



COST D43 Thematic Symposium

Colloidal Dispersions in Nanoscience
Borovets 14–15 July, 2010



**BOOK
OF ABSTRACTS**



Department of Chemical Engineering
Faculty of Chemistry, Sofia University
Sofia, Bulgaria



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Program

Tuesday, July 13th

14:00 – 20:00 **Registration** *Registration desk in hotel Samokov*

19:00 – 21:00 **Get-together party** *Restaurant of hotel Samokov*

Wednesday, July 14th

7:30 – 19:00 **Registration** *Registration desk in hotel Samokov*

Opening session COST D43 Symposium & Eufoam 2010 Conference; **Hall A (Bulgaria)**
Chair: D. Langevin

8:30 – 8:50 **P. Kralchevsky – Opening**

8:50 – 9:30 **F. Graner**

Plenary lecture: Foams as model systems: of complex fluids, of grain growth, of biological tissues

9:30 – 10:00 **N. Kristen, N. Schelero, R. von Klitzing**

D43-1/IL1: Control of foam film and wetting film stability by addition of (poly)electrolytes: electrostatics vs. ionspecificity

10:00 – 10:30 **S. Hutzler, M.E. Möbius, D. Weaire**

IL2: Foam mechanics (COST P21)

Coffee Break

Session COST D43 Symposium; Chair: B. Lindman **Hall C (Serdika)**

11:00 – 11:30 **Orlin Velev**

D43-2: Programmed Assembly and Manipulation of Complex Particles by Electric Fields

11:30 – 12:00 **Miklós Zrínyi**

D43-3: Colloidal particles that make smart polymer composites moving

12:00 – 12:30 **P.A. Kralchevsky, K.D. Danov, M.P. Boneva, N.C. Christov**

D43-4: Interactions and self-assembly of particles at liquid interfaces – new developments

12:30 – 13:00 **G. Yordanov, C. Dushkin**

D43-5: Nanoprecipitation approach in the preparation of poly(alkylcyanoacrylate) colloidal nanospheres

Lunch

Restaurant of hotel Samokov

Session COST D43 Symposium; Chair: R. von Klitzing **Hall C (Serdika)**

14:30 – 15:00 **B. Lindman, T. Nylander**

D43-6: Polysaccharide-Surfactant Interactions at Interfaces and in Bulk

15:00 – 15:25 **M. Miguel, B. Lindman, R. Dias, D. Costa, C. Moran**

D43-7: Mixtures of DNA with cationic surfactants: Gels, associative phase separation and gel nanoparticles

15:25 – 15:50 **S. Limage, M. Schmitt-Rozières, C. Dominici, J. Krägel, R. Miller, S. Vincent-Bonnieu, M. Antoni**

D43-8: Rheology of surfactant-particle mixtures

Coffee Break

Session COST D43 Symposium; Chair: M. Miguel **Hall C (Serdika)**

16:20 – 16:50 **F. Ravera, L. Liggieri, E. Santini, A. Maestro, R.G. Rubio, G. Loglio, J. Kraegel, D. Grigoriev, R. Miller**

D43-9: Rheological and structural properties of mixed layers of silica nanoparticles plus CTAB at water/air interface

16:50 – 17:20 **K.D. Danov, N.C. Christov, E.S. Basheva, P.A. Kralchevsky, Y. Zeng, R. von Klitzing**

D43-10: Structural forces in liquid films due to entrapped colloidal particles or surfactant micelles: Theory vs. experiment

17:30 – 19:30 **Poster session & light dinner**

Foyer of Hall A (Bulgaria)

Thursday, July 15th

Session COST D43 Symposium & Eufoam 2010 Conference; Chair: L. Ligierra **Hall A (Bulgaria)**

- 9:00 – 9:40 **O. Velev**
Plenary lecture: Foam superstabilization and functionalization by particles with engineered structure and properties
- 9:40 – 10:10 **T. Horozov**
Invited lecture IL6: Solid particles in thin liquid films
- 10:10 – 10:40 **S. Stoyanov, E. Pelan, V.N. Paunov**
Invited lecture IL7: Foams stabilised by shape anisotropic particles

Coffee Break

Session COST D43 Symposium; Chair: M. Zrínyi **Hall C (Serdika)**

- 11:10 – 11:40 **G. Toquer, T. Zemb, D. Shchukin, H. Möhwald**
D43-11: Ionic physisorption on bubbles induced by pulsed ultra-sound
- 11:40 – 12:10 **E. Mileva, D. Arabadzhieva, P. Tchoukov, I. Grozev, B. Soklev, R. Todorov**
D43-12: Impact of Adsorption Layers on Foam Film Drainage Kinetics
- 12:10 – 12:35 **T.D. Gurkov, J. K. Angarska, K. Tachev, W. Gaschler**
D43-13: Statistics of Rupture in Relation to the Stability of Thin Liquid Films with Different Size
- 12:35 – 13:00 **N. Mucic, V. Pradines, V.B. Fainerman, E.V. Aksenenko, J. Krägel, R. Miller**
D43-14: Adsorption of alkyl trimethyl ammonium bromides at the water/air and water/hexane interfaces

Lunch

Restaurant of hotel Samokov

Session COST D43 Symposium; Chair: T. Zemb **Hall C (Serdika)**

- 14:30 – 15:00 **M. Fanun**
D43-15: Properties of microemulsions with mixed nonionic surfactants and citrus oil
- 15:00 – 15:25 **E.D. Tzika, M. Christoforou, S. Pispas, V. Papadimitriou, S.G. Sotiroudis, E. Leontidis, A. Xenakis**
D43-16: Olive oil-based w/o nano-emulsions: a novel biomimetic system for studying oxidative enzymatic reactions
- 15:25 – 15:50 **S. Limage, M. Schmitt, C. Dominici, M. Antoni**
D43-17: From polymorphous to spherical dispersed phase transition in water/oil emulsions

Coffee Break

Session COST D43 Symposium; Chair: O. Velev **Hall C (Serdika)**

- 16:20 – 16:50 **L. Isa, E. Amstad, K. Kumar, M. Textor, E. Reimhult**
D43-18: Assembly of hard sphere and hard core-soft shell nanoparticles at liquid-liquid interfaces for patterning and functional materials
- 16:50 – 17:20 **J. Katrik, R. Škrabana, D. Mislovičová, P. Gemeiner**
D43-19: Interaction of Lectin-Modified Surface with Glycoproteins on Surface Plasmon Resonance Biochip
- 17:20 – 17:30 **P. Kralchevsky**
Closing of the COST D43 Symposium

17:30 – 19:00 **Poster session** *Foyer of Hall A (Bulgaria)*

20:00 – 24:00 **Gala dinner** *Restaurant of hotel Samokov*

Friday, July 16th

Session Eufoam 2010: Modern applications; Chair: Th. Karapantsios

Hall A (Bulgaria)

9:00 – 9:40 **A. Lips**
Plenary lecture: Successes and future challenges for foam science

9:40 – 10:10 **M. Edirisinghe, E. Stride**
Invited lecture IL11: Bubbling, foaming and capsule preparation

Session: Emulsions as bi-liquid foams; Chair: Th. Karapantsios

10:10 – 10:40 **A. Colin**
Invited lecture IL12: Flow of concentrated emulsions

Coffee Break

**Session Eufoam 2010: Foam Stability: Drainage, Coarsening, and Coalescence;
Chair: R. Miller**

Hall A (Bulgaria)

11:10 – 11:40 **R. Krastev**
Invited lecture IL13: Gas permeability of single foam films

11:40 – 12:00 **J. Goyon, F. Bertrand, G. Ovarlez, O. Pitois**
O22: Study of shear induced drainage of foamy emulsions through MRI

12:00 – 12:20 **A. Delbos, O. Pitois, E. Lorenceau, M. Vignes-Adler**
O23: Forced foam flow through a pore

12:20 – 12:40 **B. P. Binks, P. D. I. Fletcher, M. P. Gahagan, E. L. Sharp**
O24: Non-aqueous foams in lubricating oil systems

12:40 – 13:00 **F. Garcia-Moreno, A. Stocco, I. Manke, J. Banhart, D. Langevin**
O25: X-ray tomography of aqueous foams

Lunch

Restaurant of hotel Samokov

Parallel Session Eufoam 2010: Experimental Techniques; Chair: M. Adler

Hall A (Bulgaria)

14:30 – 14:50 **K. Niranjana, C. Jimenez-Junca, J.-C. Gomy, A. Sher**
O26: Non-isothermal destabilization of steam injected milk foams: characterization and interface visualization

14:50 – 15:10 **R.A. Kil, Q.P. Nguyen, W.R. Rossen**
O27: Determining trapped gas in foam in porous media from CT images

15:10 – 15:30 **R.M. Guillermic, M. Erpelding, I. Ben Salem, B. Dollet, J. Crassous, A. Saint-Jalmes**
O28: New experimental results on foam acoustics

15:30 – 15:50 **A. Bretagne, V. Leroy, C. Derec, F. Elias**
O29: Probing foams with ultrasound

**Parallel Session Eufoam 2010: Physical Chemistry of Foams, Thin Liquid Films;
Chair: S. Stoyanov**

Hall B (Rodina)

14:30 – 14:50 **D. Varade, D. Carriere, W. Drenckhan, E. Rio, A. Stocco, D. Langevin**
O30: Superstable foams made from catanionic surfactant mixtures

14:50 – 15:10 **L.N. Arnaudov, S.D. Stoyanov, S.A. Semerdzhiev, M.A. Cohen Stuart**
O31: Highly efficient interface-assisted colloid fabrication

15:10 – 15:30 **C. Stubenrauch**
O32: Mixtures of n-dodecyl- β -D-maltoside and hexaoxyethylene dodecyl ether - surface properties, foam films, and foams

15:30 – 15:50 **T. Gambaryan-Roisman**
O33: Dynamics of free liquid films during formation of polymer foams

Coffee Break

Closing session Eufoam 2010; Chair: M. Adler

Hall A (Bulgaria)

16:20 – 16:50 **L.K. Shrestha, K. Ariga, K. Aramaki**
Invited lecture IL14: Highly stable nonaqueous foams in glycerol-based nonionic surfactant/oil systems

