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Group of Complex Fluid Physics

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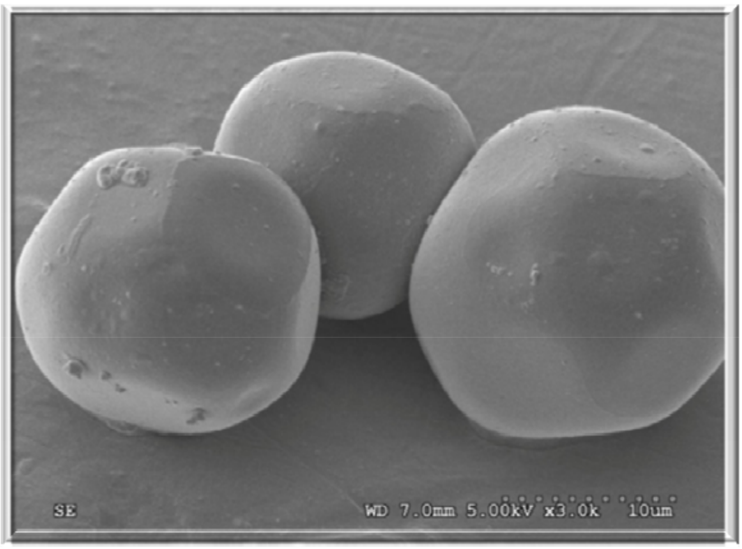

BOOK OF ABSTRACTS

12th EUROPEAN STUDENT CONFERENCE

UNIVERSITY OF ALMERÍA, SPAIN

July 15-18, 2009

ESC 2009

EUROPEAN STUDENT CONFERENCE

July 15-18, 2009

University of Almeria
Spain

BOOK OF ABSTRACTS

Group of Complex Fluid Physics
Group of PhotoCoordination Chemistry

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EUROPEAN COLLOID AND INTERFACE SOCIETY

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CONFERENCE SECRETARIAT

Group of Complex Fluid Physics
Department of Applied Physics
University of Almería
E-04120 Almería, Spain
Phone: +34 950015910; FAX: +34 950015477;
e-mail: esc2009@ual.es Web: http://www.ual.es/congresos/esc2009/

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WELCOME TO ESC2009, WELCOME TO ALMERIA

The European Student Colloid Conferences is a series of international conferences promoted by the European Colloid and Interface Society. The aim of this scheme is to give PhD students the opportunity to present and discuss their work on an international conference in a relaxed atmosphere.

We are sure the three days we will share in Almería will be fruitfully from a scientific point of view. Additionally, we think this conference is going to be a good opportunity to meet people that in the near future will be responsible for the Colloidal Science in Europe and the rest of the world.

Besides the scientific program, we try to give the participants the opportunity to know the marvellous Almería's natural areas and Spanish culture.

The Local Committee

STUDENT ECIS 2009

TIME	WEDNESDAY 15th	THURSDAY 16th	FRIDAY 17th
9:15-9:30		**Session 3A** **Session 3B**	**Session 6A** **Session 6B**
9:30-9:45			
9:45-10:00			
10:00-10:15			
10:15-10:30			
10:30-10:45	**Registration**		
10:45-11:00			
11:00-11:15	**Opening**		
11:15-11:30			
11:30-12:00	**Session 1A**	**Coffee break**	**Coffee break**
12:00-13:30		**Inauguration**	**Session 7A**
13:30-15:30	**Lunch**	**Lunch**	**Lunch**
15:30-15:45	**Session 2A**	**Session 4A** **Session 4B**	**Session 8A**
15:45-16:00			
16:00-16:15			
16:15-16:30			
16:30-16:45			
16:45-17:00			
17:00-17:15			Going to Hotel
17:15-17:30			
17:30-18:30	Coffee and **Posters**	Coffee and **Posters**	
18:30-18:45	**Brian Vincent Talk**	**Session 5A** **Session 5B**	
18:45-19:00			Travel to Escullos' Castle from Indalico Hotel
19:00-19:15			
19:15-19:30			
19:45			Conference Dinner
21:00	Barbecue on the beach	Spanish “Tapeo” at the city centre	
21:30			Flamenco Show
22:45			Cocktail
24:00			Return to Almeria

***18th Trip to Cabo de Gata Natural Park**

A and **B** means Room A and Room B

CONFERENCE SCHEDULE

Wednesday, July 15th

10:30-11:00 **Registration**

11:00-11:30 **Opening and Welcome**

Session 1A

11:30-11:45	*Joao*	*Almeida*	*Assessment Of Gemini Surfactants As Skin Penetration Enhancers*
11:45-12:00	*Craig*	*James*	*The Physicochemical Characterisation Of Polymer Therapeutics- Solution Conformation Of Hydrophobically Modified HPMA Copolymers*
12:00-12:15	*Jonas*	*Carlstedt*	*Cyclodextrins In DNA-CTAB Complex Decompaction*
12:15-12:30	*Maxime*	*Delhorme*	*Modelling Acid-Base Properties Of Clays : The Role Of Electrostatics*
12:30-12:45	*Björn*	*Persson*	*Self Assembly Of Bovine Lactoferrin*
12:45-13:00	*Olga*	*Krivosheeva*	*Interfacial Behaviour Of Small Amphiphilic Proteins (Hydrophobins)*
13:15-13:30	*Anaïs*	*Rocher*	*Effects Of Temperature On Water-In-Oil Emulsions Stabilised Solely By Wax Microparticles*

13:30-15:30 **Lunch**

Session 2A

15:30-15:45	*Agnieszka*	*Nowacka*	*Humectants In Hydration Of Lipid Membranes*
15:45-16:00	*Benjamin L.*	*Holt*	*The Effect Of Oil Phase Polarity On The Properties Of Emulsions Stabilised Solely By Silica Nanoparticles*
16:00-16:15	*Szilvia*	*Joó*	*Characterization Of Humic Substances By Particle Size Distribution And Zeta-Potential Measurement*
16:15-16:30	*Elise*	*Lejeune*	*Self-Assembling Amphiphilic Diblock Copolymers : A Dynamic Behaviour?*
16:30-16:45	*Angela*	*Chemelli*	*Loading And Release In Nanostructured Dispersions*
16:45-17:00	*John*	*Janiak*	*The Aqueous Phase Behavior Of Polyion-Surfactant Ion Complex Salts Mixed With Nonionic Surfactants*
17:00-17:15	*Anna*	*Jansson*	*Dynamic Electron Microscopy Studies Of Supramolecular Biomaterials*
17:15-17:30	*Gemma*	*Talbot*	*Investigating The Solubility Mechanism Of Ethylene Oxide Oligomers In Fluorinated Liquids*

17:30-18:30 **Coffee and Posters**

18:30-19:30 **Brian Vincent talk**
Room A

21:00 **Barbecue on the beach**

Thursday, July 16th

Session 3A

09:15-09:30	*Paola*	*Occhipinti*	*Interaction Studies Of Synthetic Polymers Within Mucin Solutions: Use Of Pulsed-Gradient Spin-Echo NMR And Small Angle Neutron Scattering*
09:30-09:45	*Rafael*	*Contreras*	*Au@pNIPAM Hybrid Particles: Effect of the Crosslinker on the Surface Plasmon Resonance*
09:45-10:00	*Marina*	*Sintyureva*	*Aggregation And Chromonic Liquid Crystal Formation*
10:00-10:15	*Joakim*	*Stenhammar*	*Electric Multipole Moment Fluctuations In Polar Liquids*
10:15-10:30	*John*	*Russo*	*Reversible Gels Of Patchy Particles: Role Of The Valence.*
10:30-10:45	*Francisco José*	*Rossier-Miranda*	*Nano-Fibril Reinforced Food Grade Microcapsules*
10:45-11:00	*Gesche*	*Graf*	*Self-Assembly Of Asymmetric Single-Chain Bolaphospholipids*
11:00-11:15	*Anne-Sophie*	*Robbes*	*Tuning The Dispersion Of Magnetic Fillers In Nanocomposites*
11:15-11:30	*Li*	*Ran*	*Effect Of Ca^{2+} And Ph On Foam Behaviour Of Sodium Alkyl Benzene Sulphonate Solutions*

Session 3B

9:15-9:30	*Chayuda*	*Chuanuwatanakul*	*Controlling Microstructure Of Ceramic Particle Stabilized Foams*
9:30-9:45	*Rasmus*	*Bodvik*	*Temperature Responsive Cellulose Derivatives*
9:45-10:00	*Juan*	*Zhou*	*Phase Behaviour Of Colloidal Sphere - Polymer Mixtures*
10:00-10:15	*Kaizhong*	*Fan*	*The Interaction Between Multi-Charged Organic Salt And Poly Vinyl Pyridine Microgel Particles*
10:15-10:30	*Awatef*	*Testouri*	*Hexagonally Close-Packed Bubble Structures In Chitosan Gels*
10:30-10:45	*Karl M.*	*Reed*	*Production Of Janus Particles Using Particle-Stabilised Emulsions*
10:45-11:00	*Melanie*	*Pretzl*	*Micromechanics And Adhesion Properties And Of Smart Polymeric Microballoons Studied By Colloidal Probe AFM And Microinterferometry*
11:00-11:15	*Angeliki*	*Tsigkri*	*Squeezing F-Actin: A Microscopy Study*

11:30-12:00 **Coffee break**

12:00-13:30 ***Conference Official Inauguration***

13:30-15:30 **Cocktail**

Thursday, July 16th

Session 4A

15:30-15:45	*Wulff*	*Pascal*	*Water-Fuel-Microemulsions*
15:45-16:00	*Rory*	*Anderson*	*Generic Routes To Nanoparticle Formation In Aqueous Solution*
16:00-16:15	*Petru*	*Niga*	*Surface Spectroscopy Of Series Of Unsaturated Fatty Acids At Liquid – Air Interface*
16:15-16:30	*Nathan*	*Nicholas*	*The Influence Of Shape Directing Molecules On The Nanostructure Of Zinc Oxide During Dissolution*

16:30-16:45	*Moheb*	*Nayeri*	*The Scattering Intensity Of Polydisperse Colloidal Sphere Dispersions*
16:45-17:00	*Laura*	*Mely Ramírez*	*Flattened Polymer Colloids And Resulting Assemblies*
17:00-17:15	*Eva*	*Max*	*AFM Single-Hair-Force Spectroscopy: “In-Situ” Measurements*
17:15-17:30	*Tingting*	*Liu*	*Interfacial Tension, Interfacial Rheology And Chemical Crosslinking Of Cationic Thermosensitive Microgels At The Oil / Water Interface*

