M. Matsubara, X. Zeng, F. Liu, G. Ungar, H. Nakamura, and A. Muramatsu. 2012. J. Am. Chem. Soc. 134: 808.

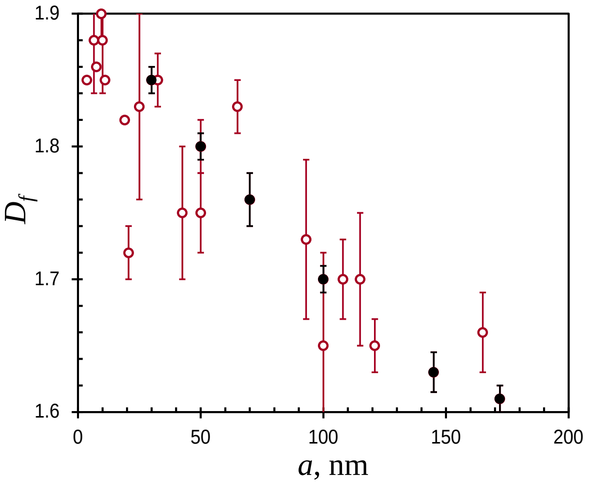
Fractal Dimension of DLCA Clusters Depends on Size of Primary Particles

Hua Wu[1]*, Marco Lattuada[2], and Massimo Morbidelli[1]

[1] – *Institute for Chemical and Bioengineering, Department of Chemistry and Applied Bioscience, ETH Zurich, 8093 Zurich, Switzerland*
[2] – *b. Adolphe Merkle Institute, University of Fribourg, 1723 Marly 1, Switzerland*
* - hua.wu@chem.ethz.ch

It is well known [1] that clusters generated from colloidal aggregation driven by Brownian motion are typical fractal objects with the fractal dimension in the range of D_f = 1.75-1.85 under the diffusion-limited cluster aggregation (DLCA) conditions. However, after systematically analysing the D_f values for the DLCA clusters determined experimentally from the scattering structure factor in the literature, we have found that the fractal dimension decreases significantly as the primary particle radius increases, as shown in **Fig. 1** (open circles). To verify such a finding, we have properly designed the DLCA experiments under density-matched conditions, using different radii of the primary particles, and determined the fractal dimensions of the generated clusters. Our results have well confirmed that the fractal dimension of the DLCA clusters indeed decreases as the primary particle radius increases (see filled circles in **Fig. 1**). To explore the mechanism leading to such dependence, we have performed intense computations through the full T-Matrix theory [2], and we conclude that this is not related to the effect of the intra-cluster multiple scattering on the slope of the scattering structure factor. The large fractal dimensions of the clusters generated by very small nanoparticles could be explained by thermal restructuring due to their low bonding energies. On the other hand, since the D_f values for the DLCA clusters obtained from numerical simulations (e.g., Monte-Carlo), where no thermal restructuring is taken into account, are always larger than 1.7, the fractal dimensions D_f<<1.7 for large primary particles in **Fig. 1** are difficult to explain. It follows that the physics behind the phenomenon in **Fig. 1** is still unknown.

Fig. 1 The D_f values of the DLCA clusters determined in this work (˜) together with those collected from the literature (š) based on the power-law regime of the scattering structure factor, plotted as a function of the primary particle radius, *a*.



Literature:

1. Lin M.Y., Lindsay H.M., Weitz D.A., Ball R.C., Klein R., Meakin P. 1989. Universality in colloid aggregation. Nature 339: 360-362.
2. Mackowski D.W., Mishchenko M.I. 1996. Calculation of the T matrix and the scattering matrix for ensembles of spheres. J. Opt. Soc. Am. A 13: 2266-2278.

Influence of Shape and Reactants Affinity On Self-Diffusiophoresis of Catalytically Active Colloids

Mihail N. Popescu [1]*, Mykola Tasinkevych [2,3], Siegfried Dietrich [2,3]

[1] – *Ian Wark Research Institute, University of South Australia, Adelaide, AUSTRALIA*
[2] – *Max Planck Institute for Intelligent Systems, Stuttgart, GERMANY*
[3] – *Institute for Theoretical Physics IV, University of Stuttgart, Stuttgart, GERMANY*
* - Mihail.Popescu@unisa.edu.au

One approach to achieve self-propulsion at the microscale consists of transforming chemical free energy into mechanical work [1]. An asymmetric decoration of a colloid with a catalyst, which promotes an activated reaction in the surrounding liquid medium, can generate dynamical concentration gradients and, via interfacial interactions, lead to self-phoresis. Such catalytically active colloids are expected to be used for, e.g., active sensing or cargo transport at the micro-scale. We discuss here analytical and numerical results for two model systems (see Fig. 1), focusing on the case of self-diffusiophoresis [2] and highlighting the influence of shape, catalyst decoration, and reactants/products affinity for the colloid surface on the emerging motion.

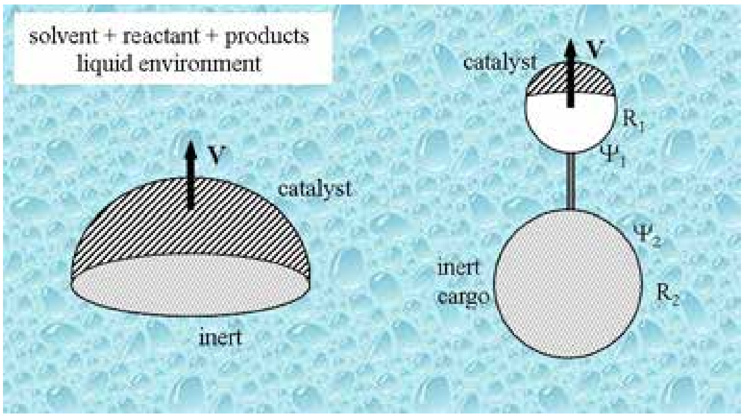


Fig. 1 A hemispherical active colloid (left) and an active carrier-cargo system (right).

The first example is a hemispherical active colloid; this shape is axi-symmetric but does not posses fore-aft symmetry. Its velocity depends on the direction of motion, which is decided by the overall repulsive or attractive character of the effective interactions between the reactants/products and the colloid. The second example is a catalytically active spherical particle (carrier) connected by a thin rigid rod to a spherical, catalytically inert particle (cargo). Generalizing previous results [3], here we discuss this system in the most general setting of different radii (R_1, R_2), reactants-surface interactions (Y_1, Y_2), and as a function of the catalyst coverage. The connection with recent experimental realizations [4] is also critically discussed.

Literature:

1. Sengupta Samudra, Ibele Michael E., Sen Ayusman. 2012. Fantastic Voyage: Designing Self-Powered Nanorobots. Angew. Chem. Int. Ed. 51: 8434–8445.
2. Golestanian Ramin, Liverpool Tanniemola B., Ajdari Armand. 2005. Propulsion of a Molecular Machine by Asymmetric Distribution of Reaction Products. Phys. Rev. Lett. 94: 220801(1-4).
3. Popescu Mihail N., Tasinkevych Mykola, Dietrich Siegfried. 2011. Pulling and pushing a cargo with a catalytically active carrier. EPL 95: 28004(1-6).
4. Baraban Larysa *et al*. 2012. Transport of cargo by catalytic Janus micro-motors. Soft Matter, 8: 48-52.

Hierarchically Structured, Double Inverse Composite Opals[#]

Markus Retsch[1,*], Ulrich Jonas[2,3]

[1] - *University of Bayreuth, Physical Chemistry – Polymer Systems, Universitätsstr. 30, 95447 Bayreuth, Germany*

[2] - *University of Siegen, Macromolecular Chemistry, Adolf-Reichwein-Strasse 2, 57076 Siegen, Germany*

[3] - *Foundation for Research and Technology - Hellas (FORTH), Institute of Electronic Structure & Laser (IESL), Bio-Organic Materials Chemistry Laboratory (BOMCLab), Nikolaou Plastira 100, Vassilika Vouton, P.O.Box 1527, 71110 Heraklion, Crete – Greece*

[#] - *experiments performed at the Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

* - markus.retsch@uni-bayreuth.de

Hierarchically structured materials prepared from colloidal particles as building blocks or templating objects are currently investigated for a vast range of potential applications. In this direction, we have been studying various strategies to prepare colloidal hierarchies, and present here a versatile and simple method to fabricate porous composite materials with a hierarchical ordering on several length scales. The fundamental templating motifs are colloidal assembly structures, which can be conveniently accessed by well-established convective assembly methods. We demonstrate the preparation of inverse opal structures with a range of materials, such as SiO_2, TiO_2, and Al_2O_3 (Fig. 1). Furthermore, this host matrix can be further infiltrated and modified by a second type and size of particles, yielding a drastically finer structured, intercalated phase with a superlattice. Yet, this second phase can serve as a template to be replicated into a sophisticated porous material.

These sequential infiltration and removal steps allow for a flexible combination of inorganic solid phases. Their multi-level structuring at several length scales holds promise for applications in catalysis or photovoltaics, where hierarchically structured interfaces play a crucial role.

Finally, the complex hierarchical material can be inverted to its polymer replica by monomer infiltration and polymerization.

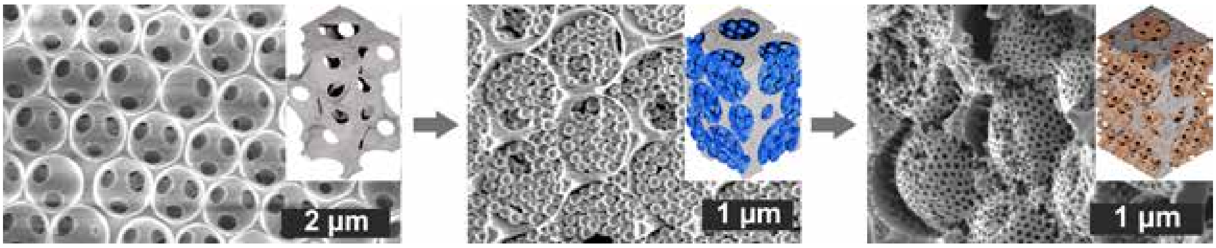


Fig. 1 Fabrication scheme of double periodic inverse opals based on multiple colloidal self-assembly steps.