16:50 – 17:10 **N. Denkov**
Closing and presenting next Eufoam 2012 conference

List of Poster presentations

- | | | |
|-----|--|---|
| P1 | J. Chen, R. Vogel, S. Werner, G. Heinrich, D. Clause, <u>V. Dutschk</u> | Influence of the particle type on the rheological behaviour of Pickering emulsions |
| P2 | J. Chen, R. Vogel, G. Petzold, D. Clause, <u>V. Dutschk</u> | Rheological behaviour of aqueous suspo-emulsions stabilized by alumina nanoparticles and emulsifier |
| P3 | <u>Sergio Gómez-Graña</u> , A. Guerrero-Martínez, Luis M. Liz-Marzán | Effect of novel gemini surfactants on the self-assembly of gold nanorods into standing superlattices |
| P4 | <u>Nina V. Kaneva</u> , Ceco D. Dushkin | Photocatalytic activity of nanostructured thin films and powders of ZnO mixed with zinc ferrite(III) |
| P5 | <u>L. Krasteva</u> , K. Papazova, C. Dushkin, D. Dimitrov | Ga- and Cu-doped ZnO thin films synthesised by sol-gel process for sensor applications |
| P6 | <u>Bozhidar I. Stefanov</u> , Ceco D. Dushkin | Novel integrated reactor for tests of the photocatalytic activity of immobilized thin films of TiO ₂ and nickel modified TiO ₂ under UV and visible light |
| P7 | <u>Z. Bedzhova</u> , G. Yordanov, C. Dushkin | Colloidal poly(butylcyanoacrylate) particles prepared by polymerization and nanoprecipitation: a comparative study of methods |
| P8 | <u>P. Vasileva</u> , B. Donkova, C. Dushkin | Synthesis of starch-stabilized silver nanoparticles and their application as a LSPR-based hydrogen peroxide sensor |
| P9 | <u>M. Żubrowska</u> , K. Wojciechowski, W. Wróblewski, R. Krastev | Effect of Type of Anion on the Thickness of Foam and Emulsion films Stabilized with CTAB |
| P10 | <u>A. Sharipova</u> , S. Aidaro-va, N. Mucic, A. Javadi, V. Dutschk, R. Miller | Dynamic and equilibrium interfacial tensions of alkyl sulfates of different alkyl chain lengths at the water/oil interface |
| P11 | K.D. Danov, <u>E.S. Basheva</u> , P.A. Kralchevsky, K.P. Ananthapadmanabhan, A. Lips | Oscillatory-structural and depletion forces due to charged surfactant micelles: theory vs. experiment |
| P12 | <u>E.K. Kostova</u> , T.D. Gurkov, W. Gaschler | Thickening of Polymer-Stabilized Aqueous Dispersions under Compressional Stress |
| P13 | <u>M.P. Boneva</u> , K.D. Danov, N.C. Christov, P.A. Kralchevsky | Attraction between particles at a liquid interface due to the interplay of gravity- and electric-field-induced interfacial deformations |
| P14 | P. Kralchevsky, <u>S.S. Kirkova</u> , K.D. Danov, A.J. Post, K.P. Ananthapadmanabhan | Solubility of fatty acids (C12 – C18) in micellar solutions of anionic and zwitterionic surfactants |
| P15 | <u>K.G. Marinova</u> , R. Stanimirova, M.T. Georgiev, N. Alexandrov, E. Basheva | Co-adsorption in solutions of BSA and β-casein studied by solution exchange experiments with pendant bubbles and thin films |

D43-1

Control of foam film and wetting film stability by addition of (poly)electrolytes: electrostatics vs. ionspecificity

Nora Kristen, Natascha Schelero, Regine v. Klitzing

*Stranski-Laboratorium, Institut für Chemie, TU Berlin, Str. d. 17.Juni 124, D-10623 Berlin, Secr. TC
9, fax: +49 30 31426602, klitzing@mailbox.tu-berlin.de*

The (de)stability and functionality of thin liquid films plays an important role in processes and technical applications like foaming, emulsification and flotation. Within this work the stability of single films is tuned by the addition of different electrolytes and polyelectrolytes. The films are either free-standing (*foam films*) or supported by a solid substrate (*wetting films*) and they are formed from aqueous surfactant solutions. The interactions between film surfaces are determined in a thin film pressure balance (TFPB). By this method equilibrium measurements of a disjoining pressure isotherm (disjoining pressure vs. film thickness) are determined. The disjoining pressure is a quantitative measure for the interactions between the two opposing film interfaces, including repulsive electrostatic, attractive van der Waals and steric contributions [1].

Usually the addition of low molecular salt like NaCl leads to a thinning of the aqueous film due to screening of the electrostatic interactions. But not only the ionic strength, also the type of added ion has a pronounced effect on the film thickness and stability. For instance a “simple” water wetting film becomes thicker and more stable by adding NaI instead of NaF at a fixed ionic strength [2]. It is explained by a stronger adsorption of I⁻ ions at the film surface in comparison to F⁻ ions due to differences in the hydration shell. Similar trends are observed for foam films and wetting films formed from surfactant solutions. Surprisingly, also an SDS film is thicker and more stable after addition of NaI instead of NaF, which means that negatively precharged surfaces can be even more negatively charged by the addition of chaotropic (water breaking) anions.

The addition of polyelectrolytes leads to another effect beside electrostatic screening and ionspecificity: Complexation between the surfactant and the polyelectrolyte at the film surfaces becomes important. For instance, with a cationic surfactant like C_nTAB a film with positively charged surfaces is formed. After addition of polyanions, the surface charge is assumed to be reversed. In both cases, a (thick) Common Black Film (mainly stabilized by electrostatic forces) is formed due to the electrostatic repulsion of the two interfaces [3]. But what happens at the isoelectric point where the surface charge is zero? Is a (thin) Newton Black Film (mainly stabilized by steric forces) formed or does the film break? Results on the stability of films with different polyelectrolyte concentrations are presented. In order to distinguish between hydrophobic and hydrophilic interactions polyelectrolytes of different hydrophobicity are studied. The effect of polymers on surface charge is compared to the influence of their monomers.

An overview on the effect of low molecular electrolytes and polyelectrolytes with respect to electrostatics and ion specificity will be given.

[1] R. v. Klitzing, *Adv. Coll. Interf. Sci.* **2005**, 114/115, 253

[2] K. Ciunel, N. Schelero, R. v. Klitzing, *Faraday Disc.* **2008** 141, published on web.

[3] B. Kolaric, W. Jäger, G. Hedicke, R. v. Klitzing, *J. Phys. Chem. B*, **2003**, 107, 8152.

[4] N. Kristen, V. Simulescu, A. Vüllings, A. Laschewsky, R. Miller, R. v. Klitzing **2009** *J. Phys. Chem. B* 113 7986.

[5] N. Kristen, R. v. Klitzing *Soft Matter* **2010** 6 849.

D43-2

Programmed Assembly and Manipulation of Complex Particles by Electric Fields

Orlin D. Velev

*Department of Chemical and Biomolecular Engineering,
North Carolina State University, Raleigh, NC 27695
odvelev@unity.ncsu.edu; <http://crystal.che.ncsu.edu/>*

We will discuss how external AC fields could be used to assemble and manipulate complex engineered particles on any size scale. Examples of dielectrophoretic manipulation of nanoparticles, microparticles of varying complexity and live cells will be presented. The structures that could be assembled on a chip include microwires from metallic nanoparticles, switchable photonic crystals, and biocomposite "wires" and membranes. We will discuss the interactions leading to the assembly of such structures, ways to simulate the dynamics of the process and the effect of particle size and conductivity on the type of structure obtained. One class of objects of specific interest for field-driven assembly includes Janus and "patchy" metallodielectric particles. We will report how Janus particles consisting of a dielectric hemisphere and a conductive one could be driven by dielectrophoresis with planar electrodes into new types of staggered chains and anisotropic crystals. Patchy metallodielectric particles in AC fields form new types of networks and crystals of unusual symmetry by pre-programmed quadrupolar and hexapolar interactions. Finally, we will discuss how an additional level of complexity can be engineered to turn miniature semiconductor diode "particles" into prototypes of self-propelling micromachines and micropumps. The diodes suspended in water propel themselves electroosmotically when a uniform AC electric field is applied across the container. These "active particles" suggest rudimentary solutions to problems facing self-propelling microdevices, including harvesting power from external sources, internally controlled movement, and potential for a range of additional functions.



D43-3

Colloidal particles that make smart polymer composites moving

Miklós Zrínyi

*Semmelweis University, Faculty of Pharmacy, Department of Pharmaceutics,
H-1092 Budapest, Hőgyes Endre u.7, HUNGARY,
E-mail: mikloszrinyi@gmail.com*

Electric-, and magnetic field sensitive polymer gels and elastomers are soft smart materials whose elastic- and thermodynamic properties are strong function of the field strength imposed upon them. Colloidal (nano-) particles with special electric and magnetic properties are built into flexible polymer matrix. The particles couple the shape of the gel (or elastomer) to the external fields. Shape distortion occurs instantaneously and disappears abruptly when electric- or magnetic field is applied or removed, respectively. Giant deformational effect, field controlled elastic modulus, non-homogeneous deformation and quick response to magnetic- and electric field open new opportunities for using such materials for various applications. The development of smart polymer composites that show spinning in static uniform field will also be presented. The rotating disk acts like micro sized motors with tunable angular frequency.

References:

- [1] Filipcsei G, Csetneki I, Szilágyi A and Zrínyi M: Magnetic Field-responsive Smart Polymer Composites, *Advances in Polymer Science*, Oligomers, Polymer Composites, Molecular Imprinting, Ed. Springer-Verlag Berlin Heidelberg, pp. 137-189 (2007)
- [2] Antal M, Filipcsei G, Zrínyi M., *Composites Science and Technology*, **67** 13, (2007), 2884-2885.