Session *4 B*

15:30-15:45	*Asad*	*Ayoubi*	*Structures Formed By Block Copolymers Containing Amphiphilic Repeating Units*
15:45-16:00	*Malin*	*Morin*	*Peptide-Lipid Interaction: Competitive Binding To Liposomes And Polymer-Stabilized Disks*
16:00-16:15	*Oscar*	*Rojas-Carillo*	*Ionic Liquid-Modified Microemulsions: A New Template For The Synthesis Of Gold Nanoparticles*
16:15-16:30	*Hirosayu*	*Mizuno*	*Sulphated Proteoglycans Are Responsible For The Sacrificial Bonds In Red Claw Lobster (Cherax Quadricarinatus) Gastroliths*
16:30-16:45	*Neus*	*Vilanova García*	*Synthesis Of Silica Microcapsules With Embedded Magnetic*
16:45-17:00	*Daniel*	*Kluge*	*Mechanical Properties Of Self-Assembled Mesoscale Fibers*
17:00-17:15	*Ann-Catrin*	*Johnson*	*Aggregation Of Colloidal Silica: Combined SAXS And Electro Spray Analysis*
17:15-17:30			

17:30-18:30 **Coffee and Posters**

Session 5A

18:30-18:45	*Oznur*	*Kaftan*	*Investigation Of Multivalent Interactions Between Host-Guest Molecules By Colloidal Probe Force Spectroscopy*
18:45-19:00	*José Guadalupe*	*Ibarra Armenta*	*Testing A Modified Model Of The Poisson–Boltzmann Theory That Includesion Size Effects: Monte Carlo Simulation Study.*
19:00-19:15	*Martin*	*Trulsson*	*Interactions Between Surfaces Immersed In Multivalent Or Macroionic Salt Solutions*
19:15-19:30	*Nienke*	*Geerts*	*Flying Colloidal Carpets*

21:00 **Spanish "Tapas" at the city centre of Almeria**

Friday, July 17th

Session 6A

09:15-09:30	*Cesar*	*Gonzalez Serrano*	*Scalable Sorting Of Colloidal Spheres*
09:30-09:45	*Nisha*	*Doshi*	*Mixtures Of Platelets And Spheres In Coating Applications*
09:45-10:00	*Yannan*	*Cui*	*Comparison Of Aqueous Clay Suspensions*
10:00-10:15	*Miguel*	*Comesaña-Hermo*	*Cobalt Nanoparticles Stabilized With Rhodamine B: Complete Study Of Luminescent And Magnetic Properties*
10:15-10:30	*Silvia*	*Vilchez Maldonado*	*Studies On The Incorporation Of Polymeric Nanoparticles On Textiles*
10:30-10:45	*Malika*	*Boukherissa*	*Effect Of Ionic Liquids On Asphaltenes Precipitation From Petroleum Fluids*
10:45-11:00	*Carolina Denis*	*Aubéry Torres*	*Optimization Of Reaction Conditions For The Synthesis Of Mn-Zn Ferrite Nanoparticles Using W/O Microemulsions As Confined Reaction Media*
11:00-11:15	*Miguel Jesus*	*Aranda Rascón*	*Effect Of Finite Ion Size On The Electrokinetic Properties Of Suspended Charged Particles*
11:15-11:30	*Bodil*	*Ahlstrom*	*Depletion Interactions Within The Asakura-Oosawa-Vrij Model.*

Session 6B

09:15-09:30	*Anne-Laure*	*Fameau*	*Self Assembly Of Hydroxylated Fatty Acids In Solution : From Volume To The Interface.*
09:30-09:45	*Andreas*	*Fall*	*Ordering Of Nano Fibrillated Cellulose (NFC)*
09:45-10:00	*Johanna*	*Bailey*	*Heterogeneous Polycondensation Reaction In Aqueous Environment*
10:00-10:15	*Marion*	*Collinet-Fressancourt*	*Development And Physico-Chemical Properties Of "Balanced Catalytic Surfactans"*
10:15-10:30	*Julien*	*Bongono*	*Estimation Of Agglomerate Fractal Dimension In Aqueous Suspensions Using Neural Network*
10:30-10:45	*Olesya*	*Myakonkaya*	*Control Over Microemulsions With Solvent Blends*
10:45-11:00	*Ying*	*Zhu*	*New Family Of "Green" Hydrotropes Derived From Isosorbide: Regio-Isomeric Effets On The Amphiphilic Behaviours*
11:00-11:15	*Gelen*	*Rodriguez*	*Effect Of Bicellar Systems In Stratum Corneum Lipids*
11:15-11:30	*Wissam*	*Moussa*	*Structuration Of Amphiphilic Comb-Like Copolymers Based On Styrene In Aqueous Solution Studied By Scattering Techniques*

11:30-12:00 **Coffee break**

Friday, July 17th

Session 7A

12:00-12:15	*Roberta*	*Acciaro*	*Fluorescein Release From Thermoresponsive Microgel - Cellulose Fiber Thin Films*
12:15-12:30	*Alejandro*	*Vilchez Villalba*	*Preparation And Characterization Of Tio2 Nanoparticles, By The Sol-Gel Method And Study Of Its Photocatalytic Activity*
12:30-12:45	*Malik*	*Vikash*	*Controlling The Size, Shape, Magnetic Properties And Crystal Morphology Of Magnetic Nanoparticles*
12:45-13:00	*Marco*	*Braibanti*	*Effect Of Coil To Globule Transition On The Electrostatic Repulsion Of Pnipam-Microgels*
13:15-13:30	*Domenico*	*Truzzolillo*	*Effective Interaction Between Polyelectrolyte-Colloid Complexes:*
13:30-13:45	*Carmen Lucia*	*Moraila Martinez*	*Why Does Contact Angle Depend On The Method Of Measurement?*
13:45-14:00			

14:00-15:30 **Lunch**

Session 8A

15:30-15:45	*Morgan*	*Durand*	*From Micro To Macroemulsion Formulation: Three-Phase Behaviour Of Terpene / Non-Ionic Surfactant / Water Systems*
15:45-16:00	*Niklas*	*Nordgren*	*Surface Interactions Between Functional Biomimetic Thin Films*
16:00-16:15	*Marco*	*Heinen*	*Theory, Simulation And Experiments On The Short-Time Dynamics Of Chargestabilized Colloidal Suspensions*
16:15-16:30	*Gabriel*	*Espinosa Pérez*	*Polyelectrolytes/Surfactant Complexation In Bulk And At The Air-Water Interface: Case Of Dna And Carboxymethylcellulose*
16:30-16:45	*Magdalena Cristina*	*Stanciu*	*Viscosity And Fluorescence Studies Of Some Cationic Amphiphilic Polysaccharides*
16:45-17:00	*Joanna*	*Thorne*	*Influence Of Organic Solvents On The Hydrodynamic Diameter Of Hydrophobically-Modified Poly (N-Isopropylacrylamide)-Based Microgeles*

18:45 ***Travel to "Los Escullos" Castle from Indalico Hotel***

19:45-21:15 **Conference Dinner**

21:30-22:15 **Flamenco Show**

22:30 h **Cocktail**

24:00 h **Return to Hotel**

POSTERS LIST

P01	Celine	Villate	Release Kinetics And Mechanism Of A Dispersed Species In Water-In-Oil Emulsions.
P02	Martin	Trulsson	Interactions Between Surfaces Immersed In Multivalent Or Macroionic Salt Solutions
P03	Laure	Pasquini	Elaboration And Properties Of Nano Dispersions Of Ionic Liquids
P04	Ying	Zhu	New Family Of “Green” Hydrotropes Derived From Isosorbide: Regio-Isomeric Effets On The Amphiphilic Behaviours
P05	Simon	Wongsuwarn	Microrheology Of Droplets Of Pnipam Microgel Dispersions
P06	Maria	Martínez Rodríguez	Study Of Preparation And Stabilization Of O/W Bitumen Emulsions
P07	Angeliki	Tsigkri	Squeezing F-Actin: A Microscopy Study
P08	Carolina	Tomczyk	Competition Between Demixing And Percolation Effects In Colloidal Suspensions
P09	Seyed	Tabaei	Lipid-Membrane Permeation Measured With Surface Plasmon Resonance
P10	Francesca	Speranza	X-Ray Reflectometry Of Semi-Fluorinated And Hydrogenated Surfactants On Mica
P11	Oscar	Rojas-Carillo	Ionic Liquid-Modified Microemulsions: A New Template For The Synthesis Of Gold Nanoparticles
P12	Jorge	Rodrigues	Effect Of Solvent Quality On Rheology Of Micelles Of Modified Triblock Copolymer
P13	Karin	Reijmar	Effekt Of A-Helical Peptides On Liposome Structure And Leakage
P14	Melanie	Pretzl	Micromechanics And Adhesion Properties And Of Smart Polymeric Microballoons Studied By Colloidal Probe Afm And Microinterferometry
P15	Jonas	Nordström	Colloidal Fumed Silica In Electrolytes - Aging And Transport Properties In A Surface Modified System
P16	Abdul Hakim	Jangher	Physicochemical Characterization Of Stimuli Responsive “Smart” Polymers
P17	Katarzyna	Makyla	The Linoleic Acid Influence On Molecular Interactions In Cholesterol/Phospholipid Membranes
P18	Katarzyna	Makyla	The Temperature Influence On The Surface Properties Of Galactolipids Obtained From Wheat Callus Cultures
P19	Cherng Leing	Lee	Some Colloidal Studies Of Overbased Engine Oil Additives
P20	Anna	Jansson	Dynamic Electron Microscopy Studies Of Supramolecular Biomaterials
P21	Richard	Hanes	Move it, shake it, anyway you want it: Building optical tweezers to initiate nucleation in colloids
P22	Agnieszka	Cwaliñska	Microcapsules Used As A Component Of Dentals Composites
P23	Marion	Collinet-Fressancourt	Development And Physico-Chemical Properties Of "Balanced Catalytic Surfactans"
P24	Anna	Angus-Smyth	Adsorption From Polymer/Surfactant Mixtures At An Expanding Liquid Interface
P25	Angela	Carvalho	Fluorescence Quenching Study Of A Fluorene-Phenylene Copolymer Induced By Nitroaromatic Compounds
P26	Marina	Sintyureva	Aggregation And Chromonic Liquid Crystal Formation
P27	Joakim	Stenhammar	Electric Multipole Moment Fluctuations In Polar Liquids
P28	Moheb	Nayeri	The Scattering Intensity Of Polydisperse Colloidal Sphere Dispersions
P29	Carmen Lucia	Moraila Martinez	Design of an Experimental Apparatus to Measure Equilibrium Contact Angle of Liquid Drops Placed on Solid Surfaces (Wettability) using Controlled Vibration
P30	Marco	Laurenti	Fluorescent Interpenetrated PNIPAM Polythiophene Microgel
P26	Olesya	Myakonkaya	Control Over Microemulsions With Solvent Blends
P27	Ignacio	Perez Mazuecos	Formation Of Microgel From DOM (Dissolved Organic Matter) In Aquatic Ecosytems
P28	Andres	Granados Del Águila	Multilayer Silica Deposition By Atmospheric Plasma
P29	Manuel	Serrano Ruiz	Water Soluble Organometallic Microgels With A Non Lineal Structure
P30	Mery	Mallqui Ayala	Synthesis Of Geles Using Water Soluble $Cp(Conhcme_3)_2$ Containign Allenylidene Ruthenium Complexes
P31	Nazira	Jadagayeva	Organometallic Gels Containing $[(PTA)_2cpru–X–Rucp(PTA)_2–Au(CN)_4–]_N$ Framework (PTA=1,3,5-Triaza-7-Phosphaadamantane; X=NCS^-, N_3^-)
P32	Mounia	Chaara	Water-Soluble Mpta-Ruthenium(Ii) Derivatives: Synthesis, Unprecedented Photochemical Behaviour And Catalytic Activity (Mpta = N-Methyl-1,3,5-Triaza-7-Phosphaadamantane)