Literature:

1. Retsch, Markus; Jonas, Ulrich, **2013**, "Hierarchically Structured, Double-Periodic Inverse Composite Opals", *Advanced Functional Materials*, doi: 10.1002/adfm.201300803

Growth and Heterogenous Aggregation of Calcium Silicate Hydrate: Insight from Statistical Mechanics

Christophe Labbez [1]*, Maxime Delhorme [1,2], Bo Jönsson[2], Martin Turesson[1], André Nonat[1]

[1] *– Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS, Université de Bourgogne, F-21078 Dijon Cedex, France*
[2] *– Theoretical Chemistry, Lund University, POB 124, SE-221 00 Lund, Sweden*
* - Christophe.labbez@u-bourgogne.fr

Calcium silicate hydrate (C-S-H) are negatively charged nano-platelets that confer the cohesive properties of concrete due to ion-ion correlations [1]. C-S-H are produced during the reaction of cement hydration which consist in the progressive dissolution of cement clinker (mainly tri-calcium silicate). C-S-H nucleates onto the dissolving surface of clinker grains and C-S-H platelets grow until they have reached a very limited size [2]. The hydration proceeds as long as the supersaturation with respect to C-S-H is maintained with a continuous germination/growth of new platelets that grow next to the previous ones forming a network. The aggregation of the platelets onto the clinker surface is strongly oriented and depends on the ionic content of the solution. Low pH and low calcium concentration promotes a lateral aggregation of platelets (i.e. next to each other) and a high calcium concentration and pH promotes an axial aggregation of the platelets (i.e. on top of each other) [3]. Both the limited growth of individual C-S-H platelets and their aggregation mode are intriguing observations. In particular, the main question is whether these processes are controled by kinetics or by thermodynamics. In this contribution, we explore these processes at the level of the full primitive model (explicit colloids and ions) by a combination of Monte Carlo and molecular dynamics simulations [4]. In the low coupling regime, i.e., weakly charged platelet in presence of low salt concentration, the growth of a single platelet is found to be limited by its own internal repulsion dominated by the counterion entropy. For a strongly coupled system, that is with high charge density and multivalent counterions, the energetic interactions become relatively more important and the entropy of the system plays less role. As a consequence, the electrostatic interactions gradually become less of a hindrance for growth and in extreme cases electrostatics actually promotes the growth. On the other hand, at high calcium concentration and strong C-S-H charge, the axial aggregation is found, in good agreement with experiments, to be favored as a result of the formation of platelets stacks onto the surface. Finally, at low calcium concentration and weak C-S-H charge, the energetic interactions are found to be strong enough to promote the adhesion of the platelets to the surface but not between themselves. As a result, the surface is found to be rapidly covered by platelets, again in good agreement with experiments.

1. B. Jönsson, A. Nonat, C. Labbez, B. Cabane, and H. Wennerström, Langmuir 21, 9211 (2005)
2. S. Garrault, E. Finot, E. Lesniewska, and A. Nonat, C. R. Acad. Sci. Paris 327, 213 (1998)
3. S. Garrault and A. Nonat, Langmuir 17, 8131 (2001)
4. M. Delhorme, Thermodynamics and Structure of Plate-Like Particle Dispersions, Ph.D. thesis, Lund University-Burgundy University, Lund, 2012.

Molecular Dynamics Simulations of the Spherical Electrical Double Layer of a Soft Nanoparticle

Sergio Madurga [1]*, Miroslava Nedyalkova [2], Stoyan Pisov [3], Isabel Pastor [1],
Eudald Vilaseca [1], and Francesc Mas [1]

[1] *– Physical Chemistry Department and Research Institute of Theoretical and Computational Chemistry (IQTCUB) of the University of Barcelona (UB), 08028 Barcelona, Catalonia, Spain*
[2] *– Faculty of Chemistry, University of Sofia, 1164 Sofia, Bulgaria*
[3] *– Faculty of Physics, University of Sofia, 1164 Sofia, Bulgaria*
* - s.madurga@ub.edu

Molecular dynamics simulations were performed to study the ion and water distribution around a spherical charged nanoparticle [1]. A soft nanoparticle model (Fig. 1) was designed using a set of hydrophobic interaction sites distributed in concentric spherical layers. Four charged nanoparticle models were studied in NaCl and $CaCl_2$ salt solutions at different concentrations. A series of simulations covering different conditions was carried out to evaluate the effect of the surface charge, valence of counterion, and concentration of added salt. Different permeability was observed for Na^+ and Ca^{2+} ions. Monovalent ions are more accumulated inside the nanoparticle surface, whereas divalent ions are more accumulated just in the plane of the nanoparticle surface sites. The increasing of the salt concentration has little effect on the internalization of counterions, but significantly reduces the number of water molecules that enter inside the nanoparticle.

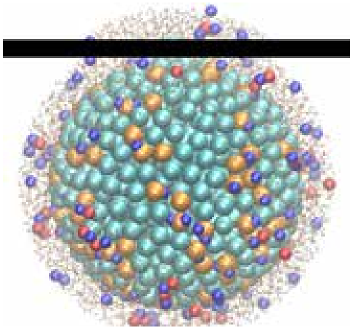


Fig. 1 *Snapshot of a simulation of the −100e charged nanoparticle in 1 M NaCl solution. Only water molecules, Na+ ions (in blue), and Cl− ions (in red) close to 1.0 nm from the nanoparticle surface are displayed*

Literature:

1. M. Nedyalkova, S. Madurga, S. Pisov, I. Pastor, E. Vilaseca, and F. Mas, 2012, J. Chem. Phys. 137, 174701.

Acknowledgements:

The authors gratefully acknowledge support of this research by the Spanish Ministry of Science and Technology (Project No. CTM2009-14612) and by the Generalitat de Catalunya (Grant Nos. 2009SGR465 and XRefQTC). M.N. thanks the HPC-Europa2 project (Project No. 228398) for financial and technical support, as well as the European Commission Capacities Area–Research Infrastructures Initiative.

Understanding the Formation of Metal Colloids

Jörg Polte [1]*

[1] *Humboldt-Universität zu Berlin, Brook-Taylor-Strasse , 12489 Berlin, Germany*
* - joerg.polte@hu-berlin.de

Colloidal nanoparticles have attracted much attention due to their unique properties and promising applications. Synthetic procedures are known and have been investigated since Faraday’s ground-breaking experiments about gold colloids more than 150 years ago.[1] However, a profound understanding of the underlying nanoparticle formation processes is still missing.[2]

Recently, we introduced novel setups and techniques which enable the determination of the size evolution and concentration of colloidal nanoparticles throughout the growth process. These technical developments have been the key to determine the growth mechanisms of several metal colloid syntheses. [3]-[6]

The comparison of the different mechanisms reveals fundamental principles of nanoparticle growth that are in contrast to present nucleation and growth theories. For the investigated systems it was shown that growth is only governed by colloidal stability whereas a process of nucleation has no significant effect on the final particle size distribution. Instead, a novel model is presented that provides a comprehensive understanding of the fundamental principles of colloidal nanoparticle growth. Exemplified for gold, silver and palladium nanoparticles, it will be demonstrated that the gained mechanistic knowledge allows improving and developing strategies for size controlled syntheses of nanoparticles without additional stabilizing agents.

In summary, three major issues in colloidal science are addressed: (i) experimental techniques and methods to investigate nanoparticle formation processes in-situ and time resolved; (ii) fundamental principles of nanoparticle growth deduced from mechanistic information of several nanoparticle syntheses;(iii) precise size control of colloidal metal nanoparticles.

Literature:

1. Faraday, Michael, 1857, The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light, Philosophical Transactions of the Royal Society of London, 147, 145-181.
2. Xia, Y., Xiong, Y, Lim, B, and Skrabalak, S.E., 2009, Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics?, Angewandte Chemie International Edition, 48, 1, 60-103.
3. Polte, J., Emmerling, F., Radtke, M., Reinholz, U., Riesemeier, H., and Thünemann, A.F., 2010, Real-Time Monitoring of Copolymer Stabilized Growing Gold Nanoparticles, Langmuir, 26, 8, 5889-5894.
4. Polte, J., Ahner, T.T., Delissen, F., Sokolov, S., Emmerling, F., Thünemann, A.F. and Kraehnert, R., 2010, Mechanism of Gold Nanoparticle Formation in the Classical Citrate Synthesis Method Derived from Coupled In Situ XANES and SAXS Evaluation, J. Am. Chem. Soc., 132, 4, 1296-1301.
5. Polte, J., Erler, R., Thünemann, A.F., Emmerling, F., and Kraehnert, R., 2010, SAXS in combination with a free liquid jet for improved time-resolved in situ studies of the nucleation and growth of nanoparticles, Chem. Comm., 46, 48, 9209-9211.
6. Polte, J., Tuaev, X., Wuithschick, M., Fischer, A., Thuenemann, A.F., Rademann, K., Kraehnert, R., and Emmerling, F., 2012, Formation Mechanism of Colloidal Silver Nanoparticles: Analogies and Differences to the Growth of Gold Nanoparticles, ACS Nano, 6, 5791-5802.

Size Control of Gold Nanorods by the Interaction with Surfactant Molecules

Yoshiko Takenaka [1]*, Hiroyuki Kitahata [2,3], Norifumi L. Yamada [4], Hideki Seto [4], Youhei Kawabata [5], Takuya Ohzono [1].

[1] – *Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST).*
[2] – *Department of Physics, Graduate School of Science, Chiba University.*
[3] – *PRESTO, JST.*
[4] – *KENS & CMRC Institute of Materials Structure Science, High Energy Accelerator Research Organization.*
[5] – *Department of Chemistry, Tokyo Metropolitan University.*
* - takenaka.yoshiko@aist.go.jp

Gold nanorods are one-dimensional gold crystals [1]. The aspect-ratio (AR: ratio between length and diameter) of gold nanorods is one of the most important parameters for industrial application. For instance, low-AR (AR < 10) gold nanorods are useful for chemical sensors and medical probes, on the other hand, high-AR (AR > 20) gold nanorods are expected for electrodes, nanogap electrodes and nanorod arrays. However the industrial applications of high-AR gold nanorods are less advanced than those of the low-AR gold nanorods. It is because the method on controlling size and the high-yield synthesis of high-AR nanorods has not been enough established, compared to the case of low-AR gold nanorods. It is therefore important to achieve both size-controlled high-AR nanorods and their high-yield synthesis for the industrial application. In this presentation, we will show the size control (diameter and length) of high-AR gold nanorods by the interaction with surfactant molecules.

It is well known that gold nanorods are synthesized with the reduction of Au ions in a surfactant solution [1]. To reveal the determination mechanism of gold-nanorod diameter, we synthesized nanorods in octadecyltrimethylammonium bromide (OTAB) solution by seeding method. The growth process was observed with scanning electron microscopy (SEM). The surfactant self-assembly in a growth solution was observed with small-angle neutron scattering (SANS) and was determined by fitting the scattering profiles. These results indicated that the gold-nanorod diameter is affected by the curvature of the surfactant bilayer covering the nanorod surface (**Fig. 1**) [2]. In addition to the determination mechanism of gold-nanorod diameter, that of gold-nanorod length will be also discussed from the viewpoint of the effect of the number of crystal nuclei and the stability of Au ion before the crystallization [3].