D43-4

Interactions and self-assembly of particles at liquid interfaces – new developments

Peter A. Kralchevsky, Krassimir D. Danov, Mariana P. Boneva and Nikolay C. Christov

*Department of Chemical Engineering, Faculty of Chemistry, Sofia University,
BG-1164 Sofia, Bulgaria; Email: pk@lcpe.uni-sofia.bg*

The attachment of a particle to the boundary between two fluid phases is usually accompanied by interfacial deformation near the particle. The overlap of such two deformations gives rise to lateral capillary interaction between the particles. As a rule, the lateral capillary force between similar particles is attractive, brings about particle aggregation, and plays an important role in the production of various two-dimensional structures.¹ The liquid interface around an adsorbed colloidal particle can be undulated because of roughness or heterogeneity of the particle surface, or due to the fact that the particle has non-spherical (e.g. ellipsoidal or polyhedral) shape. In such case, the meniscus around the particle can be expanded in Fourier series, which is equivalent to a superposition of *capillary multipoles*, viz. capillary charges, dipoles, quadrupoles, etc. We derived convenient asymptotic formulas for the force and energy of interaction between capillary multipoles of arbitrary orders.² Furthermore, we established that for *uniform* distribution of the surface charges, the electrocapillary attraction is weaker than the electrostatic repulsion so that the net force is repulsive. The derived analytical expressions for the electrocapillary and electro-dipping forces provide a simple and convenient way for their estimation.³ If the surface-charge distribution is *anisotropic*, it induces a saddle-shaped deformation in the liquid interface around each particle. This deformation, which is equivalent to a capillary quadrupole, decays relatively slow. Its interference with the gravity-induced isotropic meniscus around the other particle gives rise to a long-range attractive capillary force, $F \sim 1/L^3$ (L – interparticle distance). The obtained agreement between the experimental and theoretical curves indicates that the experimentally observed strong attraction can be explained as a hybrid interaction between gravity-induced “capillary charges” and electric-field-induced “capillary quadrupoles”.⁴

1. P.A. Kralchevsky, K.D. Danov, Interactions between particles at a fluid interface, In: *Nanoscience: Colloidal and Interfacial Aspects*, V. M. Starov, Ed.; Taylor & Francis, New York, 2010; Chapter 15.

2. K.D. Danov, P.A. Kralchevsky, Capillary forces between particles at a liquid interface: General theoretical approach and interactions between capillary multipoles, *Adv. Colloid Interface Sci.* **154** (2010) 91–103.

3. K.D. Danov, P.A. Kralchevsky, Interaction between like-charged particles at a liquid interface: Electrostatic repulsion vs. electrocapillary attraction, *J. Colloid Interface Sci.* **345** (2010) 505–514.

4. M.P. Boneva, K.D. Danov, N.C. Christov, P.A. Kralchevsky, Attraction between particles at a liquid interface due to the interplay of gravity- and electric-field-induced interfacial deformations, *Langmuir* **25** (2009) 9129–9139.

D43-5

Nanoprecipitation approach in the preparation of poly(alkylcyanoacrylate) colloidal nanospheres

G. Yordanov, C. Dushkin

*Laboratory of Nanoparticle Science and Technology, Faculty of Chemistry, University of Sofia “St. Kliment Ohridski”, 1 “James Bourchier” Blvd., 1164 Sofia, Bulgaria
Email: chem_gbg@yahoo.com*

Colloidal nanospheres of poly(alkylcyanoacrylate) are one of the most perspective drug carriers for treatment of cancer, intracellular infections and other severe diseases [1-3]. Since their first appearance in 1979 [1], these nanospheres have been prepared by the emulsion polymerization method using alkylcyanoacrylate monomers. This method has some drawbacks, such as poor control of the molecular weight of formed polymer and particle size distribution, as well as using acidic polymerization medium, in which some drugs may be unstable. Also, the high chemical reactivity of alkylcyanoacrylate monomers may lead to deactivation of sensitive drugs in the course of polymerization. With the aim to resolve some of these problems, we present here the utilization of nanoprecipitation approach for the preparation of pure and drug-loaded colloidal nanospheres of poly(alkylcyanoacrylate). This method is based on the preliminary synthesis of a polymer, which is further dissolved in water-miscible organic solvent and then added to a water solution of a stabilizer to form colloidal nanospheres of average sizes 200-300 nm. This approach is suitable for the entrapment of hydrophobic drugs inside the poly(alkylcyanoacrylate) nanospheres. Since no chemical reactions take place during the nanosphere formation, this approach is suitable also for the entrapment of chemically unstable and highly reactive drug molecules. Moreover, the nanoprecipitation approach has the advantage that the characteristics of used polymers do not depend on the conditions of nanosphere preparation.

References:

- [1] P. Couvreur, B. Kante, M. Roland, P. Guiot, P. Bauduin, P. Speiser, *J Pharm Pharmacol* **31** (1979) 331-332.
- [2] C. Vauthier, C. Dubernet, E. Fattal, H. Pinto-Alphandary, P. Couvreur, *Adv Drug Deliv Rev* **55** (2003) 519-548.
- [3] H. Pinto-Alphandary, A. Andremont, P. Couvreur, *Int J Antimicrob Agents* **13** (2000) 155-168.

D43-6

Polysaccharide-Surfactant Interactions at Interfaces and in Bulk

Björn Lindman and Tommy Nylander

Physical Chemistry 1, Lund University, PO Box 124, 221 00 Lund, Sweden

Bjorn.lindman@fkem1.lu.se

Mixed polysaccharide-surfactant systems have broad applications. A review of the underlying polymer-surfactant association in bulk is given. While ionic surfactants bind broadly to polysaccharides, nonionics only do so if the polymer has a lower polarity and can interact by hydrophobic interactions. Water-soluble polysaccharides, which have hydrophobic groups, form physical cross-links, hence their important use as thickeners. The rheological behaviour is strongly influenced by various cosolutes; especially strong effects are due to surfactants and both a decrease and an increase in viscosity can occur. This can be referred to mixed aggregate phenomenon and a simple model is presented. When the polysaccharide-surfactant interactions are particularly strong, an associative phase separation can occur; this and other types of phase separation phenomena are described. Furthermore, the behavior of these mixed systems on surfaces is discussed. In particular, we consider the adsorption of mixtures of ionic polysaccharides and oppositely charged surfactants on polar and nonpolar surfaces. Depending on concentration, an ionic surfactant can either induce additional polyion adsorption or induce desorption. Kinetic control of adsorption and, in particular, desorption is typical. Important consequences of this include an increased adsorption on rinsing and path dependent adsorbed layers.

D43-7

Mixtures of DNA with cationic surfactants: Gels, associative phase separation and gel nanoparticles

Maria Miguel, Björn Lindman, Rita Dias, Diana Costa, and Carmen Moran

Department of Chemistry, Coimbra University, Coimbra, PORTUGAL

** e-mail: mgmiguel@ci.uc.pt*

Keywords: DNA, surfactants, gels, gel particles, phase separation

Cationic polymers and surfactants are efficient in compacting DNA and can also be efficient transfection agents. These systems are also characterized by a strong associative phase separation. We describe the preparation of covalent DNA gels and describe their swelling-deswelling behaviour. It is found that covalent gels offer novel opportunities for monitoring DNA-cosolute interactions. Based on the associative phase separation, the preparation of novel DNA particles by mixing DNA and surfactant solutions can be achieved. The properties and DNA release characteristics of these particles are also described. A local phase separation in covalent gels can lead the formation of a surface phase, a “skin”. The different types of studies are performed for both double- and single-stranded DNA. Throughout, a stronger interaction is observed with denatured DNA. On the basis of these results and other observations it is found useful to view DNA as an amphiphilic polymer self-assembling by hydrophobic interactions.

D43-8

Rheology of surfactant-particle mixtures

S. Limage^(a), M. Schmitt-Rozières^(a), C. Dominici^(b), J. Krägel^(c), R. Miller^(c), S. Vincent-Bonnieu^(d), M. Antoni^(a)

^(a) Institut des Sciences Moléculaires de Marseille UMR CNRS 6263

^(b) Centre Pluridisciplinaire de Microscopie Electronique et de Microanalyse, Marseille

^(c) Max Planck Institute of Colloids and Interfaces - Potsdam-Golm - Germany

^(d) European Space Agency, Noordwijk

This work is the continuation of a study concerning solid-stabilized water-in-paraffin emulsions, for which the dispersed phase is composed of CTAB and silica nanoparticles [1]. Observations of these emulsions through optical tomographic microscopy have highlighted the existence of a transition in the shape of the droplets, from spherical to polymorphous [2]. Scanning electron microscopy investigation of these emulsions revealed that this droplets deformation origins in the formation of a microstructure [3] bridging the droplet from part to part, as shown on figure 1.

The aim of the present work is to study bulk rheology properties of the dispersed phase only, in order to underline a possible network of silica nanoparticles. To carry out these measurements, a double gap concentric cylinder is used. Oscillatory measurements are performed.

The results have evidenced significant modification of the rheological behavior depending on the ratio of surfactant and nanoparticles concentrations [4]. A domain where the mixtures behave like visco-elastic media shows up. Outside this domain, mixtures have viscous properties. The changes in the bulk rheology characteristics are related to an organization of the nanoparticles generated by synergistic effects between surfactant and nanoparticles.

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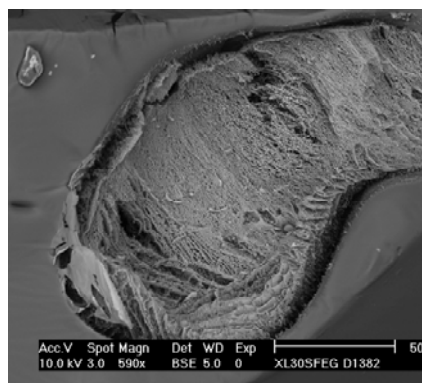


Figure 1: SEM picture of a droplet of W/O emulsion. The dispersed phase is composed of 0.05g/L CTAB and 25g/L SiO₂.

D43-9

Rheological and structural properties of mixed layers of silica nanoparticles plus CTAB at water/air interface

F. Ravera¹, L. Liggieri¹, E. Santini¹, A. Maestro², R. G. Rubio², G. Loglio³

J. Kraegel⁴, D. Grigoriev⁴, R. Miller⁴

¹*CNR-Institute for Energetics and Interphases, Genoa, Italy*

²*Department of Physical-Chemistry, Universidad Complutense, Madrid, Spain*

³*University of Florence, 50019 Sesto Fiorentino (Firenze), Italy*

⁴*MPI for Colloids and Interfaces, Potsdam-Golm, Germany*

Email: f.ravera@ge.ieni.cnr.it

Composite systems of nanoparticles and surfactants are increasingly investigated in relation to potentialities in foam technology because of their effectiveness in controlling the bubble coalescence and the lamellae stability. In this context, the interaction between particles and fluid interfaces is studied also concerning the effect on interfacial tensions and dilational rheology.

Dispersions of nanometric colloidal systems in association to a cationic surfactant, CTAB, have been investigated in the last years as model systems. In fact, as CTAB adsorbs to a large extent on the silica particle surface, it is possible to obtain different degrees of particle hydrophobicity by tuning the ratio between CTAB and silica content. According with previous works [1, 2], the transfer/attachment of nanoparticles to fluid interfaces, driven by particle hydrophobicity, may have an effect on interfacial tension and dilational rheology.