ABSTRACTS

STUDIES ON THE INCORPORATION OF POLYMERIC NANOPARTICLES ON TEXTILES

Silvia Vílchez-Maldonado[1,2]***, Gabriela Calderó***[2,1]***, Núria Azemar***[1,2]***, Conxita Solans***[1,2]

[1] *Instituto de Química Avanzada de Cataluña (IQAC), Consejo Superior de Investigaciones Científicas (CSIC). Jordi Girona 18-26, 08034 Barcelona, (Spain)*

[2] *Centro de Investigación Biomédica en Red en Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Barcelona, (Spain)*

The increasing demand of new functional textiles from different professional areas has prompted the use of several novel technologies in the textile industry. In that respect nanotechnology plays an important role, since the development of nanomaterials and their application as nanocoatings, nanocapsules or nanoparticles allows producing innovative textiles (e.g. clinic textiles, protective clothing, textile materials for medical applications, etc.). The objective of this research was to incorporate polymeric nanoparticles in textiles using mild conditions. Polymeric nanoparticles were prepared in O/W nano-emulsions from a preformed hydrophobically modified polysaccharide (HMPS) by the solvent evaporation method. The HMPS nanoparticles of spherical morphology and an average size of 180 nm were incorporated to the fabric by physical methods (pad-dry-cure) taking advantage of their affinity by the textile surface. The presence of HMPS nanoparticles in the cotton fabric was evaluated by SEM. No changes were observed in the size and morphology of the nanoparticles after their incorporation in the fabric. Moreover, the cotton appearance did not suffer any change after the treatment. In order to confer a future functionality to the textile, preliminary studies on the incorporation of a sunscreen agent to the polymeric nanoparticles have been also carried out to provide protective properties to the textile against UV radiation.

DEPLETION INTERACTIONS WITHIN THE ASAKURA-OOSAWA-VRIJ MODEL

***B. Ahlström* and J. Bergenholtz**

Department of Chemistry, University of Gothenburg, SE-412 96 Goteborg, Sweden

The phase behaviour of colloidal fluids is important not only for practical applications; it is also of great fundamental interest. Colloidal particles interacting with moderately strong attraction can undergo both equilibrium and non-equilibrium transitions. While the former is well known, an example of the latter is physical gelation. Gelation has been observed experimentally in several, very different colloidal system and appears to be a common phenomenon in systems characterized by short-range attractions that woukd be expected to undergo phase separation. Insted, phase separation is interrupted and dynamically arrested structures result. Clearly, the knowledge of both the microstructural and dynamical behaviour as well as the precise characterization of the equilibrium phade diagram is important for the investigation of the nature of gel phase. Here computer simulation and theory serve as important tool. In this project and extensive simulitation study of colloidal system interacting via so-called depletion interaction [1] is performed. These system can, for example, be a mixture of non-adsorbing polymers and hard-sphere like colloids. Such system are usually complex fluids and simplified model systems, like the Asakura-Oosawa-Vrij (AOV) model [2-4], play important roles provided they capture some of the essential features of the experimental systems. Here, within the AOV model, a varity of Monte Carlo simulation techniques are used to determine the micro structure and phase behaviour of these systems. Partucular focus is placed on Gibbs Ensemble Monte Carlo, in which Monte Carlo moves that are unphysical from a Brownian dynamics point of view can be used to coax the system pst gelation, reaching what appears to be near-equilibrated coexisting phases, In addition, Widom-like particle insertion are used to generate the complete pair-level microstructure from implicit-polymer simulations.

References:

[1] S.M. Ilett, A. Orrock, W.C.K. Poon, and P.N. Pusey, Phys. Rev. E, 1995, 51, 1344

[2] S. Asakura and F. Oosawa, J. Chem. Phys., 1954, 22, 1255

[3] S. Asakura and F. Oosawa, J. Polym. Sci., 1958, 33, 183

[4] A. Vrij, Pure & Appl. Chem., 1976, 48, 471

[5] B. Ahlström and J. Bergenholtz, J. Phys.: Condens. Matter, 2007, 19, 036102

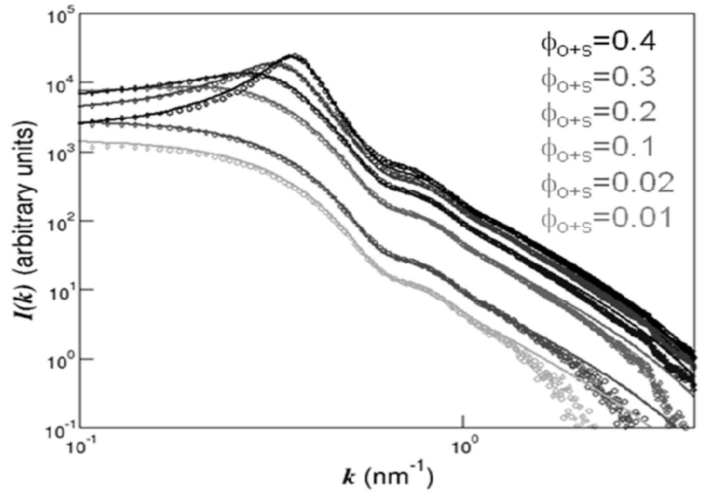
THE SCATTERING INTENSITY OF POLYDISPERSE COLLOIDAL SPHERE DISPERSIONS

***Moheb Nayeri*[1], *Malin Zackrisson*[2] *and Johan Bergenholtz*[1]**

[1]*Department of Chemistry, University of Gothenburg*
[2]*The Adolphe Merkle Institute and Université de Fribourg, Switzerland*

Small-angle scattering provides a means of microscopic characterization of a wide range of systems. It is a powerful probe of structure and interactions in colloidal systems. Analysis of scattering results from disordered systems of colloidal particles often proceeds by making quantitative comparisons with well-defined models. Here such a model is constructed for the scattering intensity of polydisperse systems of core-shell and multilayered hard spheres. Two internal distributions of scattering contrast are considered, each of which leads to an analytical expression for the scattering intensity when the size polydispersity is handled through a Schulz distribution. The first corresponds to multilayered spheres governed by a single polydispersity index, for which the shell thicknesses vary in proportion to the particle size, and the second corresponds to core-shell-structured spheres of uniform shell thickness. In addition, an effective hard-sphere diameter is introduced to capture effects of extra excluded-volume interactions. With these extensions a wider range of colloidal sphere systems can be modeled, including vesicles, microemulsions and composite particles of core-shell and layered internal structures.

In the figure below it is shown that there is very good agreements between fits obtained by one of the models and small-angle X-ray scattering data on oil-in-water microemulsions near emulsification failure, where a range of properties of the system is known to be captured by hard-sphere models.



SAXS intensity data as a function of wave vector for $C_{12}E_5$ based microemulsions, with increasing oil+surfactant volume fractions, from bottom-to-top along the right hand side. Here the good agreement between the fits and the data shows that the scattering intensity of these micro-emulsions also follows hard-sphere behavior up to rather high droplet concentrations.

FLUORESCENCE QUENCHING STUDY OF A FLUORENE-PHENYLENE COPOLYMER INDUCED BY NITROAROMATIC COMPOUNDS

A. C. P. Almeida[(a)]***, H. D. Burrows***[(a)]***, S. M. Fonseca***[(a)]***, L. Marques***[(b)]***, A. T. de Almeida***[(b)]***,***
and R. Mallavia[(c)]

[a]*Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal*
[b]*Departamento de Engenharia Electrotécnica e de Computadores, Universidade de Coimbra, 3030-290 Coimbra, Portugal*
[c]*Instituto de Biología Molecular y Celular, Universidad Miguel Hernández, Elche 03202, Alicante, España*

Conjugated polyelectrolytes are a new class of materials with applications ranging from molecular electronic devices to sensors. We have become particularly interested in their sensing properties. Fluorescence techniques have valuable applications in this area because of high sensitivity, which can be enhanced to the sub-μg level by amplified fluorescence quenching and using luminescent conjugated polymers and polyelectrolytes [1]. Because of international concern about security and terrorist attacks, there is an increasing need for new and more sensitive detection techniques for explosives. Nitroaromatics, such as trinitrotoluene, are a particularly important group of compounds, and their high electron affinities also make them strong fluorescence quenchers. We have studied the quenching of the fluorescence of the fluorene-phenylene cationic alternating copolymer poly-(9,9-bis (6'-N,N,N-trimethylammonium) hexyl) - fluorene phenylene) bromide (HTMA-PFP [2]) by nitroaromatics in both solution and polymer films. Results will be presented on the effect of the nitroaromatic structure on quenching behaviour and suggestions made on possible design of an optical sensor for these compounds, and of the relevance of the nature of the conjugated polyelectrolyte.

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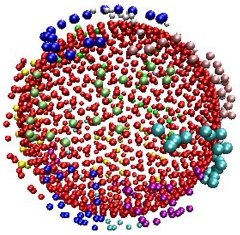
EFFECTIVE INTERACTION BETWEEN POLYELECTROLYTE-COLLOID COMPLEXES: DOUBLE LAYER THEORY AND DETAILED MC SIMULATIONS

D. Truzzolillo*, ***S. Sennato*, F. Bordi*, F. Sciortino****

** Dipartimento di Fisica, Università di Roma "La Sapienza"*
Piazzale A. Moro 5, I-00185 - Rome (Italy) and INFM CRS-SOFT, Unita' di Roma [1]



In the last year we studied by means of Dynamic Light Scattering and Electrophoretic measurements the influence of the temperature on a suspension of polyelectrolyte-colloid complexes showing how this parameter influences the phenomena of reentrant condensation and charge inversion that characterize the stable cluster phase [1] which is obseved in this systems. Through MC simulations, we showed that this behaviour in free salt solutions is well described by an extension of the double layer theory [2] to heterogeneously charged particles. Within this framework, the cluster growth may be viewed as a thermally activated process. The effects of lateral correlations between adsorbed chains on the interaction between the complexes have not yet completely explored, as well as the influence of the flexibility and valence of the ionizable groups of the polymer and of the surface charges on the overall observed behaviour of these systems. Via detailed MC simulations we investigated the role that some of these parameters have on the effective electrostatic interactions between the complexes, comparing these results with the prediction of the double layer theory. We focused our attention on the influence that charge discretization has on the structural properties of the polyelectrolyte adsorbed layer and on the mean force between decorated particles, aiming to predict the effects of charge spacings (on polymers and on particle surface) on the reentrant condensation and charge inversion.