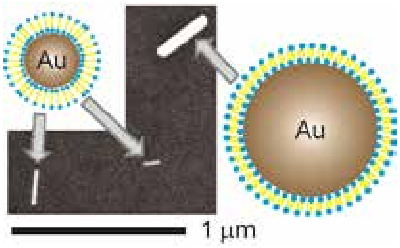


Fig. 1 SEM image of gold nanorods and the schematic illustrations of the cross-section of each gold nanorod with surfactant bilayer.

Literatures:

1. Murphy, C. J. et al. 2011. Gold Nanorod Crystal Growth: From Seed-Mediated Synthesis to Nanoscale Sculpting. Curr. Opin. Colloid Interface Sci. 16: 128-134.
2. Takenaka, Y. et al. 2011. Growth of Gold Nanorods in Gelled Surfactant Solutions. J. Colloid Interface Sci. 356: 111-117.
3. Takenaka, Y. et al. submitting.

Optimized Laboratory System for the Investigation of Colloidal Systems

Peter Mario Worsch[1]*, Andreas Keilbach[1]

[1] – *Anton Paar GmbH, Graz, Austria*
* - peter.worsch@anton-paar.com

Colloidal systems (e.g. surfactants, dispersions, emulsions etc.) are intensively investigated systems in current science. Consequently, an essential point is the careful characterization of these systems in-situ. The small angle X-ray scattering (SAXS) technique offers precise and fast measurements to investigate parameters such as size, shape, inner structure and interaction effects of particles. Thus, SAXS is a complementary method to TEM, AFM, or NMR techniques.

In the past,SAXS measurements were mainly performed at synchrotron facilities.Thanks to recent developments, laboratory instruments have become an excellent alternative(**Fig. 1**).

We are going to present the latest developments and trends in the field of laboratory SAXS instruments as well as novel techniques in sample positioning which are commonly known from synchrotron measuring stations.

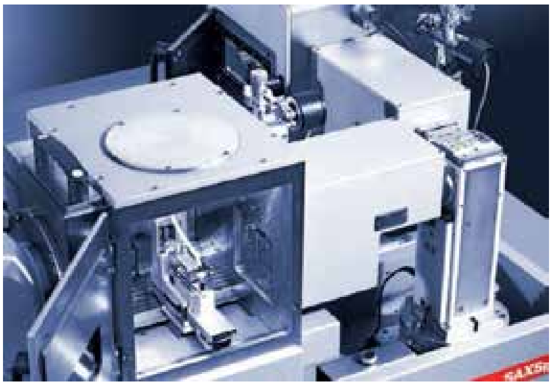


Fig. 1:SAXS measurements on lab systems are an excellent alternative to Synchrotrons

Literature:

1. SchnableggerHeimo, Singh Yashveer, “A Practical Guide to SAXS: Getting acquainted with the principles”,2011, ISBN-13 9783900323882

From Paper to Electronic:
How to convert pure Cellulose into a Working Electrode

Cristina Giordano*, Zoe Schnepp, Stefan Glatzel

Max Planck Institute of Colloids and Interfaces, Am Muehlenberg 1,
14424 Golm-Potsdam, Germany
* - Cristina.Giordano@mpikg.mpg.de

Microelectronics can be considered thequintessenceof the age of information technology. Its processing is however often highly integrated, far from open access in the process chain, and hardlyadaptable.In this sense, functional printing techniques have been identified as the most promising approach for simpler and cost effective electronics.However, for a full development, still some problems have to be overcome, e.g. the use ofthermallyunstablesupportsstrongly hinders the integration in processeswere high temperatures are required. The combinationof printing techniques with well-established high temperature processing methods is then a key requirement for future microelectronics.

To overcome these challenges without sacrificing simplicity, we set up a remarkably easy, low costs and general procedure to turn ordinary cellulose into microstructuredgraphenenano-assemblies, usinga paper support and an iron-basedcatalytic ink as two reactants to generate functional carbon/ceramic arrays (namely $Fe_3C@C$)[1].As the catalyst can be printed on the paper, these materials are also available in 2D-patterned arrays, e.g. for microstructured electrodes *via* facile ink-jet processing techniques and can be also used for further modification,e.g.electro-deposition of copper(**Fig. 1**).

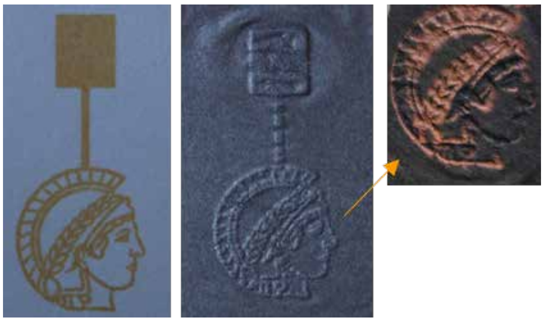


Fig. 1 Preparation of the patterned electrode, from left to right:printed iron-based ink on paper,after thermal treatment to convert the ink into carbon/ceramic arrays, and after metal deposition.

Literature:

1. Glatzel Stefan, Schnepp Zoe, Giordano Cristina, 2013. From paper to structured carbon electrodes by inkjet printing. Angew. Chem. Int. Ed., 52, 2355-2358

Acknowledgements: We gratefully thank Prof. M. Antonietti for discussion and the Max Planck Society for funding.

Stable Capsules Formed by Polyelectrolyte Coated Liposomes

Marta Ruano[1], Hernán Ritacco, José E.F. Rubio, Ramón G. Rubio[1,*]and Francisco Ortega[1]

[1]*Department of Physical Chemistry, Faculty of Chemistry, Complutense University, 28040-Madrid, Spain.*
* - rgrubio@quim.ucm.es

Nano- and microcapsules are important as delivery systems as well as microreactors. [1] It has been frequent to make them by using microparticles as templates, coating it with polymers, and finally dissolving the template. In the case of inorganic templates the last step implies to work under chemically aggressive conditions (e.g. use of HF for silica particles). In the case of polymer templates it cannot be ensured that all the polymer chains have diffused out of the capsule.[2] In this communications we describe a simple method to coat liposomes (neutral or charged) with polyelectrolytes and/or nanoparticles using the layer-by-layer method. Figure 1 illustrates the coating procedure.

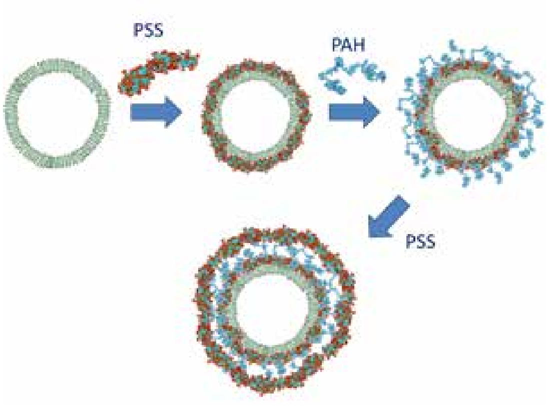


Figure 1: Scheme of the coating process of a liposome using the layer-by-layer method. PAH: poly(diallyl dimethyl ammonium) chloride. PSS: sodium poly(styrene sulfonate).

Different pairs of polyelectrolytes (PAH, PSS, PGA, PLL) and also charged latex particles have been used for building the multilayers. Mixtures of phospholipids (DOPC, DPPC) and a cationic (DODAB) have allowed us to use both cationic liposomes (DOPC+DODAB) over a broad surface charge density range, and zwitterionic liposomes. The number of layers and the nature of the polymers determine the diffusion through the wall of the capsule, as well as its stability. Capsules with up to ten polymer layers have been produced that remained stable for months, and resisted centrifugation. The structure of the coatings has been studied by light and neutron scattering techniques.

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[1] Caruso, F.L, *J. Amer. Chem. Soc.* **1998,** 120, 1
[2] Sukhorukov, G.D.; Donath, E.; Davis, S. *Polymers Adv. Technol.* **1998**, 9, 8

Controlling Structure and Surface Properties of LbL Multilayers

Piotr Batys [1]*, Paweł Weroński [1]

[1] – *Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,*
Niezapominajek 8, 30-239 Krakow, Poland
* - ncbatys@cyf-kr.edu.pl

We present our computational research of the layer-by-layer (LbL) self-assembling process of colloidal particles [1]. Experimental research using this technique, excellent for fabricating multilayers with certain characteristics, has often been reported in the literature. Procedures for the LbL assembly are relatively simple and can be automated. Hence, the usage of this method in various fields has significantly increased over the past few years. Because of major practical importance, mono- and bi-layer deposition of particles has extensively been studied. However, despite their increasing significance for the preparation of nano-structured porous materials, functional multilayers of more than two particle layers are less discussed in the literature and thus less known [2, 3]. Therefore, we have conducted in-depth analysis of the structure and surface properties of the LbL multilayers. For this purpose we have generated five multilayer structures of monodisperse spherical particles according to a generalized model of random sequential adsorption of hard spheres. The multilayers, each created at a different single-layer surface coverage, are of similar thickness. We have analyzed the variation of multilayer thickness with the number of adsorbed layers. We have also calculated the root-mean-square roughness of the multilayers as a function of the number of adsorption cycles. Finally, we have determined the specific surface area of the porous films as a function of the distance from the solid substrate. Our results suggest that the multilayer thickness is directly proportional to the number of adsorption cycles. The average single-layer thickness grows asymptotically with the single-layer coverage. We have also found that with the number of adsorbed layers the multilayer roughness increases to an asymptotic value. We have observed oscillatory variations of the multilayer specific surface area, decaying exponentially with the distance from the substrate. The decay length of the oscillation increases exponentially with the surface coverage. Our results suggest that all the film characteristics strongly depend on the method of its preparation and can be controlled by manipulating the single-layer surface coverage or deposition time. The results can be useful for efficient designing multilayers with desired properties.

Literature:

1. P. Batys, P. Weroński, (2012), Modeling of LbL Multilayers with Controlled Thickness, Roughness, and Specific Surface Area. J. Chem. Phys. 137, 214706.
2. Z. Adamczyk, P. Weroński, J. Barbasz, (2008), Formation of Multilayerd Structures in the Layer by Layer Deposition of Colloid Particles. J. Colloid Interface Sci. 317, 1.
3. D. Lee, M. F. Rubner, R. E. Cohen, (2006), All-Nanoparticle Thin-Film Coatings, Nano Lett. 6, 2305.