Results are here presented for this system at the water/air interface. For interfacial properties' characterisation different techniques have been adopted: drop/bubble profile analysis, capillary pressure tensiometry and capillary waves. In this way a quite broad frequency range has been accessed, from 10⁻² Hz to 103 Hz, allowing for a better understanding of the dynamic mechanisms governing such composite interfacial layers. The tensiometric techniques have been associated to an experimental study using the Brewster Angle Microscopy which provided interesting information about the formation of non-regular structures at water/air surface during compression and expansion cycles and the influence of the hydrophobicity grade of the particles on the area - surface pressure isotherm acquired during these cycles.

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D43-10

Structural forces in liquid films due to entrapped colloidal particles or surfactant micelles: Theory vs. experiment

Krassimir D. Danov,¹ Nikolay C. Christov,¹ Elka S. Basheva,¹ Peter A. Kralchevsky,¹

Yan Zeng,² and Regine von Klitzing²

¹*Department of Chemical Engineering, Faculty of Chemistry, Sofia University,
BG-1164 Sofia, Bulgaria*

²*Stranski-Laboratorium für Physikalische und Theoretische Chemie, Technische Universität Berlin, D-10623 Berlin, Germany
Email: kd@lcpe.uni-sofia.bg*

We carried out experiments with films formed from aqueous solutions of two nonionic surfactants, Brij 35 and Tween 20, which contain spherical micelles of diameters in the range 7–9 nm. From the measured contact angles, we determined the micelle aggregation number and volume fraction. In addition, from the measured disjoining-pressure isotherms we determined the micelle diameter.¹ By colloidal-probe atomic-force microscope (CP-AFM), we measured the oscillatory-structural surface force.² The latter force is due to the layer-by-layer expulsion of the micelles from the liquid film. The experimental data agree very well with the theoretical predictions for hard-sphere fluids. While the experiment gives parts of the stable branches of the force curve, the theoretical model allows reconstruction of the full oscillatory curve. In the case of Brij 35, at concentrations < 150 mM spherical micelles are present and the oscillation period is close to the micelle diameter, slightly decreasing with the rise of concentration. In the case of Tween 20, the force oscillations are almost suppressed, which implies that the micelles of this surfactant are labile and are demolished by the hydrodynamic shear stresses due to the colloidal-probe motion. The comparison of the results for the two surfactants demonstrates that in some cases the micelles can be destroyed by the CP-AFM, but in other cases they can be stable and behave as rigid particles. This behavior correlates with the characteristic times of the slow micellar relaxation process for these surfactants.² We investigated also the predictions of different quantitative criteria for stability-instability transitions, having in mind that the oscillatory forces exhibit both maxima, which play the role of barriers to coagulation, and minima that could produce flocculation or coalescence in colloidal dispersions (emulsions, foams, suspensions).¹

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D43-11

Ionic physisorption on bubbles induced by pulsed ultra-sound

Guillaume Toquer,¹ Thomas Zemb,^{1,2} Dmitry Shchukin,² Helmut Möhwald²

¹*Institut de Chimie Séparative de Marcoule, UMR5257, 30207 Bagnols-sur-Cèze, France,*

²*Max Planck Institute for Colloids and Interfaces, 14424 Potsdam, Germany.*

E-mail: thomas.zemb@icsm.fr

Ion flotation processes involves the use of bubbles in order to separate ionic species from a mixed solution. Bubble interfaces let to assume null curvature at the molecular scale, whose selective ion adsorption might be more easily investigated than with liquid-liquid extraction. In contrast to a classical flotation set-up, where bubbles are introduced via a glass frit, we use here a controlled sono-device generating cavitation bubbles which are initially absolutely clean. The advantage is to be faster with a small device. The liquid phase resulting from the coalescence of the overflowing foam is enriched in some ions versus the initial brine. We show here that this effect follows the Hofmeister series and can be attributed to a weak adsorption of hydrated ions at the surfactant-water interface. The selectivity of alkali metals physisorbed at interfaces is analysed through the concentrations of competing ions remaining in solution by inductively coupled plasma optical emission spectrometry. Cationic selectivity, which is independent of the method for obtaining foam, is discussed via the Gibbs free energy difference for bulk to hydrated surfactant monolayer. Relative values of effective adsorption energies are determined versus sodium ions taken as reference and correspond to 1-3% of the total hydration free energy.

D43-12

Impact of Adsorption Layers on Foam Film Drainage Kinetics

E. Mileva, D. Arabadzhieva,

P. Tchoukov, I. Grozev, B. Soklev, R. Todorov

Institute of Physical Chemistry, Bulgarian Academy of Sciences;

Email: mileva@ipc.bas.bg

Aqueous solutions of various ionic and nonionic amphiphilic substances are extensively studied via combined application of profile analysis tensiometry and microinterferometric thin liquid film instrumentation. The impact of adsorption layers is traced for concentrations two orders of magnitude lower than CMC (premicellar solutions) to about an order of magnitude above CMC (micellar solutions). The systematic investigation of the drainage of foam films obtained from these solutions show that the dependencies of basic kinetic parameters of the films on the amphiphilic concentration go in synchrony with the changes in the adsorption layer properties. In the low-concentration range the presence of smaller crumbly aggregates (premicelles) is detected, which plays a significant role for the kinetic stability of the films. In the high-concentration domain the micellar entities affect mainly the stability of the thin liquid films.

The importance of the described trend of research is related to providing better insight into the initial stages of self-assembling phenomena and into the factors that determine the drainage and the stability of thin liquid films. The results have implications for the correct prediction and understanding of the properties and the behaviour of foam systems.

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D43-13

Statistics of rupture in relation to the stability of thin liquid films with different size

T. D. Gurkov¹, J. K. Angarska², K. Tachev², W. Gaschler³

¹Department of Chemical Engineering, Faculty of Chemistry, University of Sofia, Bulgaria

²Faculty of Natural Sciences, University of Shumen, 9712 Shumen, Bulgaria

³BASF SE, 67056 Ludwigshafen am Rhein, Germany

E-mail: tg@lcpe.uni-sofia.bg

We study the stability and the thinning behavior of foam films in the presence of ionic surfactants (Dowfax, abietic acid) and polymer (cationic starch). Using the method of capillary cell at low pressures (20-50 Pa), combined with interference microscopy, we measured the film thickness vs. time, the critical thickness of rupture, and the lifetime of films with different sizes. The film behavior is characterized by two separate stages: at first, there is a hydrodynamic thinning without rupture; afterwards, film rupture occurs as a stochastic process. The measured lifetimes in an ensemble of films are scattered in a certain range. We found that the statistical behavior of the rupture process is well described by a specific distribution, which resembles the Gaussian curve. By means of theoretical considerations, this distribution is related to the probability for film rupture as a result of fluctuations. The relevant parameters of the distribution (mathematical expectation, standard deviation of the lifetime, etc.) are obtained by calculation. Fitting of experimental data for the film statistics is performed (Fig. 1). This permits one to find the average lifetime at the stochastic stage; thus, thinning and rupture are distinguished. The size dependence of the overall lifetime is interpreted in view of these two stages; the critical thickness was also taken into account. The rate of film thinning is discussed in relation with the degree of interfacial mobility and the film size. This work may be relevant to understanding the stability of fluid dispersions in dependence of the particle size.

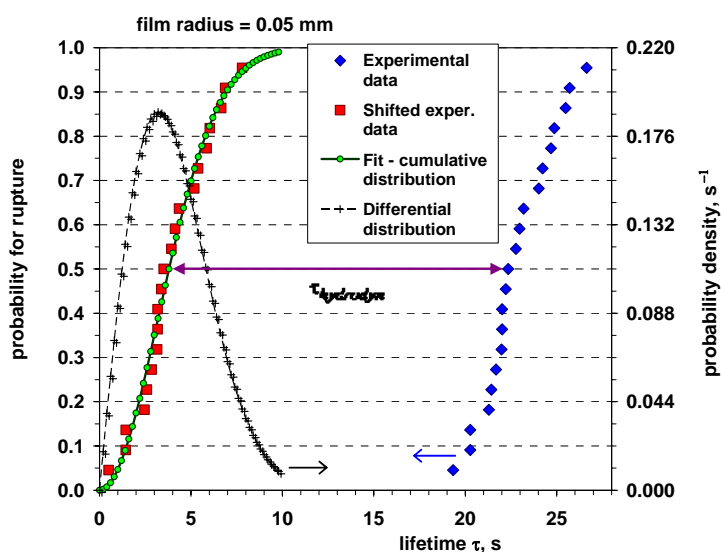


Fig. 1. Thin liquid film statistics.

D43-14

Adsorption of alkyl trimethyl ammonium bromides at the water/air and water/hexane interfaces

N. Mucic¹, V. Pradines^{1,2}, V.B. Fainerman³, E.V. Aksenenko⁴, J. Krägel¹ and R. Miller¹

¹ Max Planck Institute für Kolloid- und Grenzflächenforschung, 14424 Postdam, Germany

² Laboratoire des IMRCP, 31062 Toulouse, France

³ Medical University Donetsk, 16 Ilych Avenue, 83003 Donetsk, Ukraine⁴ Institute of Colloid Chemistry of Water, 42 Vernadsky Avenue, 03680 Kiev, Ukraine

Email: Mucic@mpikg.mpg.de

Surface and interfacial tension have been measured at the water/air and water/hexane interfaces for a series of alkyl trimethyl ammonium bromides (C_nTAB) of different chain length (C₁₀, C₁₂, C₁₄ and C₁₆) by using drop and bubble profile analysis tensiometry (PAT-1, SINTERFACE) [1]. The surface/interfacial tension isotherms are discussed on the basis of different adsorption models taking into account the average activity of all ions present in solution. We used the classical Frumkin model and also a modified one with consideration of the intrinsic compressibility [2]. The adsorbed amount and the molar area of C_nTAB at the water/hexane interface are functions of the chain length, as it was proposed recently for the water/air interface [3]. The present alkane molecules at the water/oil interface are incorporated in the surfactant layer and appear as a kind of competitive adsorption for the short chain surfactants (C₁₀ and C₁₂) while for the longer ones (C₁₄ and C₁₆), the attraction interactions between the hydrophobic chains of the adsorbed surfactant are strong enough to replace the solvent molecules from the interface. At low surface pressure the adsorption behaviour at the water/hexane interface shows peculiarities not observed at the water/air interface.