Moreover, as called by double layer theory [2], we point out the existence of an already known effective short-range attraction [3] between complexes causing the destabilization of such colloidal suspensions. Right now, we are working on the effect of the charge discretization on this "multipole" attraction in different environmental conditions (salt concentration and temperature). We are also studying the effect of ionic strength on the charge ordering of the adsorbed polymer layer with the perspective to have further insight onto the the phenomenology that the increasing of this parameter produces by the microscopical point of view. This aspect of our simulation work is aimed to give an interpretation to experimental results we have already obtained studying liposome-polyelectrolyte complexes [4] at different simple salt concentrations.

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EFFECT OF FINITE ION SIZE ON THE ELECTROKINETIC PROPERTIES OF SUSPENDED CHARGED PARTICLES

M. J. Aranda-Rascón, J. J. López-García, J. Horno

Departamento de Física, Universidad de Jaén, Campus de Las Lagunillas, Ed. A-3, 23071, Jaén, Spain

Electrokinetic properties are powerful analytical tools in colloidal science, being often used for the characterization of colloidal systems. This is why theoretical models relating these phenomena to the system parameters have been developed in the last century. According to the classical description of colloids, suspended particles are surrounded by a perfectly smooth uniform surface density of fixed charge, ions are considered to be point charges, and the suspending medium is represented by a continuum characterized by macroscopic permittivity and viscosity values (Standard Electrokinetic Model). Despite its almost universal use, the classical model fails to predict crucial experimental trends: ζ potential values calculated from experimental electrophoretic mobility, conductivity increment, and permittivity increment data using this model usually do not coincide with one another. The most common way to address these difficulties is to consider that the surface of the particle is more complex than assumed by the model: it is either surrounded by a thin layer where the ion density is determined by adsorption isotherms or the particle surface is rough or hairy so that both fixed charges and free ions populate the surface layer. Although these generalizations solve some deficiencies of the classical model, they usually worsen the interpretation of experimental data for high electrophoretic mobilities. Furthermore, they address surface properties that are specific of each particular particle-electrolyte solution combination, so that they include a series of adjustable parameters.

In previous works [1,2] we presented a simple modification of the Standard Electrokinetic Model that takes into account the finite size of ions in the electrolyte solution. In the first we presented numerical results for the equilibrium properties while, in the second, we calculated the effect of the excluded ion volume on the electrophoretic mobility. In this contribution, we calculate the conductivity increment and present a detailed interpretation of the mobility and conductivity increment results, based on the analysis of the equilibrium and field induced ion concentrations and of the convective fluid flow in the neighborhood of the particle surface. We show that the inclusion of the ion size effect generally improves the predictions of the Standard Model: both the electrophoretic mobility and the conductivity increment increase. We also show that the excluded volume effect is not negligible even for weakly charged particles.

Financial support for this work by MEC (project FIS2006-4460), FEDER funds, and Junta de Andalucía (projects FQM-410 and FQM-3893), of Spain, is gratefully acknowledged.

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Title: Competition between demixing and percolation effects in colloidal suspensions

COMPETITION BETWEEN DEMIXING AND PERCOLATION EFFECTS IN COLLOIDAL SUSPENSIONS

R. Vavrin*[1], *J. Kohlbrecher*[1], *A. Wilk*[1,2], *K. Tomczyk*[3], *M. P. Lettinga*[3], *M. Ratajczyk*[2], *J. Buitenhuis*[3], *G. Meier*[3]

1) Laboratory for Neutron Scattering, ETH Zurich & Paul Scherrer Institut,
5232 Villigen PSI, Switzerland
2) Institute of Physics, Adam Mickiewicz University,
Umultowska 85, 61-614 Poznań, Poland
3) IFF, Weiche Materie, FZ-Jülich, Postfach 1913, 52428 Jülich, Germany

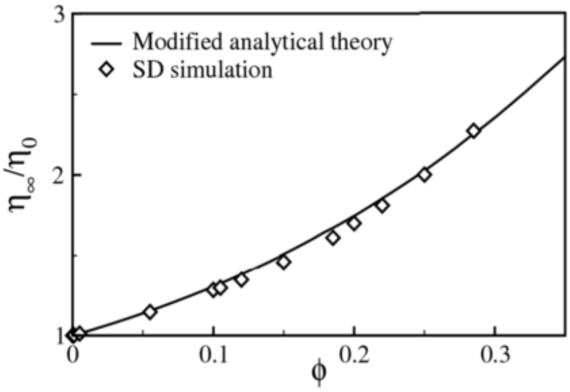
We have investigated a dispersion of octadecyl grafted silica particles in toluene, which are known to exhibit liquid-liquid phase separation and percolation depending on temperature T, pressure P and concentration φ. The competition beteween demixing and percolation was investigated by time-resolved Small-Angle Neutron Scattering (SANS) and Diffusing Wave Spectroscopy (DWS) under high pressure conditions. The latter method is capable to distinguish between ergodic and non-ergodic states and thus allows finding out percolation structures. We have investigated several concentrations around the percolation threshold and at lower volume fractions to find characteristic signatures for either demixing or percolation. We also have applied pressure jumps to overcome the coexistence quickly in order to compare this with a slow variation of the pressure. As tenetative interpretation we find that percolation effects set after the system has undergone critical slowing down. Thus the proposed equality between demixing and percolation can not be confirmed with our experiments.

THEORY, SIMULATION AND EXPERIMENTS ON THE SHORT-TIME DYNAMICS OF CHARGESTABILIZED COLLOIDAL SUSPENSIONS

***M. Heinen*, P. Holmqvist, G. Nägele**

Institut für Festkörperforschung, Teilinstitut Weiche Materie, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
E-mail: m.heinen@fz-juelich.de and A. Banchio CONICET and FaMAF, Universidad Nacional de Córdoba, Argentina

Suspensions of charged colloidal particles are well-explored model systems in soft-matter physics, with realisations such as silica, polystyrene or latex spheres in an aqeous or organic solvent. These particles are known to interact sterically by a hard-core repulsion, electrostatically by a screened Coulomb repulsion, and hydrodynamically via the embedding solvent. Examples of these systems can be found also in biophysics where suspensions, e.g., of proteins or short DNA fragments, can be modelled by soft-matter physics methods. In the present study, we apply analytical theories for the equilibrium microstructure and short-time dynamics of charged spheres, in comparison with our results from (dynamic) light scattering experiments (DLS), Monte Carlo (MC), and Stokesian Dynamics (SD) computer simulations. In the first part of our work, we explore the performance of a modified version of an integral equation scheme for the static structure factor due to Snook and Hayter, which corrects for a counterion-penetration effect. The results of this so-called particle background rescaled mean spherical approximation (PBRMSA) are shown to reproduce with high accuracy the results from our static light-scattering experiments as well as our MC simulations, over a wide range of system parameters. The PBRMSA static structure factor is used as input to an analytical theory of the shorttime dynamics developed by Beenakker and Mazur. This dynamic theory, which is based on an expansion in fluctuations of the renormalized density, allows to calculate short-time diffusion properties and the sedimentation velocity, as well as the high-frequency limiting viscosity of suspensions both of neutral and charged particles. For charged particles, we show that an appropriate self-term correction has to be introduced into the theory. With this correction, the results for the highfrequency viscosity and the short-time diffusion function of charged particles are in good agreement with our SD simulations and our DLS experiments, for all considered densities and salt concentrations. High-frequency limiting viscosity of a suspension of charged spheres at low salinity versus particle volume fraction.



High-frequency limiting viscosity of a suspension of charged spheres at low salinity versus particle volume fraction

STRUCTURES FORMED BY BLOCK COPOLYMERS CONTAINING AMPHIPHILIC REPEATING UNITS

Asad Ayoubi M.* *, U. Olsson*, A. Khokhlov** and L. Piculell*

**Division of Physical Chemistry, Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden*

***Faculty of Physics, Moscow State University, Moscow 119899, Russia*
(Mehran.Asad_Ayoubi@fkem1.lu.se)

For a diblock copolymer (poly-A and poly-B) the thermodynamic incompatibility between A and B blocks drives a microphase separation in the melt, in which alternating A-rich and B-rich microdomains appear, in order to maximize and minimize the contact between similar and dissimilar A and B blocks, respectively. The phase behavior of undiluted (bulk) linear diblock copolymer is determined by three experimentally controllable factors: the overall degree of polymerization N, overall volume fraction of A component fA and the A-B segment-segment (Flory-Huggins) interaction parameter χ. Usually the phase diagrams are plotted as χN vs. fA, where χN unifies the energetic and entropic contributions in a single parameter. At a fixed Xn (fixed overall polymer length and fixed chemical components) by increasing fA one experimentally observes the appearance of i) A-spheres arranged in a body-centered cubic lattice in B-matrix, ii) A-cylinders arranged in a hexagonal lattice in B-matrix, iii) region of gyroid phase and iv) alternating A and B lamellae, in accordance with mean-field theory predictions1,2. Very recently Khokhlov et al3 reported some computer simulation results of diblock copolymers where one of the blocks contains amphiphilic repeating units, such that one part of each unit interacts athermally (zero χ parameter) with the other block, whereas the other part of the amphiphilic repeating unit has a strongly repulsive interaction (strongly positive χ parameter). The amphiphilic block is predicted to give a new morphological variation in block copolymer phase separation, featuring thin channels and slits of amphiphilic units penetrating through the matrix of a major nonpolar components, rather than spherical micelles. The physical origin of this morphology is the interfacial activity of the amphiphilic monomer units, which forces them to be located in the regions of maximum concentration gradient. We are seeking to test these theoretical predictions by experimental techniques. For this purpose a diblock copolymer poly(styrene)-b-poly(methacrylic acid) (PS-b-PMAA) has been chosen in which the PMAA part represents the amphiphilic block. Samples are prepared by melt shear aligning and small angle X-ray scattering (SAXS), as well as transmission electron microscopy (TEM) and atomic force microscopy (AFM), are used in order to characterize the structures of these block copolymers.