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Polymer Coatings Containing Nanosized Selective Sorbents for Prevention Radionuclides from Spreading

Svetlana Bratskaya[1]*, Veniamin Zheleznov[1], Dmitry Marinin[1], Risto Koivula[2], Risto Harjula[2], Anna Musyanovych[3], Alla Synytska[4], Frank Simon[4], Valentin Avramenko[1]

[1] – *Institute of Chemistry FEBRAS, Vladivostok, Russia*
[2] – *University of Helsinki, Finland*
[3] – *Max-Planck-Institute for Polymer Research, Mainz, Germany*
[4] – *Leibniz-Institut für Polymerforschung Dresden e.V., Germany*
* - sbratska@ich.dvo.ru

Here we discuss a promising approach to prevent spreading of radioactive materials from contaminated surfaces via formation of stable impermeable polymeric films, which are able to trap radionuclides selectively and significantly reduce their mobility in the environment. The approach is based on immobilization of nanosized selective inorganic sorbents (transition metal ferrocyanides, tetravalent oxides, barium/calcium sulfates etc.) into film-forming latexes. Commercial siloxane-acrylate latex (Scientific-Production Association "Astrokhim", (Elektrostal, Moscow Region, Russia) and a series of poly(siloxane) latexes with particle size 108±10 nm varying in content of surface functional groups (carboxylic or amino groups) were used for immobilization of selective sorbents. It was shown that transition metal ferrocyanides could be synthesized directly in the presence of latex particles using carboxylic functional groups as anchoring centers for divalent metal ions sorption and further growth of ferrocyanides nanocrystals. The content of surface functional groups has been identified as a crucial parameter affecting stability of the materials.

The effects of composition, pH, and media salinity on the sorption properties of the selective sorbents immobilized in latex particles toward ^{137}Cs, ^{63}Ni, and ^{90}Sr have been investigated. The dust-suppressing formulations with different latex solid contents varying in composition of latex particles and type of selective sorbents were prepared. Conditions of coatings formation by spray-drying method were optimized via variation of number of pushes, distance from the surface, and solid content of latex in dispersions. Homogeneity, thickness, and topography of the coatings were monitored using SEM, Nanofocus and MicroGlider techniques. It was shown that despite high variations in thickness of spray-dried coatings, the full surface coverage was reached after spraying latex dispersions with solid content >5% and drying for 3-6 h. Efficiency of coatings to prevent radionuclides spreading was investigated in leaching tests on contaminated quartz sand. It was shown that the degree of radionuclides leaching from uncoated sand and sand coated with latex dispersions reached up to 80% after 6 h of contact with leaching solution, while immobilization of selective sorbents into the latex allowed reducing radionuclides leaching from coated surface to <1.5%.

Acknowledgements: Financial support for ERANET-Russia project (STProject-144) of the 7th EU Research Framework Programme is gratefully acknowledged.

Surface Coatings of Water-insoluble, but Water-responsive, Internally Structured Polymer-surfactant Films

Charlotte Gustavsson[1]*, Joaquim Li[1], Karen Edler[2], Lennart Piculell[1]

[1]*Division of Physical Chemistry, Lund University, Sweden*
[2]*Department of Chemistry, University of Bath, United Kingdom*
* - charlotte.gustavsson@fkem1.lu.se

We present a facile method to produce water-insoluble, water-responsive and internally structured surface coatings via deposition of polyion-surfactant ion "complex salts" dissolved in ethanol. The combination of hydrophobic domains and water-responsive structural transitions suggests triggered release of solubilized compounds as a possible future application of such films. Polymer-surfactant coatings are not readily made by established strategies, such as layer-by-layer deposition. However, since complex salts are soluble in ethanol [1, 2], it is possible to cast a film by simply spreading an ethanolic solution onto a surface. Good wettability is found for a variety of hydrophilic and hydrophobic surfaces. When an initially dry surface film is exposed to water, it immediately responds by adsorbing water and swelling, but it does not dissolve. The structures of the complex salt coatings can be controlled by varying the polyion and/or surfactant ion, by adding a co-surfactant or, interestingly, by controlling the water activity. As the water content increases the structure may change, for example, from hexagonal to micellar cubic.

A knowledge-based design of structured coatings is possible thanks to previous systematic bulk phase studies of mixtures containing C_nTAPA complex salts (alkyltrimethylammonium ions paired with polyacrylate) [2, 3]. SAXS studies confirm that the same structures are present in the thin surface films as in the corresponding bulk phases. Figure 1 shows SAXS profiles for a $C_{12}TAPA_{6000}$ film at increasing water contents. The observed phase changes are reversible upon drying. Incorporation of a water-insoluble long-chain alcohol results in a water-swellable lamellar film.

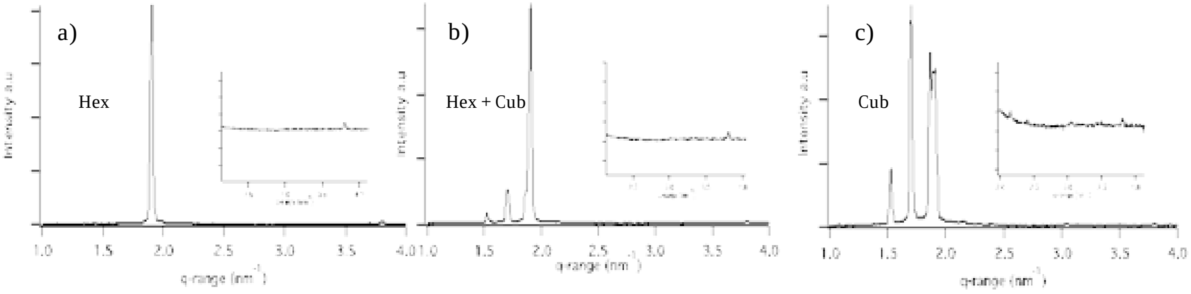


Figure 1. SAXS profiles for $C_{12}TAPA_{6000}$ 1 min (a), 10 min (b) and 15 min (c) after exposure to water.

Literature:

1. Antonietti Markus, Förster Stephan, Zisenis Mathias, Conrad Jürgen. 1995. Solution viscosity of polyelectrolyte-surfactant complexes: polyelectrolyte behavior in nonaqueous solvents. Macromolecules 28, 2270-2275
2. Silva Bernardes Juliana, Piculell Lennart, Loh Watson. 2011. Self-assembly of polyion-surfactant ion complex salts in mixtures with water and n-alcohols. J.Phys.Chem.B 115, 9050-9058
3. dos SantosSalomé, Gustavsson Charlotte, GudmundssonChristian, LinsePer, PiculellLennart. 2011. When do water-insoluble polyion-surfactant ion complex salts “redissolve” by added excess surfactant?. Langmuir 27, 592-603.

Polyelectrolyte Brushes with Charge Gradient: A Neutron Reflectometry Study

Ralf Köhler [1,2]*, Zuleyha Yenice [1], Jan Genzer [3], Regine v.Klitzing [1]

[1] – *University of Technology Berlin, Dept. Chemistry, Stranski-Lab, Berlin, Germany*
[2] – *Helmholtz Center Berlin, Inst. Soft Matter and Functional Materials, Germany*
[3] – *North Carolina State University, Chemical and Biomolecular Engineering, Raleigh, USA*
* - ralf.koehler@helmholtz-berlin.de

Polyelectrolyte (PE) brushes are macromolecular films which are grafted to a substrate. Due to their unique properties, as specific adsorption, permeability and stimuli-responsive behavior, PE-brushes can be used for surface modification. For instance, poly-[2-(dimethylamino) ethyl methacrylate] (PDMAEMA), a weak polyelectrolyte with pH-dependent properties, shifts its protonisation when pH is varied, or converts into a strong PE by quaternisation.

The PDMAEMA-brushes were gradually quaternised with deuterated iodomethane. Deuterium allows labelling the quaternised sites within the brushes for neutron reflectometry (NR) without altering their chemistry. NR was applied to detect the inner structure, density, and thickness of the brush after quarternising. Due to the deuterium-labelling it can additionally monitor the charge distribution in the brush, laterally and vertically to the substrate. The brushes are fully extended (swollen) in saturated water vapour (D2O).

Fig. 1 Scattering Length Density (SLD) profiles of swollen PE-brushes: Decreasing thicknesses and SLDs of the brushes at different sample positions (red to blue: high to low quaternisation).

Our results present a decrease of the SLD of the brushes in lateral direction, i.e. in direction of preparation. This reduction indicates a distinct decrease of charged sites, which are labelled with deuterated methyl groups of high SLD. At the same time, the vertical distribution of charges seems widely homogeneous along the brush chain. Brush thickness and also the water content of the brushes are simultaneously increased with degree of quaternisation. The origin of these effects might be, on one side, a more pronounced intermolecular and intramolecular electrostatic repulsion and a higher water affinity of the quaternised sites of the brush, on the other side.

Charge gradients are promising surface modifications, allowing a unidirectional functionalisation of thin films. Beside the aspect as tool for surface modification, the tunable internal interactions of PE-brushes will also give new inside into the complex interplay of soft matter interactions.

Acknowledgements:

Financial support by the German Research Foundation (DFG) in the framework of the IGRTG 1524 (SSNI) is gratefully acknowledged. Beamtime was provided by HZB Berlin.

Frictional Behaviour of Nanotextured Surfaces: Challenging Ancient Amontons' laws of Friction

Benoit Quignon*, Sean A. Davis, and Wuge H. Briscoe

School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom
* - benoit.quignon@bristol.ac.uk

Due to miniaturisation of modern devices, their reliability and durability becomes friction limited. Recent advances in the fabrication of nanostructured surfaces with tuneable topographic properties, along with advances in analytical tools such as the friction force microscopy, now enable the study the frictional properties of well-defined nanostructured surfaces at the nanoscale. In this study, we have studied the frictional behaviour of nanotextured surfaces bearing Aluminium Oxide nanodomes[1] (*cf.* Fig. 1) and Zinc Oxide nanorods[2] of varying topographic dimensions by Friction Force Microscopy (FFM).

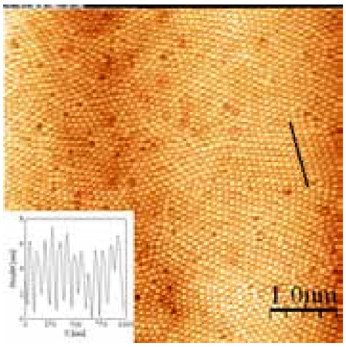


Fig. 1. AFM micrograph of a nanodome-textured surface (a section height profile is shown in inset). The diameter of the nanodomes varied between 20 nm and 200 nm.