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D43-15

Properties of microemulsions with mixed nonionic surfactants and citrus oil

Monzer Fanun

Colloids and Surfaces Research Laboratory, Al-Quds University, P.O. Box 51000

East Jerusalem, Palestine

Email: Fanunm@gmail.com

Water/propylene glycol/sucrose laurate/ ethoxylated mono-di-glyceride/citrus oil microemulsion systems were formulated and characterized using electrical conductivity, dynamic viscosity, dynamic light scattering, small angle X-ray scattering, and cryogenic transmission electron microscopy. The solubilization capacity of water in the oil is dependent on the surfactants mixing ratio (w/w). Static percolation phenomena were observed in these systems, and the water volume fraction percolation threshold was determined. The activation energy of conductive flow depends on the surfactants mixing ratio. The hydrodynamic diameter of the diluted microemulsions increases with the increase in temperature. The periodicity and the correlation length of the microemulsions increase with the increase in the aqueous phase content. Cryo-TEM images of the oil-in-water microemulsions revealed the presence of spheroidal droplets of up to 10 nm diameter. It is suggested that a progressive transformation of the water-in-oil to bicontinuous and inversion to oil-in-water microemulsions occurs upon dilution with water.

D43-16

Olive oil-based w/o nano-emulsions: a novel biomimetic system for studying oxidative enzymatic reactions

Evangelia D. Tzika,¹ Maria Christoforou,³ Stergios Pispas,² Vassiliki Papadimitriou,¹ S. G. Sotiroudis,¹ Epameinondas Leontidis,³ and Aris Xenakis¹

¹*Institute of Biological Research & Biotechnology, National Hellenic Research Foundation, 48 Vas. Constantinou Avenue, 11635 Athens, Greece*

²*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vas. Constantinou Avenue, 11635 Athens, Greece*

³*Department of Chemistry, University of Cyprus, PO Box 20537, 1678 Nicosia, Cyprus*
Email: vpapa@eie.gr

Virgin olive oil (VOO) can be considered a fine emulsion of a small quantity of water dispersed in a large quantity of triglycerides, stabilized by various endogenous ionic and nonionic amphiphilic components. Water-in-oil (w/o) nano-emulsions, composed of olive oil as the continuous oil phase, have been successfully used as model biomimetic media to carry out enzymatic reactions that may naturally occur in olive oil since detectable amounts of lipoxygenase, polyphenoloxidase and peroxidase activities have been detected in olive oil samples.

Oxidative enzymatic reactions using horseradish peroxidase (HRP) were carried out in w/o nano-emulsions composed of olive oil/lecithin/1-propanol/water. The substrates used (gallic acid, octyl gallate and ABTS) span a range of hydrophobicities and possible locations in the nano-emulsion system. HRP reactivity in these systems with reference to the substrate hydrophobicity is examined. The nature of the enzyme microenvironments was examined using Dynamic Light Scattering (DLS) and Differential Scanning Calorimetry (DSC), while the location of various enzymatic substrates in the microemulsion phase was assessed by solubility measurements and by taking pressure-area isotherms of mixed monolayers of the substrates with dipalmitoyl-phosphatidylcholine (DPPC), which is a major constituent of lecithin.

D43-17

From polymorphous to spherical dispersed phase transition in water/oil emulsions

S. Limage, M. Schmitt, C. Dominici, M. Antoni

Université Paul CEZANNE, Centre Scientifique de St Jérôme, 1339, Marseille, France

Surfactants, polymers, proteins and their mixtures can be used to stabilize foams and emulsions. Since more than one hundred years it is also known that very small (micro- and nanometer sized) particles can act as emulsion stabilizers [1]. Recent investigations reported about colloidal silica dispersions with different amounts of CTAB to tune the hydrophobicity of the silica nano-particles [2,3]. One aim of these studies is to understand the effect of silica particles on the stability of diluted water-in-paraffin oil emulsions and to report about topological transition in the geometry of the dispersed phase droplets. Optical Scanning Tomography and Scanning Electron Microscopy investigations were carried out with different CTAB/silica particle mixtures [3,4]. They evidenced a transition in the shape of the droplets at a critical CTAB/silica particle ratio that is generated by the existence of microstructures. The aim of this presentation is to present the changes in this transition when adding non ionic soluble surfactant in the continuous phase.

Optical Scanning Tomography is used [5] to characterize the properties of dilute water in paraffin oil emulsions. The dispersed phase is an aqueous mixture of CTAB and silica nanoparticles while the continuous one contains non ionic surfactant (SPAN 80). A flow of one hundred grey level images are obtained to analyse each scanning shot of the considered emulsions with a precision of 1 μm . The role of SPAN80 in the geometry of the dispersed phase droplets is investigated. Depending on the concentration of CTAB, silica nanoparticles and SPAN80, a transition occurs in their geometry that changes from polymorphous to spherically when increasing SPAN concentration. This transition is controlled by the ratio $Q = [\text{CTAB}]/[\text{SPAN}]$ and is described using an identification procedure of the topology of the grey level contours of the images [3]. The precise influence of nanoparticles, CTAB and SPAN concentrations on the critical mixing ratio is determined. The transition in the shape of the droplets occurs for critical values of Q that do not strongly depend of the silica particles concentration when [CTAB] is small. For large values, a sharp increase in the critical ratio is evidenced.

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D43-18

Assembly of hard sphere and hard core-soft shell nanoparticles at liquid-liquid interfaces for patterning and functional materials

L. Isa, E. Amstad, K. Kumar, M. Textor, E. Reimhult*Department of Materials, ETH Zurich, Zurich, Switzerland**Email: erik.reimhult@mat.ethz.ch*

Self-assembly of nanometer-sized colloids at liquid-liquid interfaces is a process with huge potential for the fabrication of controlled two-dimensional structures and patterns as well as “nanomaterials”. This is due to three key factors: a) the particles are trapped at the interface, but b) retain lateral mobility and c) exhibit specific interactions. We have recently explored both how the oil-water interface can be used for unprecedented control of the assembly of colloidal masks for low-cost nanolithography and how tailored core-shell nanoparticles (NPs) with functional cores can be assembled at such interfaces. In the first area we will show how self-assembly at the liquid-liquid interface can be used for the deposition of non-close packed crystalline arrays of NPs for lithographic masks. Our approach allows us to control the spacing of particles in a wide range; we have demonstrated reproducible and homogeneous patterns with spacing between 3 to 20 particle diameters using colloids from 40 to 500 nm over mm² areas. The deposited patterns are then used as masks for the fabrication of substrates for biosensing.

While hard-shell NPs have been probed in the assembly at the oil-water interface the detailed assembly, its relation to particle chemical and physical properties and the resulting super-structure have only recently begun to be addressed. If one aims to build membrane materials which respond to external stimuli it is desirable to combine the unique properties of NPs to interact with optic, electric and magnetic fields with the multi-faceted and large structural response of polymers. To control the resulting structure of such hybrid materials the interaction between the two has to be stable and well controlled. We have recently developed a new anchor chemistry based on nitrocatechols to create ultra-stable, individually stabilized, superparamagnetic iron oxide nanoparticles (SPIONs) [1] and extended this approach to include a variety of magnetite core and polymer shell sizes as well as a large variation in shell physical and chemical properties. The result is a core-shell NP toolbox where we, e.g., can tailor core and shell size independently in the few nanometer range. We will demonstrate how the stable, well characterized properties of these NPs result in rich assembly behaviour at the oil-water interface as well as demonstrate a difference in bulk and interfacial core-shell NP stability [2]. The combination of designed SPIONs and tailored liquid-liquid interface assembly opens a perspective on design of membranes with magnetically controlled permeability.

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D43-19

Interaction of Lectin-Modified Surface with Glycoproteins on Surface Plasmon Resonance Biochip

Jaroslav Katrlík¹, Rostislav Škrabana², Danica Mislovičová¹, Peter Gemeiner¹

¹ Department of Glycobiotechnology, Institute of Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 38 Bratislava, Slovakia

² Institute of Neuroimmunology, Slovak Academy of Sciences, Dúbravská cesta 9, SK-84510 Bratislava, Slovakia

Email: katrlik@yahoo.com

Optical lectin biochips in combination with microfluidic surface plasmon resonance (SPR) was used for study of interaction of selected glycoproteins containing α -D-mannose structures with lectins concanavalin A (ConA), Lens culinaris agglutinin (LCA) and Pisum sativum agglutinin (PSA) specific for α -D-mannose. Lectin biochips were prepared by covalent immobilization on flat carboxymethylated gold surface with final lectin surface concentration 0,15 – 0,35 ng/mm². Both measurement as well as regeneration conditions were optimized. The determined dissociation constants of lectin-glycoprotein interactions were in range 10⁻⁵ - 10⁻⁷ mol/l.

D43-P1

Influence of the particle type on the rheological behaviour of Pickering emulsions

J. Chen¹, R. Vogel¹, S. Werner², G. Heinrich¹, D. Clause³, V. Dutschk^{*1,4}

¹*Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*

²*Max Rubner-Institut, Bundesforschungsinstitut für Ernährung und Lebensmittel, Institut für Lebensmittel- und Verfahrenstechnik, Karlsruhe, Germany*

³*Département Génie Chimique, Génie des procédés industriels, Université de Technologie, Compiègne, France*

⁴*EFSM group, Faculty for Engineering Technology, University of Twente, Enschede, The Netherlands*

In order to get a better understanding of potential relationships among the microstructure and stability of Pickering emulsions, rheological studies were performed using differently modified dispersible colloidal Boehmite alumina nanoparticles.

Steady state flow measurements and dynamic (oscillatory) rheological measurements on two different emulsion systems – water-in-oil (W/O) and oil-in-water (O/W) – were carried out in linear and non-linear regime. Rheological investigations were performed at different storage time.

DSC results, optical microscopic images, TEM images of these emulsion systems were additionally analysed in respect to reveal the emulsions type and their microstructure.

Pickering emulsion stabilized by rather hydrophilic particles exhibited inhomogeneous structure and exhibited relative large yield stresses and thixotropic flow behavior indicating a formation of a three-dimensional network.

Emulsion stabilized by rather hydrophobic particles with a contact angle around 90° was revealed to be an oil-in-water-in-oil multiple emulsion. The emulsion was homogenous and showed thixotropy indicating the presence of a three dimensional network, however, a phase separation slightly occurred in the storage time evaluated meaning that the stability of this emulsion need be improved.