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FLATTENED POLYMER COLLOIDS AND RESULTING ASSEMBLIES

Laura Mely Ramírez

Pennsylvania State University (USA)

Polystyrene spheres were flattened at one spot on their surface. We allowed the particles, which were 1 to 5 microns in diameter, to adhere to a glass surface, and then we raised the temperature above the glass transition temperature (Tg) of the polymer. The size of the resulting flat region depended upon the time allowed above the Tg, although at long times a limiting size was reached, such that the flattened region was a circle with a diameter 1/4 to 2/3 of the diameter of the original spheres. The size of the flattened region is explored in terms of surface tensions and polymer viscosities. The resulting flattened spheres offer interesting possibilities for strong yet flexible assemblies, and these will be discussed in this talk.

AGGREGATION OF COLLOIDAL SILICA: COMBINED SAXS AND ELECTRO SPRAY ANALYSIS

***Ann-Catrin Johnson*[1]*, *Zareen Abbas*[1] *and Staffan Wall*[1]**
***Caterina Camerani*[2]**

[1]*Dept. of Chemistry, Göteborg University, Göteborg*

[2]*Eka Chemicals AB (subsidiary of Akzo Nobel)*
SE-445 80 Bohus, Sweden.

In this project we seek to mimic the conditions during which colloidal silica nanoparticles are coagulated into stable gels after the addition of an accelerator for the grouting of geological media. Silica particles with different initial morphology, monodispersed, polydispersed and pre-aggregated were investigated in the presence of NaCl, KCl and K_2CO_3. The aggregation was monitored using ElectroSpray-Scanning Mobility Particle Sizer (ES-SMPS) combined with time resolved Synchrotron Radiation Small Angel X-ray Scattering (SR-SAXS).

The ES-SMPS system has proved to be a reliable method for accurate determination of the size distribution during aggregation of colloidal silica [1]. This technique involves a transfer of the colloidal particles from liquid phase to gas phase and a subsequent classification by means of a differential mobility analyzer (DMA). SR-SAXS technique with a stopped flow cell as the sample injector has been employed at the Elettra's SAXS beamline in Trieste, Italy, in order to really capture the very onset of gelation and to investigate the structural evolution during sol-gel transition and gel aging.

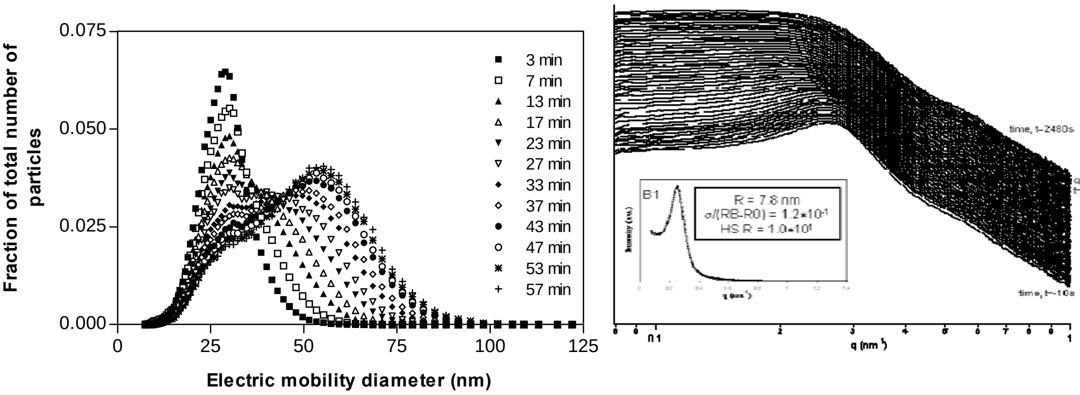

Fig.1 Aggregation of colloid silica particles (Bindzil 40/220, 0.3 M NaCl). Left panel: size distributions obtained with ES-SMPS setup, right panel: I(q) vs q (inset: I(q) vs q for Bindzil 40/220. [x] Observed data points, line fit from the Hayter Penfold charged polydisperse spherical model). In all the particle-electrolyte systems investigated in this study, very little changes were observed after the gel time. Agglomerates show the same size evolution independent of the accelerator used within the length scale measured in our experiments. The possible aggregation mechanisms are discussed by considering the fractal dimension and the invariance during gelation.

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AGGREGATION AND CHROMONIC LIQUID CRYSTAL FORMATION

Marina M. Sintyureva [a,b]***, Owen R. Lozman*** [b]***, Andrew Masters*** [a]***,***
Gordon J.T. Tiddy [a]

a) School of Chemical Engineering and Analytical Science, the University of Manchester, Sackville Street, M60 1QD, Manchester, UK; Tel. +441612008867; Fax +441613069321
b) FUJIFILM Imaging Colorants Limited, PO Box 42, Blackley, M9 8ZS, Manchester, UK

e-mail: Marina.Sintyureva@postgrad.manchester.ac.uk

Chromonic mesophases are a well-defined group of lyotropic liquid crystals with very different structures from conventional amphiphiles. While extensive research has been dedicated to the field of surfactant liquid crystals, the structural and aggregation studies of chromonics have only emerged as a topic of interest within the last few years. The main objective of this research is to explore the molecular structure within aggregates of the Edicol Sunset Yellow dye. Multiple techniques, such as optical microscopy, multi-nuclear NMR (^{1}H, ^{2}H, ^{13}C, ^{23}Na) and X-ray diffraction have been used in order to examine the solution and liquid crystalline phases. We also wish to determine the tautomeric form present in both dilute and concentrated solutions. The recent report by P.J. Collings [1] assumed the predominance of the azo form. We have measured and analysed ^{13}C NMR spectra showing that the compound exists predominantly in the hydrazone form. ^{1}H NMR helped to study the state of aggregation of the dye in solution with respect to variable concentration. The decrease in the chemical shift of the protons was observed as a result of raising the concentration, indicating the extent to which aggregation occurred over the range of compositions and providing evidence of the involvement of the whole dye molecules into the stacks. Remarkably, from proton NMR of the mesophases it is possible to obtain molecular order parameters using direct proton dipolar splittings. Optical microscopy allowed us to identify the liquid crystalline phases and to construct the phase diagram. X-ray diffraction data proved packing of the molecules into single molecule columnar aggregates. An unusual feature of the X-ray diffraction pattern of the mesophases occurred in the form of diffuse off-axis reflections at ca. 6.8 Å. It is proposed that these arise from "head-to-tail" molecular packing within the stacks, a result also predicted by recent computer simulation studies [2].

Fig. 1 **a** **b**

Figure 1 Aggregated dye molecules in chromonic nematic (N) phase **(a)** and chromonic hexagonal columnar (Mcol.) phase **(b)**.

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THE EFFECT OF OIL PHASE POLARITY ON THE PROPERTIES OF EMULSIONS STABILISED SOLELY BY SILICA NANOPARTICLES

Bernard P. Binks, Paul D.I. Fletcher and Benjamin L. Holt

Surfactant and Colloid Group, Department of Chemistry, University of Hull, Hull, HU6 7RX, UK; b.l.holt@chem.hull.ac.uk

Kenneth Wong and Pascal Beaussoubre, Firmenich SA, Geneva, P.O. Box 239, CH-1211, Switzerland; Kenneth.WONG@firmenich.com

Providing the wettability is correct, solid particles can strongly adsorb to liquid-liquid interfaces. Such particles can then be used to stabilize emulsions, with relatively hydrophilic particles stabilizing oil drops in water and relatively hydrophobic particles stabilizing water drops in oil. Silica nanoparticles hydrophobised to different extents with dichlorodimethylsilane (DCDMS) have been used to stabilize emulsions of oil and water. A novel method of emulsification has been employed in which the dry particles are added as a powder between the two liquid phases, followed by homogenization. The extent of silica hydrophobisation required to invert batch emulsions from oil-in-water to water-in-oil has been found to vary with the type of oil used. Generally more hydrophobic particles are required to invert emulsions containing oils of lower polarity. Using the surface energy components of the three homogenized phases (water, oil and particles), the extent of silica hydrophobisation required to invert the emulsions can be calculated theoretically for each of the oils used. A comparison between measured and calculated points of phase inversion reveals strong agreement, lending support to the approach taken.

MODELLING ACID-BASE PROPERTIES OF CLAYS: THE ROLE OF ELECTROSTATICS

***Maxime Delhorme*, Christophe Labbez and Fabien Thomas**

Department of Theoretic Chemistry. University of Lund. Sweden

Clays are highly anisotropic, platy aluminosilicate minerals. In general, the edges of the platelets bear protonable silanol and aluminol sites. In certain cases, isomorphic substitutions occur within the crystal lattice (Si^{4+} by Al^{3+} and Al^{3+} by Mg^{2+}), and result in a permanent negative charge on the basal surfaces. Typical titration curves of such clays obtained at different ionic strengths show a shift of the point of zero net proton charge (PZNPC) toward acidic pH when the ionic concentration is increased [1]. On contrary, clays devoid of crystalline substitutions exhibit a unique PZNPC which is the Point of Zero Charge. While it is increasingly evident that the structural charge has to play a role on the dissociation of the edge sites, the interplay between the structural and titrable charges is still a matter of debate.

In this work, we present a theoretical investigation of the titration of clays with various structural charge and anisotropy. The structural charge was chosen such as to match that of pyrophyllite (s_b = 0 e.nm^{-2}), montmorillonite (s_b = -0.7 e.nm^{-2}) and illite (s_b = -1.2 e.nm^{-2}). The calculations were carried out using a Monte Carlo method in the Grand Canonical ensemble [2] and in the framework of the primitive model. The clay particle was modeled as a perfect hexagonal platelet of thickness 1 nm and variable diameter. It consists in explicit charged hard spheres distributed on a hexagonal lattice, representing the permanent negative sites on the basal faces, and silanol and aluminol sites on the edges. Only two intrinsic constants (pK) are used. The pK for the protonation of the silanol $=SiO^- + H^+ \rightarrow =SiOH$ was set at 8, and the one of aluminol, $=AlO^{-1/2} + H^+ \rightarrow =AlOH^{+1/2}$ at 3.75. Combining the electrostatics from the crystal substitutions with the protonation constants, the simulations satisfactorily catch the shift of the PZNPC of montmorillonite when changing the ionic strength. Change in the ionic strength modulates the screening of the electrostatic interactions which results in the shift of the PZNPC. What is more, the PZNCP is found to shift toward alkaline pH upon increasing the permanent basal charge in good qualitative agreement with experimental observations following the sequence: pyrophyllite < montmorillonite < illite.

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ESTIMATION OF AGGLOMERATE FRACTAL DIMENSION IN AQUEOUS SUSPENSIONS USING NEURAL NETWORK

***Julien Bongono*, Anne Johannet, Nathalie Azéma and Pierre Gaudon**

Centre des Matériaux de Grande Diffusion. Ecole des Mines, 6 avenue de Clavières, 30319 Alès, Cedex, France.