Our results show that frictional behaviour of the nanodome textured surfaces could be described by ancient Amonton's laws of dry friction[3], however the friction coefficient was insufficient to fully characterise the frictional behaviour of such nanotextured surfaces. Pronounced stick-slip frictional characteristics are observed for all the nanodomed surfaces, with the amplitude of the stick-slip varying linearly with the applied load. We therefore proposed to define a *Stick-Slip Amplitude Coefficient* (*SSAC*) to characterise the frictional behaviour of such surfaces.

The nanorod-textured surfaces, as examined using a colloidal probe, do not however obey Amonton's first law (*cf.* Fig. 2), with a non-linear relationship between friction and load. Instead, two distinct friction-vs.-load regimes are present for certain nanorod length and density. In the first regime at low loads, the frictional force is dominated by sliding of the probe on the rods, whereas in the second regime at higher loads, the elastic bending of the rods dominates the frictional force. We thus are able to extract Young's modulus for the nanorods by fitting our frictional data, incorporating Hertzian contact mechanics.

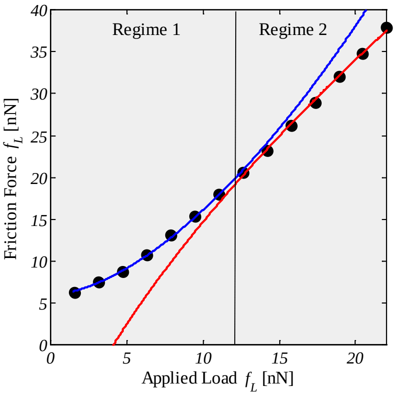


Fig. 2. Friction vs. applied load between a μm silica colloidal probe and a nanorod-textured surface.

Our results show that ancient Amontons' laws of friction, which has been found universally valid for a large number of systems, are challenged when surfaces are decorated with nanotextures.

Literature:

1. Mattia, D. *et al. J. Phys. Chem. B*, 2006. 110(20): p. 9850-9855.
2. Fuge, G.M. et al. *Chem. Phys. Lett.*, 2009. 479(1–3): p. 125-127.
3. Pilkington, G.A. *et al. PCCP*, 2011. 13(20): p. 9318-26.

Acknowledgements: M. Ashfold, B. Truscott & G. Pilkington (Bristol); D. Mattia & H. Leese (Bath); P. Claesson & E. Thormann (Stockholm)

Influence of Type of Surfactant on Degradation and Drug Release Rate from Anhydride Based Nanoparticles

Shahla Bagherifam[a,e,f], Gareth W. Griffiths [f], Gunhild M. Mælandsmo [g], Bo Nyström [e], Vasif Hasirci [a,b,d], Nesrin Hasirci [a,c,d*],

Middle East Technical University, [a] Graduate Department of Polymer Science and Technology,
[b]Department of Biological Sciences, [c] Department of Chemistry, Ankara, Turkey,
[d] BIOMATEN-Center of Excellence in Biomaterials and Tissue Engineering, Ankara, Turkey
[e] Department of Chemistry, University of Oslo, Oslo, Norway.
[f] Institute of Molecular Biosciences, University of Oslo, Oslo, Norway
[g] Institute for Cancer Research, Oslo University Hospital, University of Oslo, Oslo, Norway
* - s.b.fam@kjemi.uio.no

The main advantage of drug delivery vehicles is their possibility to carry the active agent and release it in a controlled manner after intravenous administration. This is very important in the case of therapy with cytotoxic agents such as anti-cancer drugs. In order to have nano-size delivery vehicle with optimum size and properties, different parameters such as organic solvent, surfactant type and concentration can be altered during the nanoparticle preparation process [1]. In this study the influence of surfactant type and its concentration on physical properties of nanoparticles were studied. For this purpose different surfactants and surfactant concentrations were applied to decrease the size of doxorubicin-loaded nanoparticles. The size and shape of the prepared nanoparticles were characterized by dynamic light scattering (DLS) and scanning electron microscopy (SEM), which is shown in Figure 1. The degradation and drug release profiles of prepared nanoparticles were examined in situ. Antitumor efficiency of formulated nanoparticles was also studied on MDA-MB-231 human breast cancer cells. The obtained results demonstrated that nanoparticles prepared by using polyvinyl alcohol 4% as surfactant exhibit the smallest size with smooth spherical morphology. While nanoparticles prepared by using Tween 80 exhibit a delay in degradation and drug release [2].

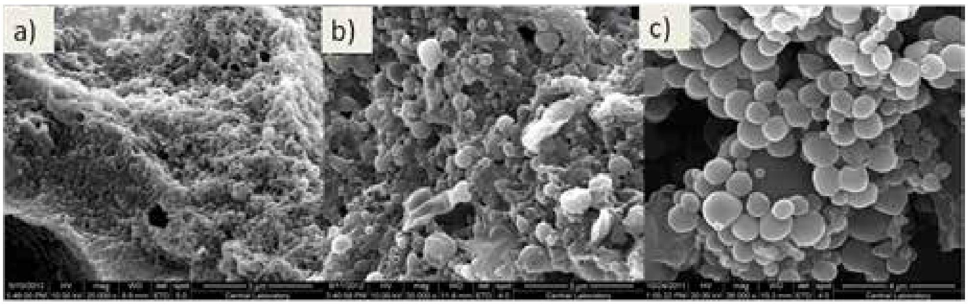


Fig. 1 . SEM micrographs of nanoparticles prepared with different surfactants. a) PVA 4%, b) PVP 4%, c) T80 4%.

Literature:

1. Chavanpatil M, Khdair A, Patil Y, Handa H, Mao G U, et al.. 2007. Polymer-surfactant nanoparticles for sustained release of water-soluble drugs. J Pharm Sci. 96: 3379-89

2. Dhanya K P, Santhi K, Dhanaraj S A, Sajeeth C I. 2011. Formulation and evaluation of chitosan nanospheres as a carrier for the targeting delivery of lamivudine to the brain. IJCP 2(05): 1-5

Studies on DNA-Cationic Surfactant Structures

Amalia Mezei[1], Ramon Pons[1]*, M. Carmen Morán[2]

[1] – *Department de Tecnologia de Tensioactius, IQAC-CSIC, Barcelona, Spain;*
[2] – *Department de Fisiologia. Facultat de Farmacia, Universitat de Barcelona, Barcelona, Spain.*
* - ramon.pons@iqac.csic.es

Nanostructured materials have opened new possibilities for application in novel sensors, biomaterials, drug delivery and delivery vehicles. In the last years increasing interest is focused on the structure of oppositely charged macromolecules and surfactants. The strong electrostatic attraction between the negative charges of DNA and the positive charge of the surfactant aggregates is forming complexes. The properties of cationic surfactants and DNA gel particles has been characterized recently [1-3]. However, the nanostructure of these complexes is still not clear. In the present communication an overview about the preparation and nanostructure of thin films based on four different cationic surfactants and DNA is proposed. Three different preparation methods were investigated, the obtained films were washed with water, dried at room temperature and analyzed by polarized light microscopy and X-ray measurements. A representative image of the textures obtained from polarized light microscopy is shown in Figure 1. The experimental results of X-ray measurements suggest a hexagonal packing in these complexes. Further insight into the structural properties of the complexes was obtained by Elemental Analysis from which the surfactant/base molar ratio was calculated. Different DNA helices to surfactant rods arrangement have been obtained in the complexes ranged to 2:1 or 3:1 depending on the surfactant structure. This research could be the basis for new drug-delivery applications of thin films.

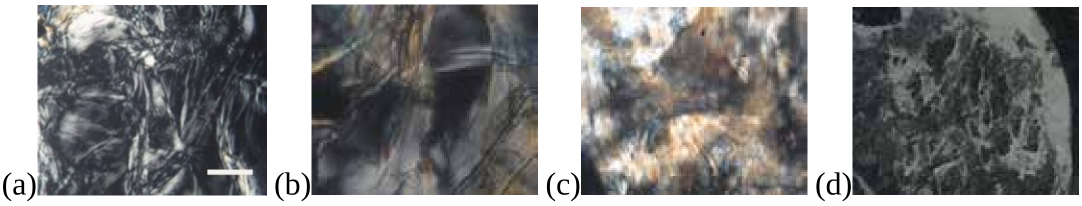


Fig. 1 Representative optical polarized micrographs of cationic surfactant-DNA complexes: (a) DNA-CTAB; (b) DNA-MTAB, (c) DNA-ALA and (d) DNA-LAM. The scale bar in (a) corresponds to 50µm.

Literature:

1. M. C. Morán, M. G. Miguel, B. Lindman, **2007,** DNA gel particles: Particle preparation and release characteristics, *Langmuir***,** 23, 6478-6481.
2. M. C. Morán, M. G. Miguel, B. Lindman, **2010,** DNA gel particles, *Soft Matter***,** 6, 3143-3156.
3. M. C. Morán, M. R. Infante, M. G. Miguel, B. Lindman, R. Pons, **2010,** Novel biocompatible DNA gel particles, *Langmuir***,** 26, 10606-10613.

Acknowledgements: This work was supported by CSIC trough a JAE-DOC2010-097 contract co-financed by FSE 2007-2013. Financial support by CTQ2010-14897 from MINECO (Spain) and 2009SGR1331 from Generalitat de Catalunya is acknowledged. M.Carmen Morán acknowledges the support of the MICINN (Ramon y Cajal contract RyC 2009-04683). Imma Carrera is acknowledged for technical assistance and Jaume Calles for IQAC SAXS-WAXS Service and the Microanalysis Service from IQAC.

Preparation of Microbial Recognition Polymer Beads via Pickering Emulsion Polymerization

Xiantao Shen, Johan Svensson Bonde, Tripta Kamra, Tongchang Zhou, Leif Bülow, Lei Ye *

Division of Pure and Applied Biochemistry, Lund University, Box 124, 221 00 Lund, Sweden
* - Lei.Ye@tbiokem.lth.se

Polymers with pre-defined molecular recognition properties have very broad applications. Introducing tailor-designed binding sites into polymers can be achieved by molecular imprinting, which is particularly suitable for small organic molecules. For large and fragile biological entities (*e.g.* virus and bacteria), it remains challenging to achieve well defined selective materials. In this work, we demonstrate that the tendency of bacteria to self-assemble at oil-water interface can be utilized to create microbial recognition sites on the surface of organic polymer beads. In the present model system, we first treated *E. coli* cells with acryloyl-functionalized chitosan, and then used the bacteria-chitosan complex to stabilize an oil-in-water emulsion (Pickering emulsion), which contained crosslinking monomer dispersed in an aqueous buffer. After polymerizing the oil phase and removing the bacteria template, we obtained well-defined polymer beads bearing bacterial imprinted sites on surface (Fig. 1). Using chemical passivation, the adsorption of bacteria by the imprinted beads could be altered, suggesting that both non-covalent interaction and shape selectivity played important roles for bacteria recognition. The method of interfacial bacteria imprinting provides a new route to achieving functional materials for separation and detection of microorganisms, and shows great potential for construction of cell-cell communication networks, biosensors, and new platforms for testing antibiotic drugs.