D43-P2

Rheological behaviour of aqueous suspo-emulsions stabilized by alumina nanoparticles and emulsifier

J. Chen¹, R. Vogel¹, G. Petzold¹, D. Clause², V. Dutschk^{*1,3}

¹*Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*

²*Département Génie Chimique, Génie des procédés industriels, Université de Technologie, Compiègne, France*

³*EFSM group, Faculty for Engineering Technology, University of Twente, Enschede, The Netherlands*

This paper focuses on the study of the rheological behavior of emulsions stabilized by differently modified dispersible colloidal Boehmite alumina nanoparticles with a non-ionic emulsifier. A polyglycerin ester of condensed castor oil fatty acids was used as an emulsifier.

Steady state flow measurements and dynamic (oscillatory) rheological measurements on two different emulsion systems – water-in-oil (W/O) and oil-in-water (O/W) – were carried out in linear and non-linear regime.

In addition, the DSC results and optical microscopic images of these emulsion systems were discussed in order to get a better understanding of relationships between rheology, microstructure and stability of the emulsion systems.

Emulsion stabilized by a combination of rather hydrophilic particles and emulsifier was an O/W emulsion. The addition of emulsifier improved the stability, however, did not show a significant influence on the flow behavior of the emulsion. The emulsion showed a complicated flow behavior, i.e. sometimes it exhibited thixotropy or antithixotropy and sometimes both of them.

Emulsion stabilized by rather hydrophobic particles and emulsifier was a W/O. This emulsion was very homogenous and exhibited very weak thixotropy. Dynamic measurements showed that G' was almost equal to G'' and both parameters were frequency-dependent indicating a viscous liquid-like system with little if any network structure.

The addition of emulsifier, the rather elastic solid-like structure of emulsion can be changed into viscous-liquid-like structure.

D43-P3

Effect of Novel Gemini Surfactants on the Self-Assembly of Gold Nanorods into Standing Superlattices

Sergio Gómez-Graña, Andrés Guerrero-Martínez,* Luis M. Liz-Marzán*

Colloid Chemistry Group. Departamento de Química-Física, Facultad de Ciencias, Universidad de Vigo, Vigo 36310 (Spain)
Email: segomez@uvigo.es

In recent years, substantial progress has been made regarding the synthesis of gold nanoparticles, motivated by the potential of nanoscale design to produce a diverse range of topologies with tailored plasmon resonances. Among them, gold nanorods (GNRs) have emerged as precisely plasmonic tunable anisotropic particles by controlling their aspect ratio, and GNR self-assembly into extended nanostructured arrays is a potential starting point for the amplification of the properties of individual components [1].

The self-assembly strategy applied to GNR building blocks is a potential starting point for the amplification of the individual plasmonic properties and/or the generation of new optical characteristics unique to the ensemble [2]. Recently, we have described the use of cationic gemini surfactants as efficient promoters of side-by-side GNRs self-assembly [3]. These double-chain surfactants, made of two hydrophobic tails and two hydrophilic headgroups linked by a spacer chain, register exceptional amphiphilic properties in comparison to conventional surfactants such as low critical micelle concentrations, strong efficiencies in decreasing water surface tension, and high adsorptivities on hydrophilic solid surfaces. All these properties make them excellent scaffolds for surfactant bilayer design of stable GNRs in water, which appears to be a key point for the formation of micron-sized superlattices of standing GNRs upon drop casting on different surfaces.

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D43-P4

**Photocatalytic activity of nanostructured thin films and powders of ZnO
mixed with zinc ferrite(III)**

Nina V. Kaneva, Ceco D. Dushkin*

*Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic
Chemistry, Faculty of Chemistry, University of Sofia, 1164 Sofia, Bulgaria*

**Corresponding author. Tel.: +359-2-8161-387;*

Fax: +359-2-962-5438

E-mail address: nhtd@wmail.chem.uni-sofia.bg (C. Dushkin)

Nanostructured thin films and powders of ZnO mixed with zinc ferrite(III), ZnFe_2O_4 , are prepared, characterized and tested as for the first time photocatalysts in aqueous solutions of dye. The decolorization kinetics of malachite green dye upon UV-light illumination is studied as a model system. The ZnO and ZnO/ ZnFe_2O_4 powders are first tested as a photocatalyst in the form of slurry. Then thin films of the same materials of the powders are prepared from polyethylene glycol/alcohol dispersions on glass substrates using the dip coating technique. The films are characterized by means of scanning electron microscopy, infrared spectroscopy and X-ray diffraction before and after annealing. Their photocatalytic activity is investigated and compared with that of the respective powders. The initial concentration of malachite green, the amount of catalyst, and the molar ratio of $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ are varied during the experiments. It is found that increasing of the amount of ZnFe_2O_4 with respect to ZnO lowers the photocatalytic activity in comparison with pure ZnO for both films and powders. The obtained results are the preliminary step toward the use of mixed ZnO/ ZnFe_2O_4 photocatalysts for the purification of water under white light illumination.

D43-P5

Ga- and Cu-doped ZnO thin films synthesised by sol-gel process for sensor applications

L. Krasteva, K. Papazova, C. Dushkin, D. Dimitrov

Laboratory of Nanoparticle Science and Technology, Faculty of Chemistry, University of Sofia, Sofia 1164, Bulgaria

Email: lussyk@hotmail.com (L. Krasteva)

During the last decade, a renewed interest has been devoted to ZnO-based materials owing to their applications in many different fields and sensors among them. As opposed to traditional deposition by physical methods, the sol-gel process offers a simple low-cost and highly controlled way for ZnO films deposition. Zinc-acetate dihydrate dissolved in 2-methoxyethanol is used as the inorganic precursor; monoethanolamine acts as a base and as a complexing agent at the same time. The precursors for the dopants are GaCl₃ and Cu-acetate, respectively. The films are obtained by dip coating on different glass or ceramic substrates. X-Ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to characterise the films. The effects of dopant concentration, type of substrate and the deposition conditions are studied. All the obtained films are polycrystalline, homogeneous and with clearly defined layer structure. The electron conductivity of the films is measured in the medium of ethanol vapours by means of a newly constructed experimental system. The presence of dopants in ZnO films alters the conductance thus affecting the gas sensitivity.

D43-P6

Novel Integrated Reactor for Tests of the Photocatalytic Activity of Immobilized Thin Films of TiO₂ and Nickel Modified TiO₂ under UV and Visible Light

Bozhidar I. Stefanov, Ceco D. Dushkin*

Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry, University of Sofia, Sofia 1164, Bulgaria

**Corresponding author. Tel.: +359-2-8161-387; Fax: +359-2-962-5438*

E-mail address: nhtd@wmail.chem.uni-sofia.bg (C. Dushkin)

We present the development and use of an inexpensive and yet fully integrated, liquid phase, batch reactor for testing the activity of immobilized, thin films, photocatalysts. The reactor is constructed around an encapsulated custom-built glass cuvette containing the catalyst sample and the solution of the model organic contaminant. The irradiation is provided by a tubular UV lamp or a white LED array fitted to the cuvette lid, while the solution is stirred by a standard magnetic stirring bar, turned around by a motor mounted inside the electronics block beneath the reactor. The concentration of contaminant is followed in-situ by an integrated photometric system using a low-power laser. In the current paper, the reactor is used to determine the effect of the incident radiation on the apparent rate constants of degradation of an organic dye (methylene blue) via thin-films of pure and modified commercial photocatalyst (Degussa P25) exhibiting visible light activity. The catalyst samples were prepared by dip-coating from a TiO₂ particle suspension to yield thin films with varied thickness/load. The suspensions for coating are made from the pure TiO₂ catalyst and also with 1 mol.% Ni(II) added. X-ray diffraction and scanning-electron microscopy are used to characterize the coatings. The catalyst performance under various UV and visible light illumination is estimated using the novel reactor system for just 1 h of experimental time: 30 min of dark adsorption of dye and 30 min of irradiation. Kinetic curves are drawn from the data and the apparent rate constants of photocatalysis are computed using a model for the space distribution of light intensity in the reactor. Film samples of different thickness of photocatalyst are examined at a good coincidence between theory and experiment. The reactor is suitable for investigation of the intrinsic properties of processes utilizing not only titanium dioxide, but also other common photocatalysts and a variety of organic pollutants.

D43-P7

Colloidal poly(butylcyanoacrylate) particles prepared by polymerization and nanoprecipitation: a comparative study of methods

Z. Bedzhova, G. Yordanov*, C. Dushkin

Laboratory of Nanoparticle Science and Technology, Faculty of Chemistry, University of Sofia "St. Kliment Ohridski", 1 "James Bourchier" Blvd., 1164 Sofia, Bulgaria

*Email: chem_gbg@yahoo.com

The poly(butylcyanoacrylate) colloidal particles are one of the best candidates for drug delivery applications [1,2]. Such colloids can be prepared by two different methods – emulsion polymerization and nanoprecipitation. In the emulsion polymerization, the monomer is polymerized in acidic aqueous medium in the presence of colloidal stabilizers. Although this method is the most popular one, it has a number of limitations. On the other hand, the use of a pre-synthesized polymer in the nanoprecipitation approach allows the successful incorporation of chemically sensitive drugs in the polymer particles. Despite of its potential advantages, there are no systematic investigations on the preparation of colloidal poly(butylcyanoacrylate) particles by the nanoprecipitation method. This report presents a comparative investigation of poly(butylcyanoacrylate) particles prepared by both emulsion polymerization and nanoprecipitation methods. The as-obtained particles are characterized for particle size distribution, zeta potential and molecular weight of polymer. The effects of different factors are studied. The colloidal particles, obtained by the two different methods, possess remarkably different characteristics, which clearly demonstrate the advantages of nanoprecipitation.

Acknowledgement:

The financial support of the Scientific Research Fund of the University of Sofia (Project 148/15.04.2010) is greatly acknowledged.

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- [2] J. Nicolas, P. Couvreur, *Wiley Interdiscipl. Rev. Nanomed. Nanobiotechnol.* **1** (2009) 111–127.