Structural characteristic of the agglomerates in aqueous suspension is studied in modeling their fractal dimension with a neural network. After a selection of input variables, a careful adjustment of the network complexity is presented in order to maximize the generalization performance of the model. Interesting results are thus presented; particularly the role of physical microscopic, mesoscopic and macroscopic variables is considered.

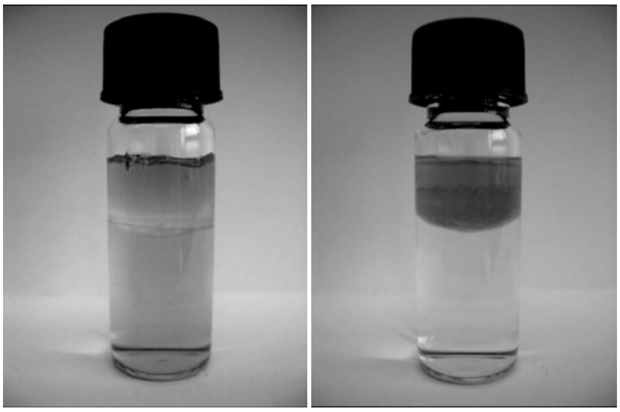
LOADING AND RELEASE IN NANOSTRUCTURED DISPERSIONS

Angela Chemelli, Otto Glatter

Karl-Franzens University Graz, Austria

In the ternary system of monoglyceride, oil and water various structures are formed depending on the composition and temperature [1]. Those phases can be dispersed in water to create so called Isasomes (internally self-assembled particles) [2, 3]. Their self-assembled internal structure, which is inverse in all cases, can be cubic, hexagonal, cubic micellar or micellar. It has a high interfacial area, which allows them to be good carrier systems for amphiphilic substances. Due to their oil and water compartments they can also host hydrophilic and lipophilic molecules. Furthermore, if substances are incorporated in the phases their stability against degradation is enhanced. These properties make them interesting as possible drug delivery systems. For the preparation of those Isasomes a method was optimized which uses relatively low energy input. Due to this preparation method also sensitive substances such as proteins can be incorporated in Isasomes. In order to be able to use Isasomes as delivery vehicles it is important to gain information about the release mechanism and possible ways to control it. For this purpose the release from the self-assembled bulk as well as from the dispersed phases is studied. As model substances hydrophilic dyes and bovine serum albumin are used.

The release is related to the diffusion within those phases. The diffusion is furthermore affected by the nanostructure as it is shown from PGSE-NMR measurements. In those measurements the self-diffusion of water in all four phases was observed. The difference in the release properties can further be used to control the release by particularly changing the nanostructure.



Sustaining release by changing the nanostructure: water is covered with self-assembled cubic phases loaded with the hydrophilic dye indigo carmine. the dye is released from the bicontinuous cubic (left picture) whereas it is entrapped in the discontinuous cubic structure (right picture).

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TESTING A MODIFIED MODEL POSISSON-BOLTZMANN THEORY THAT INCLUDESION SIZE EFFECTS: MONTECARLO SIMULATION STUDY

***José G. Ibarra-Armenta*[1], *Alberto Martín-Molina*[2], *Manuel Quesada-Pérez*[1].**

[1] Departamento de Física, Escuela Politécnica Superior de Linares,
Universidad de Jaén, 23700, Linares Jaén, Spain.
jgibarra@ujaen.es, mquesada@ujaen.es
[2] Grupo de Física de Fluidos y Biocoloides, Departamento de Física
Aplicada, Facultad de Ciencias, Universidad de Granada, 18071
Granada, Spain.
almartin@ugr.es

The Poisson-Boltzmann (PB) theory has become a valuable tool to the field of electrokinetics phenomena and electric double layer (EDL) studies since its apparition. Modified Poisson–Boltzmann (MPB) theories improving the original classical theory and leading to much precise predictions are of great importance too. In particular, in this work we focus ourselves on a MPB theory that includes ion size effects through a Langmuir-type correction and report as result an analytic charge–potential relationship accounting for such effects[1]. In previous studies it was demonstrated that the inclusion of ion size effects can yield considerable improvements for EDL theories based on PB equation where these are not included. Furthermore, the theory under analysis assumes that, the ion concentration close to the charged surface cannot exceed a determined value by the close packing fraction, as a result of the excluded volume by ions. Under this assumption, counterion concentrations smaller than the corresponding PB values are predicted. It is meaningful to test the validity of this novel theory at any level. In this case, computer simulations were chosen due to their relevance and accuracy on previous EDL studies. The obtained results prove that the analytical charge-potential expression works adequately for 1:1 electrolytes and large ions. Moreover, its predictions compared to simulation results were improved by corrections in the estimation of counterion concentration. Anyhow, theory fails for multivalent electrolytes[2].

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PHASE BEHAVIOUR OF COLLOIDAL SPHERES-POLYMER MIXTURES

Juan Zhou**, **Jeroen van Duijneveldt and Brian Vincent

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Addition of non-adsorbing polymer is a well known method for introducing attraction between colloidal particles in suspension via the depletion mechanism. There is a large body of work available on the structure and phase behaviour of the resulting systems. Mixtures of polymers and spheres of two different sizes have received very little attention so far but could be of great significance for coating formulations containing for instance latex particles and pigment particles. Different particle sizes are employed in the presence of non-adsorbing polymer in order to observe phase separation. Preliminary results on such mixtures will be presented.

FLYING COLLOIDAL CARPETS

Nienke Geerts[1] ***and Erika Eiser***[2]

FOM Institute AMOLF, Science park 113, 1098SJ Amsterdam, The Netherlands.
University of Cambridge, Department of Physics, Cavendish laboratory, Madingly Road, Cambridge CB3 OHE, United Kingdom.

The double helix of DNA consists of two negatively charged phosphate-sugar polymer chains held together by hydrogen bonds between complementary bases on each chain. This specific feature makes this biomolecule of great interest to materials science, since it allows for specific and reversible binding. This property of DNA is of particular relevance for the self-assembly of constructs that contain different sequences of single-stranded DNA (ssDNA). In 1996 Mirkin and coworkers [1] showed that ssDNA oligonucleotides can be attached to nanoparticles to direct the formation of larger assemblies. This formation is possible due to the fact that DNA prefers to be in its natural conformation: a double helix.

Besides realizing the “bottom-up” approach to build structures and devices via self-assembly by the use of DNA hybridization, this biomolecule is also used to detect specific DNA sequences or to determine mismatches within a genetic code [2,3].

While usually a binary mixture of two sets of colloids is used in the search for new materials [4-6], detection specified fields use a combination of a ssDNA-coated surface with only one set of colloids. As polymer-coated surfaces are an alternative substrate for the assembly of colloidal nanoparticles [7,8], a combination of the two could lead to novel crystalline structures.

Here we report the spontaneous formation of ordered structures in a system of DNA-coated colloids above a surface. Besides hybridization, also depletion forces are responsible for the assembly. Particles are closely packed forming hexagonal layers. In contrast to the 3D environment, only 2D crystallites emerge.

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SCALABLE SORTING OF COLLOIDAL SPHERES

Cesar Gonzalez Serrano

Pennsylvania State University (USA)

The sorting of colloidal assemblies with different sizes or densities is an issue for the scale up of colloidal technology. Sedimentation/centrifugation seems like a logical solution to the sorting problem, but a notorious fluid instability requires that the volume fraction of particles used remains small (less than about 0.001), even with a density gradient technique. We have developed an explanation for this instability. Furthermore, we have developed a simple yet very effective technique to perform sedimentation sorting of colloidal spheres. The method, which we call "effective density sorting", uses aspects of fluid dynamics, thermodynamics, and colloidal packing to achieve particle sorting.

SOME COLLOIDAL STUDIES OF OVERBASED ENGINE OIL ADDITIVES

Chern Leing Lee[1], Alexander F. Routh[1], Peter J. Dowding[2]

Department of Chemical Engineering, University of Cambridge
Infineum UK , Milton Hill, Abingdon, OX13 6BD

Overbased engine oil additives are used to neutralize acid by introducing calcium carbonate into the engine oil. These calcium carbonate particles can be stabilized in the oil medium through steric repulsion by chemically absorbed alkyl salicylate surfactant on the particle surface. Previous studies [1] suggest that the presence of water can cause alkyl salicylate surfactant to desorb from the particle surface and form novel structures in the oil medium. In this study, the structures formed by the alkyl salicylate surfactant in oil-water mixtures are investigated by optical microscopy, confocal microscopy, environmental scanning electron microscopy and X-ray diffraction. Some of the structures observed appeared to be multiple emulsions. Results from confocal microscopy suggest that some of the structures formed could be spherical reverse vesicles. Work in studying the depletion flocculation of calcium carbonate particles has also been carried out. Non-absorbing polymer such as polyisoprene was added into the engine oil to induce flocculation of the additive particles. The interaction potential between the additive particles was computed and the free energy of system is calculated by using second-order perturbation theory with the hard sphere system acting as the reference [2,3]. The model was then used to predict phase separation in the system and experimental results were compared to the phase behavior of the system predicted by the perturbation theory.

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GENERIC ROUTES TO NANOPARTICLE FORMATION IN AQUEOUS SOLUTION

***Rory Anderson*, Richard Buscall[+], Robert Eldridge, Paul Mulvaney*, and Peter Scales**

University of Melbourne, Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, Parkville, Victoria 3010, Australia.
[+]MSACT Consulting, United Kingdom.
**University of Melbourne, Bio21 Institute, School of Chemistry, Parkville, Victoria 3010, Australia.*

Nanoparticles have a diverse range of novel properties and therefore a host of potential applications that can be exploited economically, for both the consumer and niche markets. These uses may simply be an improvement on already available technology or through exploitation of their unique properties, allow for innovative and new applications. However, in order for these applications to be generally accessible, an economically viable and environmentally sustainable method of mass production needs to exist. The aim of this work is to develop a generic nanoparticle stabiliser for particle synthesis in aqueous systems. In particular this work reports the synthesis of highly concentrated and fully redispersible colloidal silver, with a mean diameter of 18nm, using a comb polymer of maleic anhydride and methoxypoly(ethylene glycol) acrylate. Investigation of potential reaction pathways yielded an optimal method through reduction of $AgNO_3$ using hydrazine in an aqueous ammonia and polymer solution at a final silver particle concentration of 2.5mol/L. The spectator species were removed using DOWEX® MONOSPHERE 550A (OH) anion exchange resin followed by drying. Through rotary evaporation it was found that the maximum solubility of these particles in water was 35wt% Ag. Analysis of the polymer-particle interactions established that complete surface coverage is required to prevent aggregation which corresponds to a $[Ag^+]:[COO^-]$ ratio of 10. After successful synthesis of materials at high concentrations using this novel comb polymer, subsequent analysis has been conducted to evaluate comb polymer architecture on its stabilisation efficacy. The parameters that were analysed include: the steric length and its relationship to DLVO models; the nature of the adsorption groups and if increasing the surface affinity would impact on final particle size; and the number of repeating units was to look at the impact of increasing polymer backbone length on stabilisation capacity.