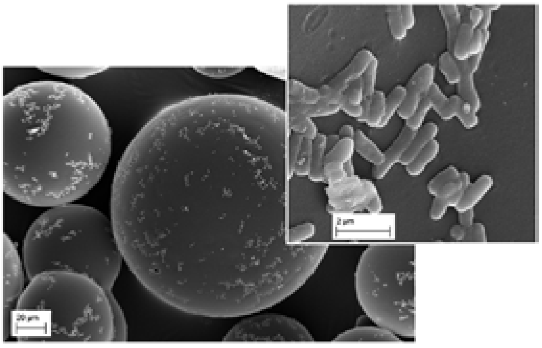


Fig. 1 Polymer beads obtained by bacteria-stabilized Pickering emulsion polymerization.

Literature:

1. Changgang Xu, Lei Ye. 2011. Clickable Molecularly Imprinted Nanoparticles. Chem. Commun. 47: 6096-6098.
2. Xiantao Shen, Lei Ye. 2011. Interfacial Molecular Imprinting in Nanoparticle-Stabilized Emulsions. Macromolecules 44: 5631-5637.

Acknowledgements:

We thank the Swedish Research Council (VR), the Swedish Research Council FORMAS and Crafoordska Stiftelsen for financial support.

Mesoporous Silica as Host for Enzymes

Krister Holmberg*, Hanna Gustafsson, Christian Thörn, Nils Carlsson, Björn Åkerman, Lisbeth Olsson

Department of Chemical and Biological Engineering, Chalmers University of Technology, 412 96 Göteborg, Sweden

* - krister.holmberg@chalmers.se

We have prepared mesoporous silica using nonionic surfactants as templating agents. The pore dimension was varied within the range 4-10 nm and three different particle sizes, 1000 nm, 300 nm and 40 nm were prepared. The immobilization rate was rapid with trypsin and with an esterase but more sluggish with lipases. The immobilized lipase showed very high activity however, much higher than lipase free in solution. The immobilized esterase exhibited a somewhat changed selectivity compared to free esterase. The entrapped enzyme was very stable towards leaching. Only a small fraction was lost on extensive rinsing with water. Enzyme immobilization into porous materials has traditionally been followed by measuring the depletion of the enzyme concentration in the surrounding aqueous phase. A novel method based on quartz crystal microbalance was developed as a way to continuously monitor the immobilization process by assessing the amount of enzyme entrapped in the pores. The immobilization efficiency is pH dependent and a method to measure the pH inside the mesoporous particles was also developed using a protein bound fluorescent probe, see Fig. 1. Fluorescence spectroscopy was also used to study the immobilization kinetics, again using a fluorescent probe covalently attached to the protein.

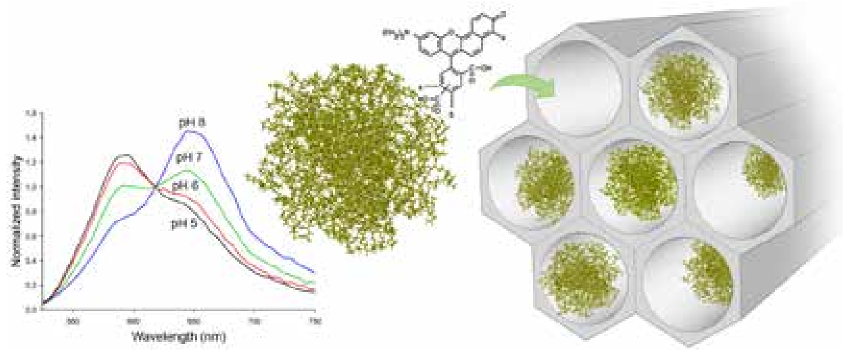


Fig. 1 Use of fluorescence labeling of an enzyme for measuring pH inside the pores of ordered mesoporous silica

Literature:

1. Thörn, Christian; Carlsson, Nils; Gustafsson, Hanna; Holmberg, Krister; Åkerman, Björn; Olsson, Lisbeth (2013) A method to measure pH inside mesoporous particles using protein-bound SNARF1 fluorescent probe, Micropor. Mesopor. Mater., 165, 240-248.

Filtration of Aqueous Suspension through Porous Medium

Anatoly Filippov [1]*, Georgiy Belyakov [2], Nikolay Baryshnikov [2], Aliya Tairova [2]

[1] – *Gubkin Russian State University of Oil and Gas, Moscow, 119991, Russia*
[2] – *Institute of Geospheres Dynamics RAS, Moscow, 119991, Russia*
* - a.filippov@mtu-net.ru

In filtration experiments (Fig.1) we used aqueous suspension containing solid particles of silicon carbide (moissanite) of 10 micron average diameter and concentration ~ 10^6cm^{-3}. The sheet of 0.9 mm foam rubber, compressed between the planes of polished glass mirrors (Fig.2), which is a braiding of polyurethane filaments with thickness of 100 microns with an average pore size of 600 microns, was used as a porous medium. The porosity of the medium was 0.93, and its permeability - 150 Darcy. Before each experiment, the porous layer was filled with water. Dissemination of the suspension into the reservoir model occurs under differential pressure created at the ends of the reservoir model using a vacuum pump. Monitoring the area of penetration of the suspension into the porous medium was conducted using a camera that records the light coming through different parts of the medium with different concentrations of filtered particles. The density distribution of the particles deposited in the pores was correlated with the distribution of brightness on the obtained photographs.

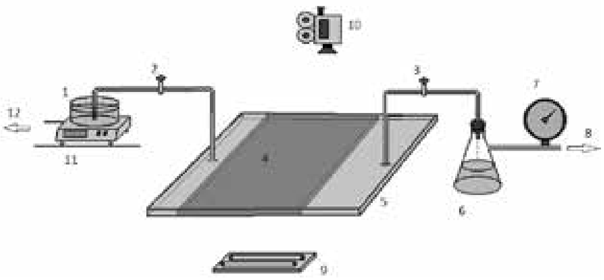


Fig. 1 The experimental setup: 1 - container with aqueous suspension, 2,3 - tubes, 4 - sheet of foam rubber, 5 - cell, 6 - buffer capacity, 7 - gauge, 8 - to the vacuum pump, 9 - backlight, 10 - camera, 11 – weighing-machine, 12 - to the computer interface.

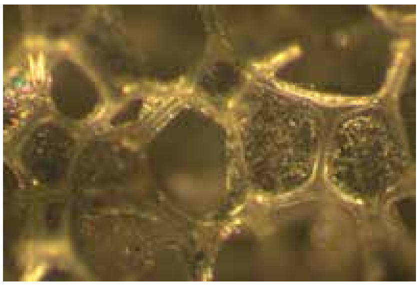


Fig. 2 Foam rubber cells with retained particles: polyurethane fibers diameter - 100 μm, average pore size - 1 mm, average particle size of silicon carbide - 10μm.

The experimental dependences of the filtration rate which is monotonically decreasing with time and the concentration profiles of the particles deposited in the foam rubber at different time were obtained. To describe the pore blocking process the probabilistic-sieve model of microfiltration [1] has been applied, which allowed us to determine physicochemical parameters of non-stationary process of aqueous suspension filtering.

Literature:

1. Filippov A., Starov V., Lloyd D., Chakravarti S., Glaser S. 1994. Sieve Mechanism of Microfiltration. J. of Membrane Sci. 89: 199-213.

Acknowledgements: This work was supported by Russian Foundation for Basic Research (projects # 11-08-01043 and 12-08-01091).

Distribution of Permeation Rates through Nanopores

Sara Marleen Hellenkamp [1]*, Vladislav Krzyzanek [2], Andreas Heuer [1], Monika Schönhoff [1]

[1] – Institute of Physical Chemistry, University of Muenster, Münster, Germany
[2] – Institute of Medical Physics and Biophysics, University of Muenster, Münster, Germany
* - s_hell07@uni-muenster.de

We study the permeation of polymer chains through the nanoporous wall of hollow capsules in dependence on properties of polymers and capsules. The capsules are prepared via Layer-by-Layer coating of silica particles and their walls have a porous structure caused by dissolution of the core. Detailed information about the wall structure, i. e. pore number and size, is available from high resolution scanning electron microscopy (SEM) (Fig. 1) [1].

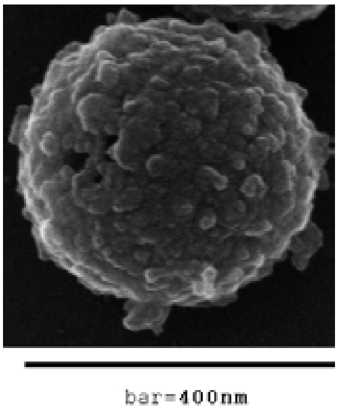


Fig. 1 SEM picture of a freeze-dried polymeric capsule

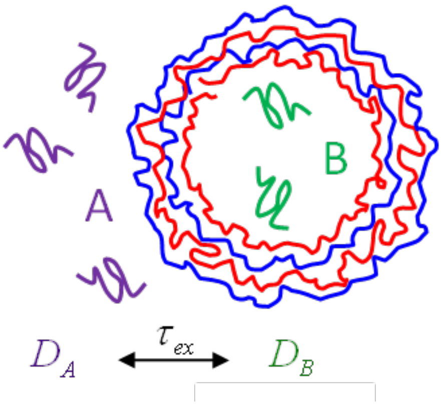


Fig. 1 Schematic illustration of the capsules and probe polymers in two sites

The main focus of this study is the exchange process between free polymers in dispersion (site A) and encapsulated chains (site B) (Fig. 2). With diffusion experiments (Pulsed Field Gradient NMR) we distinguish polymers in either site by their respective diffusion coefficients $D_{A,B}$. This exchange system can be described by the two-site model. Variation of the observation time in the regime of intermediate exchange yields the exchange time t_{ex} of chains through the porous capsule wall. The dependence of t_{ex} on molecular weight M_w has been described by a scaling law: $t_{ex} \sim M_w^n$ [2].