D43-P8

Synthesis of Starch-Stabilized Silver Nanoparticles and Their Application as a LSPR-Based Hydrogen Peroxide Sensor

P. Vasileva, B. Donkova, C. Dushkin

*Laboratory of Nanoparticle Science and Technology,
Department of General and Inorganic Chemistry,
Faculty of Chemistry, University of Sofia "St. Kl. Ohridski", Bulgaria
Email: pvasileva@chem.uni-sofia.bg*

In recent years, hydrogen peroxide (H₂O₂) has attracted more attentions in biochemical fields owing to its important role in biological systems. Most of the H₂O₂ biosensors developed till date are based on enzymes and proteins causing them to have a limited lifetime. Moreover, complex procedures are followed for sensor fabrication. Silver nanoparticles are well known for their strong interactions with light through the resonant excitations of the collective oscillations of the conduction electrons on the particles, the so-called local surface plasmon resonances (LSPR). Recent studies on hydrogen peroxide sensor based on silver nanoparticles inspired us to synthesise and examine the activity of obtained dispersion of silver nanoparticles for the preparation, characterization and calibration of LSPR-based hydrogen peroxide sensor. In this work, we developed a green synthetic procedure to obtain aqueous colloidal dispersion of starch-stabilized silver nanoparticles via reduction of silver nitrate by D-glucose under ultrasound irradiation. UV–vis spectroscopy, transmission electron microscopy and X-ray diffraction were used to give a complete characterization of the silver nanoparticles. The nanoparticles are quasi-spherical, with narrow size distribution and mean diameter of 14.4±3.3 nm. It was found that starch-stabilized silver nanoparticles obtained in our synthesis have a LSPR band at 408 nm, high colloidal stability and moderate catalytic ability for the decomposition of hydrogen peroxide. Furthermore, hydrogen peroxide induces the degradation of highly clustered silver nanoparticles by the decomposition of hydrogen peroxide. Hence, a remarkable change in the LSPR absorbance strength, which depends on the H₂O₂ concentration, was observed. As a result, the yellow colour of the silver nanoparticle–starch solution was gradually changed to transparent colour. On the basis of the abovementioned mechanism, the characterization of the LSPR-based optical enzyme biosensor was carried out. This LSPR-based optical sensor has very good sensitivity and linear response over the wide concentration range of 10⁻¹ - 10⁻⁷ mol/L H₂O₂. Furthermore, the detection limit of this sensor was found to be 1 μM, which was lower than certain enzyme-based biosensors. Therefore, this LSPR-based optical sensor for hydrogen peroxide has the potential to be applied in determination of other reactive oxygen species.

D43-P9

Effect of Type of Anion on the Thickness of Foam and Emulsion films Stabilized with CTAB

M. Żubrowska¹, K. Wojciechowski¹, W. Wróblewski¹, R. Krastev²

¹*Department of Chemistry, Warsaw University of Technology, Warsaw, Poland*

²*Natural and Medical Science Institute, Reutlingen, Germany*

Email: marta.kucharek@ch.pw.edu.pl

Quaternary ammonium salts are commonly used both in industry and for fundamental research in colloid and interface science. Highly lipophilic quaternary ammonium salts are also used as electroactive components in membrane-based ion-selective electrodes (ISE). Our previous research using CTAB (hexadecyltrimethylammonium bromide) as model quaternary ammonium salt in the presence of different inorganic anions, shows that adsorption processes at the interface may play a significant role in the mechanism of electrical signal generation of ISE. The concentration and nature of anions present in solution strongly influence surface concentrations of CTA⁺ and anions, thus altering surface potential (Hofmeister effect). Surface potentials calculated from interfacial tension data at water-air and toluene-air interfaces using STDE model of Warszynski et al. agree well with the results obtained with ISE [1].

In this contribution we present further experimental studies aiming at confirmation of the role of specific adsorption of inorganic anions in generation of electrical potential difference across the interface. We measured the thickness and velocity of film thinning of foam and emulsion films using Thin Film Pressure Balance technique (TFPB) [2]. The films were stabilized with CTAB in the presence of inorganic 1:1 electrolytes (NaBr, NaNO₃, NaF, NaClO₄). The water-air and water-toluene interfaces are expected to be positively charged by adsorption of CTA⁺ ions. This results in strong double layer repulsion between the surfaces and formation of thick films. Addition of salts decreases the repulsion according to the DLVO theory and the film thickness decreases. We observed that the change in the film thickness depends not only on the concentration of the salt in the film forming solution, but also on the type of anion.

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D43-P10

Dynamic and equilibrium interfacial tensions of alkyl sulfates of different alkyl chain lengths at the water/oil interface

A. Sharipova^{1,2}, S. Aidarova¹, N. Mucic², A. Javadi², V. Dutschk³ and R. Miller²

¹ *International Postgraduate institute “Excellence Polytech” of Kazakh National Technical University, Almaty, Kazakhstan*

² *Max-Planck institute of Colloids and Interfaces, Potsdam, Germany*

³ *University of Twente, Enschede, The Netherlands*

Ionic surfactants play an important role in many processes in practice, such as formation of emulsions and foams, flotation, wetting etc. Among ionic surfactants the sodium dodecyl sulfate (SDS) is the most famous. Among all surfactants it is most frequently studied one at the water/air interface, and there are many investigations of dynamic and equilibrium surface tensions at the aqueous solution/air interface. However, so far there are only very few interfacial tension studies of alkyl sulfates at water/oil interfaces.

In the present work the dynamic interfacial tensions of alkyl sulfates with different alkyl chain lengths (from C10 to C16) at the water/hexane interface were studied by Profile Analysis Tensiometry (PAT-1, SINTERFACE Technologies, Germany). With increasing surfactants concentration the equilibrium interfacial tension values are reached faster and faster, as expected from a diffusion controlled adsorption kinetics. The interfacial tension isotherms are analysed with different thermodynamic models. The location of the isotherms are shifted to lower concentrations with increasing alkyl chain length, however, the Traube factor is much smaller than observed for the water/air interface.

D43-P11

Oscillatory-structural and depletion forces due to charged surfactant micelles: theory vs. experiment

Krassimir D. Danov,^a Elka S. Basheva,^a Peter A. Kralchevsky,^a

Kavssery P. Ananthapadmanabhan,^b Alex Lips^b

Department of Chemical Engineering, Faculty of Chemistry, Sofia University ; 1, J. Bourchier Blvd., 1164 Sofia, Bulgaria ; Fax : +359-2-9625643, Email : kd@lcpe.uni-sofia.bg

^b*Unilever Research and Development, Trumbull, Connecticut 06611, USA*

The progress in the field of oscillatory structural forces (OSF) is impeded by the fact that it is not easy to achieve comparison of theory and experiment. We propose a relatively simple (but quantitatively accurate) semiempirical approach. We carried out experiments with films formed from solutions of ionic surfactants (see e.g. Fig. 1), which contain micelles of hydrodynamic diameter 5–6 nm. By measuring disjoining pressure isotherms and contact angles, we determine the micelle charge and aggregation number. In other words, we demonstrate that the liquid-film measurements can give information about the micelles, which is analogous to that obtainable by dynamic and static light scattering [1]. Furthermore, we investigate the predictions of different quantitative criteria for stability-instability transitions, having in mind that the oscillatory forces exhibit maxima, which play the role of barriers to coagulation, and minima, that could produce flocculation or coalescence in colloidal dispersions. Stability/instability diagrams are constructed that show the values of the micelle volume fraction, at which the oscillatory barriers can prevent the particles from coming into close contact, or at which a strong flocculation in the depletion minimum (or a weak flocculation in the first oscillatory minimum) could be observed. Thus, we demonstrate that the measurements of oscillatory structural forces combined with a (quantitative and convenient for applications) theory, can be rather informative. The results could help to understand the stability of products that contain small charged particles: in cosmetics, house-hold detergency, food and paper industries, etc.

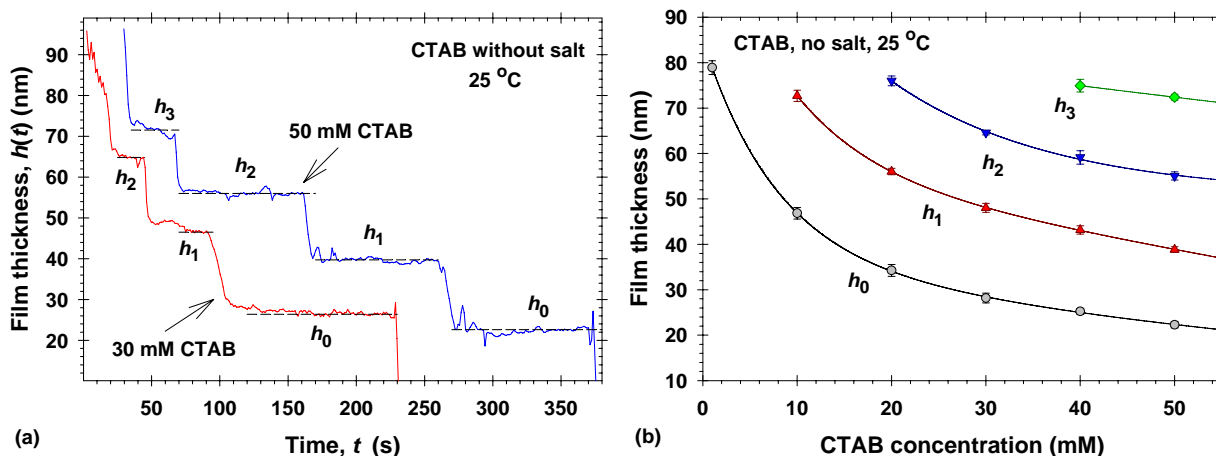


Fig. 1. (a) Stepwise thinning of foam films formed from solutions of the cationic surfactant CTAB. (b) Plot of the thickness, h_n , of a film containing n micelle layers vs. the CTAB concentration.

Reference:

[1] E. S. Basheva, P. A. Kralchevsky, K. D. Danov, K. P. Ananthapadmanabhan, A. Lips, *Phys. Chem. Chem. Phys.* 2007, 9, 5183–5198.