WATER-SOLUBLE MPTA-RUTHENIUM(II) DERIVATIVES: SYNTHESIS, UNPRECEDENTED PHOTOCHEMICAL BEHAVIOUR AND CATALYTIC ACTIVITY (MPTA = *N*-METHYL-1,3,5-TRIAZA-7-PHOSPHAADAMANTANE)

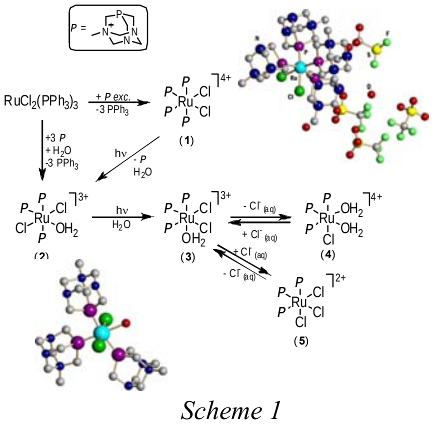
***Mounia Chaara**, Rugiada Girotti, Sonia Mañas, Vincenzo Passarelli,*
Antonio Romerosa, Manuel Serrano-Ruiz

Area de Química Inorgánica, Facultad de Ciencias, Universidad de Almería, Almería, Spain.
Organometallic and Photochemistry Laboratory for Sustainable Chemistry, CIESOL,
Almería, Spain.

The preparation of novel materials with tailored properties always rises great interest. So far a number of catalytic processes have been reported showing the enormous potential of metal-assisted syntheses. Nevertheless the design of transformations respectful towards environment and the consequent attempt to reduce the impact of industrial processes is still an open challenge. In this connection promising strategies are the use of non-contaminant reaction media, like water, and the design of catalytic transformation with high atomic economy.

On this background our research group has been interested in the synthesis and characterisation of water soluble ruthenium complexes containing phosphane ligands, namely 1,3,5-triaza-7-phospha-adamantane (PTA)[1] and 3-(diphenylphosphino) benzenesulfonate,[2] and the investigation of their catalytic activity.

Herein we report the synthesis and fully characterisation of the unprecedented water soluble ruthenium(II) derivatives shown in Scheme 1, containing the mPTA moiety, the elucidation of its photochemical behaviour and the preliminary results dealing with their catalytic activity in selected high atomic economy processes, namely the preparation of blocks for the synthesis of new polymers useful as gels. In addition the inclusion of metals into the gel structure would provide new materials with both gel and photochemical behaviour.



Scheme 1

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Acknowledgements. Funding is provided by Junta de Andalucía through PAI (research teams FQM-317) and Excellence Projects FQM-03092, the MCYT (Spain) projects CTQ2006-06552/BQU. M. Chaara thanks to MAE for a grant.

PREPARATION AND CHARACTERIZATION OF TiO_2 NANOPARTICLES, BY THE SOL-GEL METHOD AND STUDY OF ITS PHOTOCATALYTIC ACTIVITY

***A. Vílchez*[a], *C. Solans*[a], *C. Cortés*[b], *J. Esquena*[a]**

[a] *Instituto de Química Avanzada de Cataluña (IQAC), Consejo Superior de Investigaciones Científicas (CSIC), Barcelona, Spain, avvqst@cid.csic.es*
[b] *Departament I+D+I, Servià Cantó, Girona, Spain*

Titanium dioxide (TiO_2) is one of the most effective and widely used photocatalysts, and intensive studies aiming to improve its effectiveness continue. Anatase is most often synthesized by hydrothermal process or by precipitation from $TiCl_4$ or $TiOSO_4$ in aqueous medium [1]. Anatase is also frequently obtained by hydrolysis-condensation of metal-organic compounds such as titanium alkoxides in ethanol or aqueous medium [2]. Any processes affecting the formation of stable dispersions of colloidal particles are very important for industrial applications. Various methods have been used for preparing transparent sols but only few studies on photocatalytic activity of the sol itself are found in the literature. The main aim of the present work has been to control the particle size and the crystalline phase of the TiO_2 nanoparticles, as a function of temperature, pH and ageing time. The present research describes the formation of TiO_2 nanoparticles (<100nm) using a sol-gel method, based on hydrolysis and condensation of a titanium alkoxide precursor, obtaining stable sols in aqueous solution. The nanoparticles have been characterized by means of X-Ray Diffraction (XRD), Dynamic Light Scattering (DLS), and Zeta potential measurements. The XRD patterns have showed that anatase has been the main crystalline phase obtained, while the content in rutile phase increases with the ageing of the sols in acid aqueous solutions. In order to study the possible application of these sols as a photocatalysts materials, the colour-fading of methylene blue has been studied. The effect of pH and the effect of ageing on the sol photocatalytic efficiency have been evaluated.

Acknowledgements

Financial support from the Spanish Ministry of Science and Innovation, (CENIT 2007-1014 and CTQ2008-06892-C03-01 projects).

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COBALT NANOPARTICLES STABILIZED WITH RHODAMINE B: COMPLETE STUDY OF LUMINESCENT AND MAGNETIC PROPERTIES

Miguel Comesaña-Hermo[1]***, Diana Ciuculescu***[1]***, Catherine Tardin***[2]***, Serge Mazères***[2]***,***
Catherine Amiens[1]***, Bruno Chaudret***[1]

[1]*Laboratoire de Chimie de Coordination,UPR 8241-CNRS, 205*
Route de Narbonne, 31077 Toulouse, France
[2]*Institut de Pharmacologie et de Biologie Structurale, CNRS-UPS, UMR 5089, 205*
Route de Narbonne, 31077 Toulouse, France

The synthesis of nanocomposites which can hold different functionalities (as for example magnetic and luminescent properties) is a promising subject of study due to their possible implementation in different fields of nanomedicine for diagnosis or imaging. Here we present the direct synthesis of bifunctional nanoparticles composed by a metallic cobalt core with an organic luminescent molecule as unique stabilizing agent. This system presents superparamagnetic behavior and magnetization close to that of bulk cobalt. On the other hand, the fluorescent properties of the organic molecules are quenched when they are linked to the metallic surface; this phenomenon has been already reported in the case of chromophores linked to Au or Ag nanoparticles and was explained as a consequence of an energy or electron transfer process between the dye and the metallic surface[1]. Our case is particularly interesting since it is the first time that this kind of interactions are studied with a metallic-magnetic nanoparticle and we do not focus only on the changes induced on the luminescent properties of the dye but also on how this interaction could eventually affect the magnetic properties of the cobalt core, especially under irradiation. Another point of interest is that playing with the parameters of the reaction we have been able to control the shape of our nanoparticles leading to the formation of cobalt nanodisks. The control of the shape of magnetic particles has been also the center of many efforts in the past years due to the importance of this parameter for the improvement of the magnetic properties such as the magnetic anisotropy. Only few cases of anisotropic magnetic and fully metallic nanoparticles are present in literature[2, 3, 4].

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MIXTURES OF PLATELETS AND SPHERES IN COATING APPLICATIONS

<u>Nisha Doshi</u>, Dr. Jeroen van Duijneveldt, Prof. Terence Cosgrove, Dr. David Gittins and Dr.David Skuse

University of Bristol

Coatings rely on the use of titanium dioxide to scatter light due to its high refractive index. However, if the titanium dioxide particles 'bunch up' this can be detrimental to the coating. Spacers are used to prevent this. Previous research in the coating industry has found that plate-like particles such as kaolin are much more efficient at spacing than less elongated particles such as $CaCO_3$.z[1] From theories[2-6] for mixtures of particles of different shapes and sizes one would expect phase separation to occur, due to the depletion potential, but this seems contrary to what has been seen in industry.[1] In order to understand this effect we have created a model system of hard spheres and hard platelets to investigate the change in the structure of the particles as they are mixed together. An aqueous system of synthetic gibbsite ($Al(OH)_3$) platelets of ~ 250 nm diameter and alumina coated of silica spheres of diameter of ~ 35 nm (Klebosol Cal 25), as shown in Figure 1, was chosen due to there similar surface chemistry. Both these particles have been stabilised with a commercial stabiliser in water to create hard interactions between the particles. There has been little research on such mixtures, in particular for the size ratios considered here

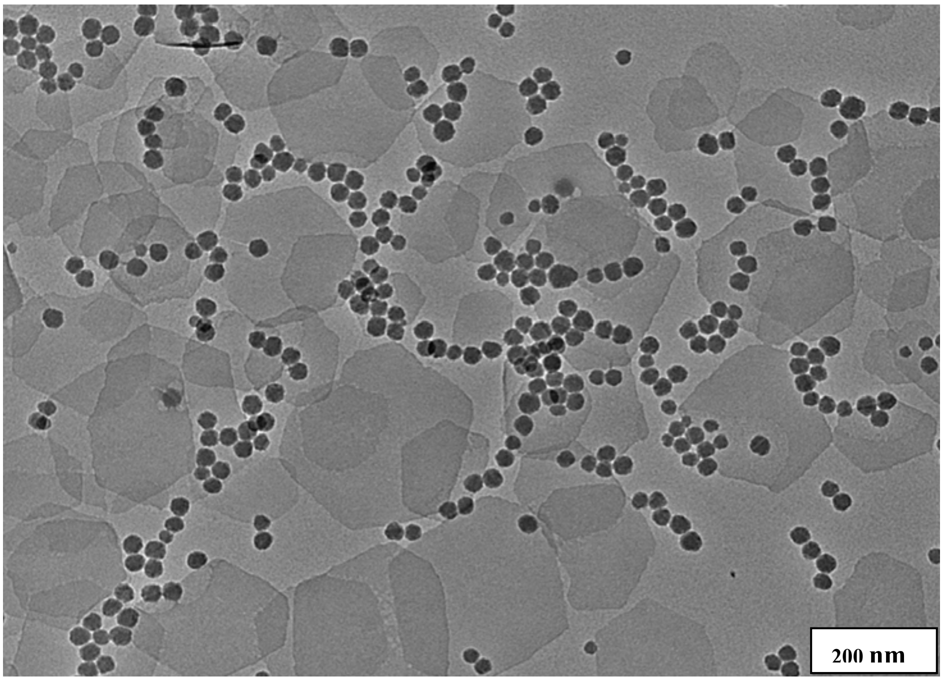

Figure 1. TEM image of a mixture alumina coated silica spheres and synthetic hexagonal gibbsite platelets.