With the information about the capsule wall structure obtained by SEM, we have investigated the effect of the heterogeneity of either the number of pores per capsule or the pore size. The distribution of pore sizes is correlated to a distribution of exchange times. We are able to describe the distribution of exchange times for the first time by varying the measurement window. With simulations of a broad exchange time distribution we could verify this interpretation.

Literature:

1. V. Krzyzanek et al, 2011. Polyelectrolyte multilayer capsules: nanostructure and visualization of nanopores in the wall. Soft Matter. 13: 7034-7041.
2. R. Choudhury et al, 2008. Scaling Law of Poly(ethylene oxide) Chain Permeation through a Nanoporous Wall. J. Phys. Chem. 112: 13245

How Superhydrophobicity Breaks Down

Periklis Papadopoulos[1]*, Lena Mammen[1], Xu Deng[1], and Hans-Jürgen Butt[1]

[1] – *Max Planck Institute for Polymer Research, D-55128 Mainz, Germany*
* - papadopoulos@mpip-mainz.mpg.de

Droplets on superhydrophobic surfaces roll off easily, leaving the surface dry and clean. This remarkable property is due to a surface geometry that favors the entrainment of air cushions beneath the drop, leading to the so-called Cassie state. The Cassie state competes with the Wenzel (impaled) state, in which the liquid fully wets the substrate. Despite the fact that thermodynamically the Wenzel state is often more stable, the geometry imposes an energy barrier that prevents the liquid from wetting the structure. A Cassie-to-Wenzel transition can be triggered by vibrations, impact, rapid deceleration, or evaporation. The transition dynamics is still poorly understood due to difficulties in monitoring the temporal evolution of the air cushion and the liquid–air meniscus between the asperities with sufficient spatial resolution.

Here, we study the Cassie-to-Wenzel transition of water drops evaporating on arrays of hydrophobic micropillars. To understand the underlying processes, we image the impalement dynamics in three dimensions by confocal microscopy (Fig. 1). As evaporation proceeds, the curvature of the drop and the Laplace pressure increase. The three-phase contact line remains pinned until the contact angle reaches the advancing contact angle of the material. Then the water slides down the pillars. Alternatively, at large pillar spacing the curved water surface can touch the bottom of the substrate triggering an instantaneous Cassie-to-Wenzel transition.

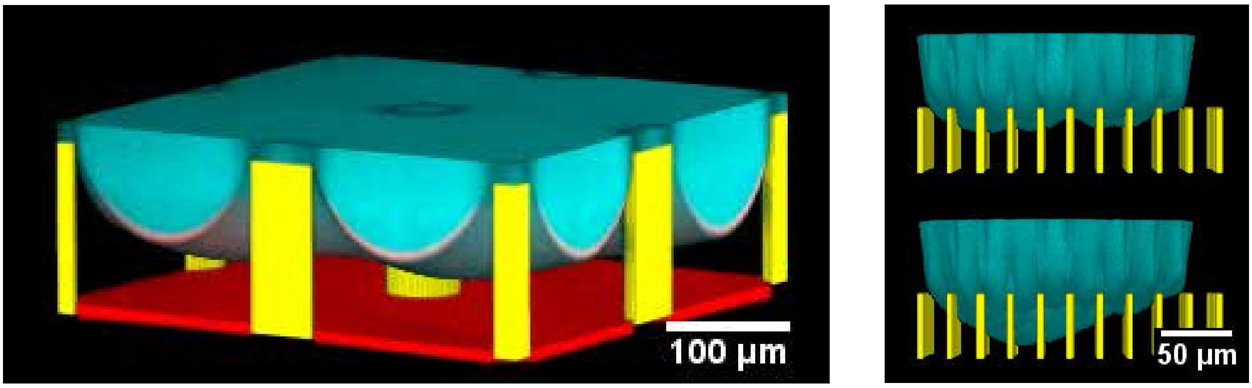


Fig. 1 (Left) A water drop (blue) on an array of pillars (yellow) during the Cassie-to-Wenzel transition. (Right) The 3D images are taken 5 s apart, showing the slow progress of the depinning mode of the wetting transition. The z axis has been magnified by a factor of 10 to show the penetration of the drop more clearly. The actual heights of the pillars are 25 (left) and 5 µm (right).

Literature:

1. Papadopoulos P., *et al.* 2012 Wetting on the microscale: Shape of a liquid drop on a microstructured surface at different length scales. *Langmuir* 28: 8392–8398.
2. Papadopoulos P., Mammen L., Deng X., Vollmer D., Butt H.-J., 2013 How superhydrophobicity breaks down. *Proc. Natl. Acad.Sci. USA* 110: 3254–3258.

Liquid Crystal-Based Emulsions for Synthesis of Spherical and Non-Spherical Particles with Chemical Patches

Frédéric Mondiot, Xiaoguang Wang, and Nicholas L. Abbott*

Department of Chemical and Biological Engineering
University of Wisconsin-Madison
Madison, Wisconsin 53706
USA
* - abbott@engr.wisc.edu

This presentation will describe the use of liquid crystal (LC)-in-water emulsions for the synthesis of either spherical or non-spherical particles with chemically-distinct domains located at the poles of the particles. The approach involves the localization of solid colloids at topological defects that form predictably at surfaces of water-dispersed LC droplets. By polymerizing the LC droplets displaying the colloids at their surface defects, we demonstrate formation of both spherical and, upon extraction of the mesogen, anisotropic composite particles with colloids located at either one or both of the poles. Because the colloids protrude from the surfaces of the particles, they also define organized, chemical patches with functionality controlled by the colloid surface.

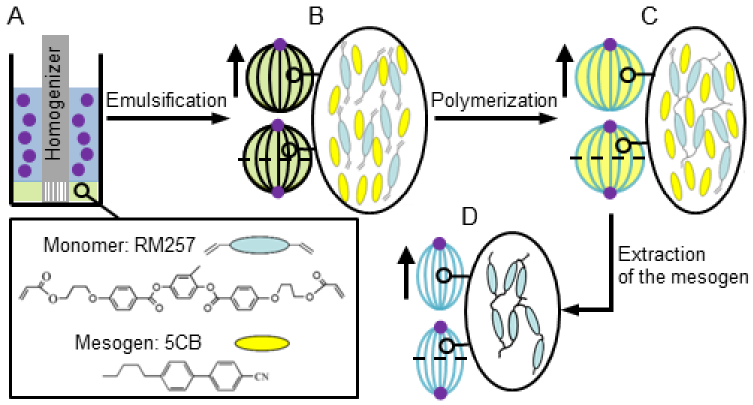


Figure 1: (A) Initial system before emulsification (blue color: aqueous phase; purple spots: colloids). (B) After emulsification, formation of bipolar nematic droplets with either 1 (dipolar symmetry) or 2 colloids (quadrupolar symmetry) located at the poles. (C) After polymerization of the monomer within the droplets, formation of spherical particles with dipolar or quadrupolar symmetry. (D) Upon extraction of the mesogen from the polymerized droplets, formation of anisotropic particles with dipolar or quadrupolar symmetry. The horizontal dashed line indicates a mirror plane in the quadrupolar composite particles.

Literature:

Mondiot, F.; Wang, X.; de Pablo, J.J.; and Abbott N.L., “Liquid Crystal-Based Emulsions for Synthesis of Spherical and Non-Spherical Particles with Chemical Patches, *Journal of American Chemical Society*, DOI 10.1021/ja4022182 (2013).

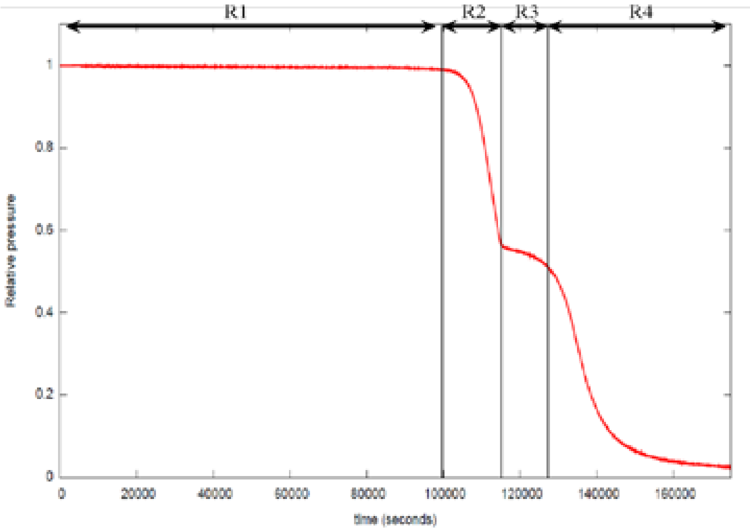
High resolution Liquid Desorption in Drying of Aqueous Suspensions

Renaud Denoyel* and Mickaël Antoni

Aix-Marseille Université, CNRS, MADIREL UMR 7246, 13397 Marseille cedex 20, France
* - renaud.denoyel@univ-amu.fr

Processes where a solid phase is obtained after complete drying of a suspension is a quiet common phenomenon observed in paintings and in industry like for example in the field of ceramics preparation. The final structure of the solid obtained is usually difficult to predict since it depends on many factors among which: chemical composition of the suspension, wetting properties, ambient conditions that are often very difficult to control. Fast drying processes will moreover generate large gradients that will make the control of local parameters, like temperature or heat transfer, even more difficult. It is therefore of importance to try control as much as possible evaporation kinetics. Differential microcalorimetry is a well suited technique to achieve this goal. This technique is indeed adapted to investigate very low flow rates (in the mg/h range) and allows a very fine tuning of both pressure and temperature.

In the present work, the drying of silicon oxide nanoparticle aqueous suspensions is studied using differential microcalorimetry. The activity of water above the drying suspension can be measured and followed in a quasi-equilibrium way as a function of the suspension concentration, going continuously from a state of suspension, where DLVO forces are involved, to that of a porous solid, where capillary forces are involved during the emptying of the pores. Four successive evaporating regimes can be identified in the desorption curve (see graph below). The first one R1, where mass transfer is governed by free water molecules as observable in pure water, corresponds to an increase of suspension concentration at nearly constant pressure. The second regime R2 is a transition between a suspension and a solid network of particles. In R3 relative pressure is governed by evaporation of capillary water and its diffusion within a progressively dense packing silicon oxide colloidal network. Finally in R4, there is no capillary water left to be extracted from this latter and water desorption from silica surface is observed.



Relative pressure as a function of time for a drying concentrated (300 g/L) silicon oxide aqueous suspension.