D43-P12

Thickening of Polymer-Stabilized Aqueous Dispersions under Compressional Stress

E. K. Kostova,¹ T. D. Gurkov,¹ W. Gaschler²

¹*Department of Chemical Engineering, Faculty of Chemistry, University of Sofia,
James Bourchier Avenue 1, Sofia 1164, Bulgaria*

²*BASF SE, 67056 Ludwigshafen am Rhein, Germany*

E-mail: ek@lcpe.uni-sofia.bg

We study the creaming stability of aqueous dispersions whose particles consist of solid fatty alcohols, and have sizes of a few μm . High stability against thickening is provided by polymers (polyacrylamide, PAM, and polyacrylic acid, PAA). Centrifugation is performed in multiple steps, each one with fixed time duration, in two ways: either with increasing rotation speed, or at one and the same rotation speed. The volume fraction of particles in the cream, ϕ , is determined from the amount of separated cream. The pressure dependence of ϕ (Fig. 1) gives information about the structure of the compressed dispersion. The change of ϕ as a function of time, at fixed acceleration, shows a typical linear dependence. The latter is related to a viscous-type drainage of liquid from the structure. The slope of the $\phi(t)$ plot increases with the rotation speed, in agreement with the expected trend, $d\phi/dt \propto \omega^2$. Information about the extent of irreversible flocculation is gained from experiments with redispersion of the cream and subsequent centrifugation, combined with microscopic observations. We discuss the influence of different factors on the creaming stability, such as the concentration of the polymers, the ratio between PAM and PAA, presence of small hydrophilic particles (Bentonite), etc.

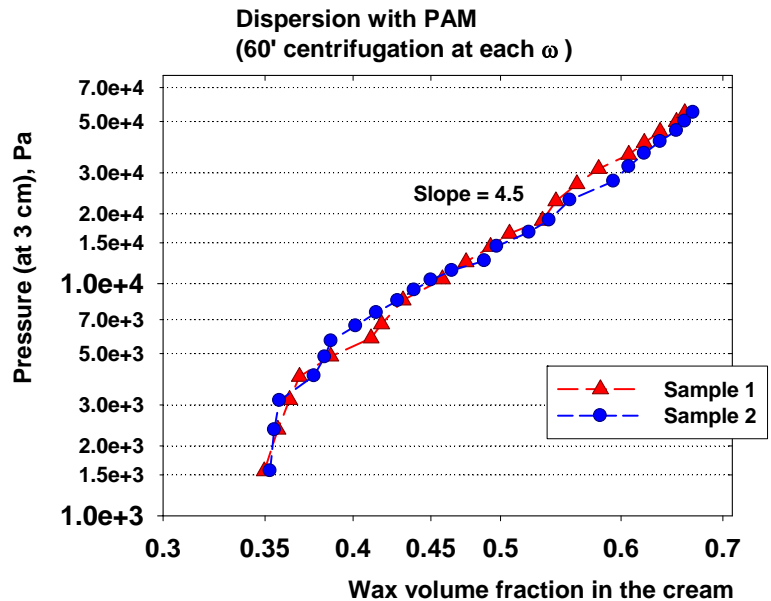


Fig. 1. Centrifugation in steps of increasing acceleration.

D43-P13

Attraction between particles at a liquid interface due to the interplay of gravity- and electric-field-induced interfacial deformations

Mariana P. Boneva, Krassimir D. Danov, Nikolay C. Christov, and Peter A. Kralchevsky

Department of Chemical Engineering, Faculty of Chemistry, Sofia University ; 1, J. Bourchier Blvd., 1164 Sofia, Bulgaria ; Fax : +359-2-9625643, Email : mb@lcpe.uni-sofia.bg

We established that the attraction between electrically charged particles attached to a water/tetradecane interface is stronger than predicted on the basis of the gravity-induced lateral capillary force.¹ The investigated particles are hydrophobized glass spheres of radii between 240 and 320 μm . Their weight is large enough to deform the liquid interface. The interfacial deformation is considerably greater for charged particles because of the electro-dipping force that pushes the particles toward the water phase. By independent experiments with particles placed between two electrodes, we confirmed the presence of electric charges at the particle/tetradecane interface. The theoretical analysis shows that if the distribution of these surface charges is isotropic, the meniscus produced by the particle electric field decays too fast with distance and cannot explain the experimental observations. However, if the surface-charge distribution is anisotropic (Fig. 1), it induces a saddle-shaped deformation in the liquid interface around each particle. This deformation, which is equivalent to a capillary quadrupole, decays relatively slow. Its interference with the gravity-induced isotropic meniscus around the other particle gives rise to a long-range attractive capillary force, $F \sim 1/L^3$ (L – interparticle distance). The obtained agreement between the experimental and theoretical curves, and the reasonable values of the parameters determined from the fits, indicate that the observed stronger attraction in the investigated system can be really explained as a hybrid interaction between gravity-induced “capillary charges” and electric-field-induced “capillary quadrupoles”.²

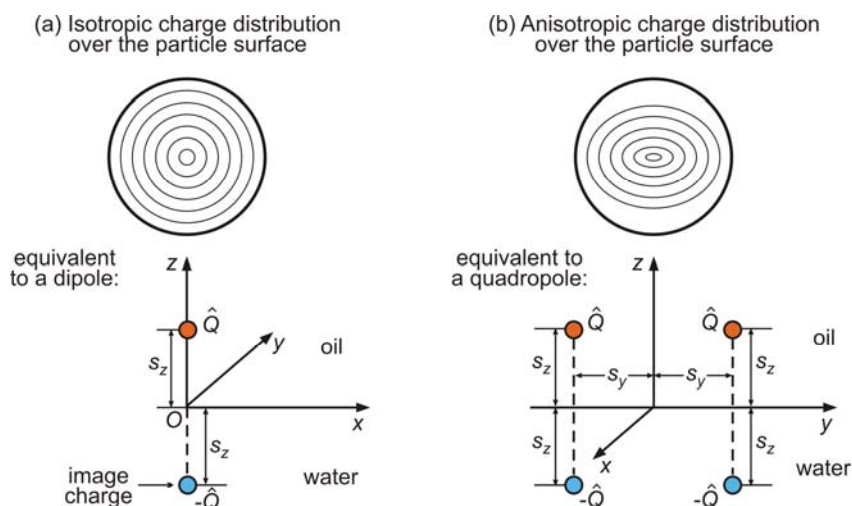


Fig. 1. Modelling of the electric field of a charged particle at an oil/water interface. (a) Isotropic surface charges – the particle can be modelled as a dipole. (b) Anisotropic surface charges – the particle can be modelled as a pair of two parallel dipoles.

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[2] M.P. Boneva, K.D. Danov, N.C. Christov, P.A. Kralchevsky, *Langmuir* 25 (2009) 9129.

D43-P14

Solubility of fatty acids (C₁₂ – C₁₈) in micellar solutions of anionic and zwitterionic surfactants

Peter A. Kralchevsky,^{1*} Sylvia S. Kirkova,¹ Krassimir D. Danov,¹ Albert J. Post,²
and Kavssery P. Ananthapadmanabhan²

¹ Department of Chemical Engineering, Faculty of Chemistry, Sofia University,
1 James Bourchier Blvd., 1164 Sofia, Bulgaria

² Unilever Research and Development, 40 Merritt Blvd., Trumbull, Connecticut 06611, USA

*e-mail: pk@lcpe.uni-sofia.bg

The fatty acids have found applications in shower gel and body wash products. Acids of chain length from C₁₂ to C₁₈ have a rather low solubility in water. However, they form mixed micelles with conventional surfactants, i.e. they become soluble in water in micellar form. The experiments indicate that a solubility limit for the fatty acids in the micellar solutions exists. Above this limit, the acids form crystallites [1,2], instead of increasing their molar fraction in the mixed micelles. The aim of our study is to determine the solubility limits of four fatty acids (C₁₂, C₁₄, C₁₆ and C₁₈) in micellar solutions of anionic and zwitterionic surfactants. For this goal, experimental data for two surfactants at four different temperatures have been obtained. Furthermore, the data were interpreted by means of a thermodynamic model of mixed micelles. The theoretical analysis indicates that the raise of the molar fraction of the fatty acid in the micelles leads to increase in the bulk concentration of free fatty-acid monomers (Fig. 1). When the latter concentration reaches the solubility limit of the respective acid in water, it forms crystallites, and the solutions become turbid. The obtained results for the solubilization constants of fatty acids in the micelles allow one to predict the micellar composition and the critical micellization concentration at different lengths of the paraffin chain and at various temperatures.

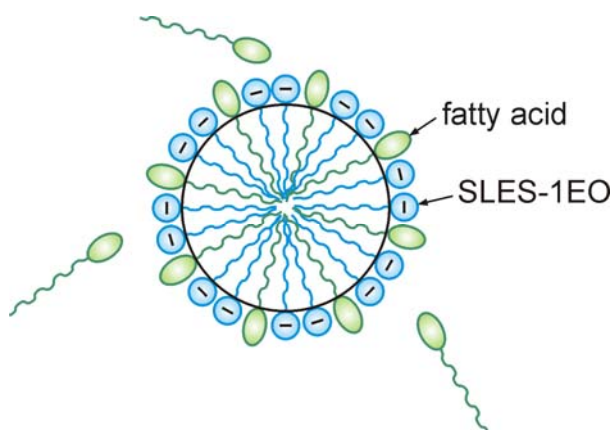


Fig. 1. Sketch of a mixed micelle of anionic surfactant and fatty acid.

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D43-P15

Co-adsorption in solutions of BSA and β -casein studied by solution exchange experiments with pendant bubbles and thin films

K.G. Marinova, R. Stanimirova, M.T. Georgiev, N. Alexandrov, E. Basheva

Dept. Chem. Eng., Chem. Fac., Sofia University, 1 James Bourchier Ave., 1164 Sofia, Bulgaria

Email: km@lcpe.uni-sofia.bg

The protein stabilizers used for aerated and emulsified foods usually represent mixtures of components with different molecular weight and structure (e.g. the different caseins and whey proteins in the milk). We present systematic experimental study of the mixed adsorption layers formed by the disordered protein β -casein and the globular one BSA (bovine serum albumin).

Set of complementary experimental methods is used to determine the properties of the adsorption layers and to analyse qualitatively the impact of the individual components: Phase exchange experiments with (i) rising bubbles to determine the surface tension by the ADSA method, combined with surface dilatational rheology measurements; and (ii) thin films observations for determination of the film thickness and stability. Mixed systems were compared to the single ones in simple foam tests as well.

Three types of mixed adsorption layers and thin films were compared: (i) formed from mixed β -casein-BSA solutions; (ii) β -casein initially adsorbed and afterwards washed and added BSA; (iii) BSA initially adsorbed and afterwards washed and added β -casein. Comparison was made with surfaces and films of the single proteins. The results showed that the surface tension and disjoining pressure in the films was determined by the casein molecules. However the surface dilatational moduli of the layers were comparable to those of the BSA layers. We hypothesize that the mixed layers of BSA and β -casein have lower surface coverage than in presence of β -casein only, which results in lower films and foams stability, respectively.

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