The time evolution of the relative pressure can be fitted with two hyperbolic tangents that allow the measurement of the characteristic time scales associated to the different evaporative regimes.

“Boat”-like Silica Supraparticles by Ionic Strength Shape Control of Evaporating Droplets

Marcel Sperling[1*], Orlin D. Velev[2] and Michael Gradzielski[1]

[1]– *Stranski Laboratorium Institut für Physikalische und Theoretische Chemie – Stranski LaboratoriumInstitut für Chemie, TU Berlin*
Straße des 17. Juni 124, Berlin, 10623, (Germany)
[2] – *Department of Chemical and Biomolecular Engineering, NC State University*
911 Partners Way, Raleigh, NC 27695-7905, (USA)
* - Marcel.Sperling@gmx.net

Supraparticles made by self-assembly of colloids are considered to offer high potential in terms of controlling structure, shape and functionality in complex colloidal systems. Especially sub-structuring of such particles and the formation of composites has been studied nowadays using materials like silica microspheres and gold nanoparticles [1]. Furthermore they can become functionalized by incorporation of functional colloidal materials and thus provide promising perspectives with respect to (bio-) analytical, medical or catalytic applications.

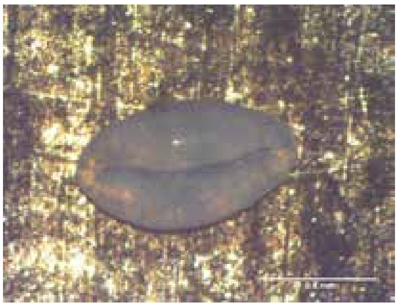


Figure 1. Fumed silica particle dried from suspension on superhydrophobic surface

In our work we concentrate on the defined manipulation of the shape of supraparticles by evaporation induced self-assembly (EISA) of colloidal suspension droplets containing fumed silica (FS) deposited on a superhydrophobic substrate. The controlled manipulation was achieved adjusting the ionic strength of the droplets containing different concentrations of FS by adding NaCl [3]. This led to the formation of anisometric supraparticles (see Figure 1), where the extent of anisometry and the shapes observed strongly depend on the ionic strength. We also propose a likely formation mechanism based on the formation of a dense FS layer at the droplet interface where the FS interactions are tuned by the NaCl concentration. The corresponding systems have been investigated by rheological, AFM, and SEM experiments.

In conclusion we present a very easy applicable and fundamental way to control the overall shape of supraparticles derived from colloidal suspensions containing FS by an easy controllable parameter, i.e., the ionic strength. In addition we could also show that this principle is also applicable for droplets containing additional PS latex microspheres, which indicates general usability of the procedure for preparing composite systems, opening the perspective of creating new types of materials with corresponding functionality.

Literature:

1. Rastogi, V.[1], Garcia, A. A[2]., Marquez, M.[3], Velev, O. D.[4], 2010. Anisotropic Particle Synthesis Inside Droplet Templates on Superhydrophobic Surfaces. Macromol. Rapid Commun. 31: 190—195.

2. Sperling, M[1]., Velev, O.D.[2], Gradzielski, M.[3], submitted

Exothermic pre-ouzo to ouzo transition: consequences on fragrance evaporation

Vera Tchakalova[1*], Thomas Zemb[2] and Daniel Benczédi[1]
[1] – *Firmenich SA, Corporate R&D, B.P. 239, CH-1211 Geneva 8, Switzerland*
[2] – *Institut de Chimie Séparative de Marcoule, UMR5257 CEA/CNRS/UM2/ENSCM, Bat 426, Marcoule, F-30207 Bagnols sur Cèze, France*
* - vera.tchakalova@firmenich.com

An Eau de Toilette (EDT) can be considered as a ternary mixture of volatile molecules, namely ethanol, water and fragrance ingredients. The evaporation kinetic of such a system depends on the composition of the ethanol-water mixture and on the solubility of fragrance ingredients in it. During its evaporation, the composition changes spontaneously and leads to variable concentration ratios between the three components of the system and thus, a variable path in “pre-ouzo” and “ouzo” domains on the ternary phase diagram. This compositional change influences strongly the ability of fragrance ingredients to partition between ethanol and water and so the performance of the EDT.

Early studies [1] of ternary mixtures based on toluene, water and 2-propanol have highlighted the existence of aggregates similar to swollen micelles in a domain of the phase diagram referred to as “pre-Ouzo” region, having well defined spinodal line separating it from the Ouzo-Region [2]. The formation of domains of typical size 2 nm as transient aggregates with same size, but shorter life-time than surfactant based-microemulsions have been confirmed by direct light [3] , X-ray and neutron scattering characterization on absolute scale [4]. The same effect was confirmed with other ternary mixtures in which component 1 and 2 are mutually miscible and component 3 is only miscible in one of them. This holds in an EDT as well, where ethanol and water are mutually miscible but fragrance ingredients are only soluble in ethanol.

The present studies demonstrate that during the EDT evaporation, a transition from unstructured ternary ethanol-rich solutions, to structured water-rich domains takes place, passing through the pre-ouzo and ouzo regions. In the pre-ouzo region, the presence of microemulsions stabilized by a highly cohesive interfacial film made from ethanol and water, encapsulates efficiently the fragrance as measured by on-line analysis of mass loss (TGA) combined to calorimetry (DSC) and gas-chromatography (GC-MS). The transition is accompanied by exothermal DSC peaks, linked to molecular transfer between the water-rich and ethanol-rich coexisting micro-domains separated by an interface and stabilized by the hydration force.

It was furthermore observed that fragrance evaporation is boosted as the water-ethanol ratio is increased. The encapsulation and the boosting effect are general for all perfumery ingredients, independent on their hydrophobicity as defined from water/octanol scale (logP). The present studies are fundamental and they provide new insights on the evaporation of fragrance/flavors in different applications (5). They can be used by perfumers to enhance the performance of their compositions.

Literature:

1. Lund G. and Holt S. L. (1980), "Detergentless water/oil microemulsions: IV. the ternary pseudo-phase diagram for and properties of the system toluene/2-propanol/water." Journal of the American Oil Chemists' Society 57(8): 264-267.
2. Vitale S. A. and Katz J. L.(2003), “Liquid droplet dispersions formed by homogeneous liquid-liquid nucleation: “The Ouzo Effect”, Langmuir, Vol. 19, pp 4105-4110.
3. Klossek ML, Touraud D, Zemb T. and Kunz W. (2012), “Structure and Solubility in Surfactant-Free Microemulsions”, Chemphyschem 13 (18): 4116-9.
4. Zemb Th. *et al.* (2012), “Formation of surfactant-free microemulsions characterized via TOF-SANS” in Proceedings of the 15th International Small-Angle Scattering Conference, Sydney, Australia, 18-23 November 2012, editors Duncan J. McGillivray, Jill Trewhella, Elliot P. Gilbert and Tracey L. Hanley, ANSTO, ISBN 1 921268 15 8
5. Tchakalova V., Zemb T. and Benczédi D (2013), “Exothermic pre-ouzo to ouzo transition: consequences on fragrance evaporation” , (submitted)

Colloid-Electrospinning for Multicompartment Materials

Daniel Crespy*

Max Planck Institute for Polymer Research
* - crespy@mpip-mainz.mpg.de

Electrospinning can be used for the fabrication of fibers from solutions or melts but also from dispersions. This interesting recent variant, called colloid-electrospinning,[1-2] is applied to immobilize and/or assemble nanoparticles into nano- or microfibers, hence yielding multicompartment materials.

We discuss here the preparation and characterization of fibers with solid or liquid nano-compartments obtained by the electrospinning of nanoparticles (Figure 1a) or emulsions. Applications of such materials include the fabrication of anisotropic particles (Figure 1b-c),[3-4] catalysis,[5] and energy conversion.[6]

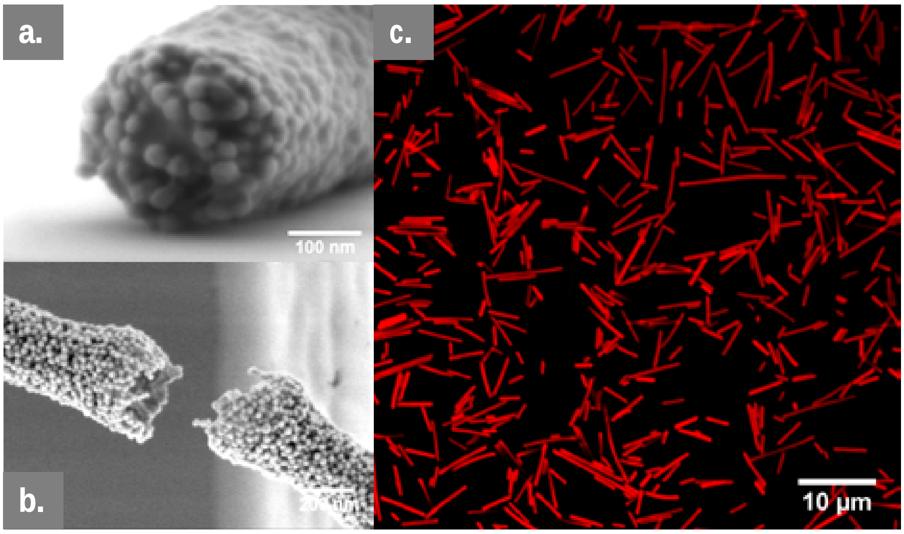


Fig. 1 SEM micrographs of **a:** a typical fiber obtained by colloid-electrospinning with high content of inorganic nanoparticles, **b:** fibers with structural and sacrificial compartments after removal of the latter. **c:** Fluorescent microscopy image of fluorescent silica microrods obtained by the simultaneous electrospinning of structural and sacrificial particular compartments.

Literature:

1. Crespy D., Friedemann, K., Popa A.M. 2012. Macromol. Rapid Commun. 23:1978.
2. Friedemann K., Turshatov A., Landfester K., Crespy D. 2011. Langmuir 27:7132.
3. Herrmann C, Turshatov A, Crespy D. 2012. ACS Macro Lett. 1:907.
4. Friedemann K, Corrales T, Kappl M, Landfester K. 2012. Small 8:144.
5. Horzum N, Munoz-Espi R, Glasser G, Demir M.M., Landfester K, Crespy D. 2012. ACS Appl. Mater. Interf. 4:6338.

6. Wohnhaas, C., Friedemann, K., Busko, D., Landfester, K., Baluschev, S., Crespy, D., Turshatov, A. 2013. ACS Macro Lett. DOI:10.1021/mz400100j