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THE INFLUENCE OF SHAPE DIRECTING MOLECULES ON THE NANOSTRUCTURE OF ZINC OXIDE DURING DISSOLUTION

Nathan J Nicholas,[1] ***George V Franks,***[1] ***William A Ducker***[2]

[1] *Department of Chemical & Biomolecular Engineering,*
University of Melbourne, Victoria, Australia

[2] *Department of Chemical Engineering,*
Virginia Polytechnic Institute, Virginia, USA

The hydrothermal growth of zinc oxide has undergone renewed interest in recent years due to the discovery that certain molecules, when introduced into the growth medium, can control the aspect ratio of single ZnO crystals. In contrast, little attention has been given to the process of dissolution and, in particular, how these same molecules affect the morphology of the etched ZnO. In this work Atomic Force Microscopy (AFM) was used to study the real time dissolution of m-plane (10-10) and c-plane (0001) ZnO under basic conditions in the presence of the known shape directing molecules tri-sodium citrate and hexamine. Attenuated Total Internal Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was then used to directly measure the bonding characteristics of these molecules to the different faces of ZnO to better understand how these molecules control crystal morphology. Results show a correlation between the selective adsorption and selective etching of the ZnO.

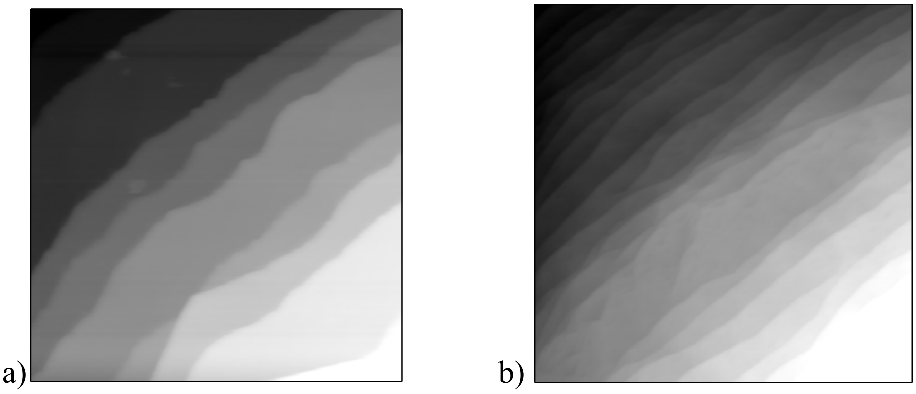

Fig 1: 10μm scans of (0001) ZnO before (a) and after (b) dissolution for 9 hours in 2MNaOH/0.1M Na_3Citrate. The citrate causes the formation of smaller basal steps by hindering dissolution in the c-direction.

ELABORATION AND PROPERTIES OF NANO DISPERSIONS OF IONIC LIQUIDS

Laure Pasquini

Laboratoire de Chimie et des Méthodologie pour l'Environment
1, bd Arago, 57070 Metz, France

Ionic liquids are selective solvents suitable for extraction and catalytic reactions. The current use of these solvents is limited by their specific properties such as, high viscosity, toxicity, and relatively high cost. We propose to use ionic liquid dispersions as an extractive medium. Ionic liquids were adsorbed on the surface of nanoparticles of metals or metal oxides. These nanomaterials may be dispersed in liquid solution and used as a reservoir of ionic liquid for extractions and catalytic reactions. The efficiency of these processes is enhanced by synergistic effects occurring between the solvent and the nanoparticle surface. Indeed, specific properties of nanoparticles and nanostructures enhance their efficiency in separation and in catalysis. In the present work we considered thermodynamic aspects of adsorption and film formation of ionic liquids on the nanoparticle surface. Several adsorption mechanisms were observed. At first, suitable, specific ligands may be adsorbed on the surface forming a protective monolayer. The second adsorption mechanism is due to strong auto structuring properties of ionic liquids. Indeed, the strong adsorption of the first layer is followed by adsorption of consecutive, numerous layers. We can obtain stable materials containing 20-40% w/w of ionic liquid. At last, materials containing a high amount of the ionic liquid may be formed by capillary forces also. In this case few nanoparticles are brought together by capillary forces resulting from the ionic liquid penetrating in the inner space of the aggregate. All described above materials allows to carry on extractions and catalytic reactions in solution with a small amount of the ionic liquid used. This technique allows to facilitate the use of ionic liquids. Moreover, extractions performed using dispersed systems present a high efficiency due to the favourable contact surface. Synergistic effect between the ionic liquid and the nanoparticle surface may enhance the efficiency of the processes. This point concerns particularly chemical reactions.

OPTIMIZATION OF REACTION CONDITIONS FOR THE SYNTHESIS OF Mn-Zn FERRITE NANOPARTICLES USING W/O MICROEMULSIONS AS CONFINED REACTION MEDIA

Carolina Aubéry, Margarita Sánchez-Domínguez and Conxita Solans

Consejo Superior de Investigaciones Científicas (CSIC, IQAC)
CIBER en Biotecnología, Biomateriales y Nanomedicina (CIBER BBN)
Jordi Girona 18-26, 08034 Barcelona, Spain.
Fax: +34 93 2045904
e-mail: catqci@cid.csic.es, msdqci@cid.csic.es, csmqci@cid.csic.es

Mn-Zn ferrites are materials which present superparamagnetic behaviour when produced at nanometric scale. Due to their magnetic and electrical properties they may find applications as components in transformers, in ferrofluid technology and as contrast enhancement agents in magnetic resonance imaging (MRI)[1,2]. The microemulsion reaction technique is one of the methods used for the synthesis of such materials, since particle size in the order of a few nanometres can be obtained. In most cases, the nanoparticles are first obtained as their hydroxide precursors, hence a calcination step (600-800ºC) is necessary to obtain a pure crystalline spinel phase. Recently, it has been demonstrated that it is possible to obtain such spinel phases at relatively low temperatures directly in the microemulsion without the need of calcination [3]. However, most of the studies reported employ microemulsions with a high concentration of ionic surfactants. In this work, microemulsion systems based on biodegradable fatty alcohol ethoxylated surfactants were employed [4]. Different reaction conditions have been explored; amongst the reaction variables considered were the initial pH for hydroxide formation, reaction time, order of reagents addition and microemulsion composition. Characterization was carried out by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and magnetization studies. Mn-Zn ferrite nanoparticles (3-5nm) with spinel structure were obtained (Fig.1); magnetization studies seem to indicate superparamagnetic behaviour. The results show that parameters such as pH have a great influence on the crystallinity of the obtained material.

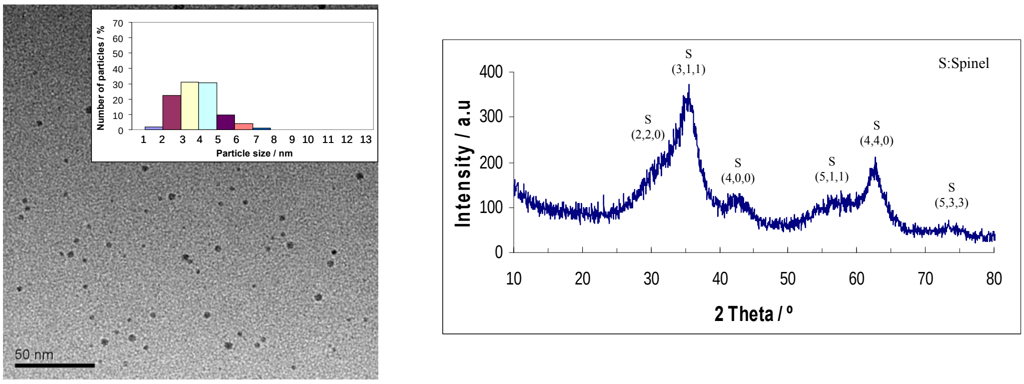

Figure 1. Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD) pattern of Mn-Zn ferrites.

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TUNING THE DISPERSION OF MAGNETIC FILLERS IN NANOCOMPOSITES

Anne-Sophie Robbes[1,2], Fabrice Cousin[1], Jacques Jestin[1], Florian Meneau[2], Olivier Sandre[3], Didier Gigmes[4] and François Boué[1]

[1]*Laboratoire Léon Brillouin (LLB), CEA Saclay, 91191 Gif-Sur-Yvette*
[2]*Synchrotron Soleil, L'Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-Sur-Yvette Cedex*
[3]*PECSA,CNRS UMR 7612, Université Pierre et Marie Curie, 4, Place Jussieu, 75252 Paris Cedex*
[4]*Laboratoire Chimie Provence, UMR 6264, Université de Provence-Centre Universitaire de Saint Jérôme, Av. Escadrille Normandie Niemen-case 542, 13397 Marseille Cedex 20*

In the past two decades, many industrial applications have encouraged research toward developing methods to reinforce polymer material with nanoparticles as fillers. The key point to tune the mechanical properties is to play on the local structure of the filler. At LLB, a model system made of polystyrene (PS) films reinforced by silica nanoparticles is studied since a few years in order to determine how the structure of the aggregates acts on the macroscopic mechanical properties of the nanocomposites. Two different systems have been considered: (i) a simple dispersion of the silica nanoparticles by mixing within the polymer matrix [1] and (ii) a dispersion of the silica nanoparticles chemically grafted by PS chains in a controlled way to improve the compatibility between the nanoparticles and the polymeric matrix [2]. This has enabled to get a good comprehension of the mechanisms involved in the reinforcement process. An alternative way of controlling aggregation by an external trigger, a magnetic field, has been also tested recently at LLB on a specific system made of magnetic nanoparticles of maghemite (γ-Fe_2O_3) in an aqueous suspension of polymer nanolatex [3]. It has shown that it is possible to design nanocomposites with anisotropic reinforcement properties. The aim of the work presented here is to merge the different approaches of the Laboratory in order to adapt the concepts of magnetically-tuned reinforcement presented in [3] to the dispersions of inorganic nanoparticles in PS such as in [1] and [2]. We use thus magnetic nanoparticles of maghemite (γ-Fe_2O_3) as filler, chemically grafted by a PS chain or not and study their dispersion within a PS matrix. For the system made of naked nanoparticles, we transfer the particles from an aqueous medium to an organic polar solvent (DMAc), which is a good solvent of the polymer, by controlling the electrostatic interactions during solvent exchange through osmotic compressions, enabling to get a controlled dispersion of magnetic particles without any aggregation in DMAc. We have then formulated the nanocomposites at various concentrations, according to the film processing defined in ref [1] for silica nanoparticles. The nanocomposites structure obtained by SANS experiments have shown that this process limits the particles aggregation in the PS matrix. Uni-axial stretch experiments performed on a film prepared under magnetic field seem to show a higher reinforcement when a strain is applied perpendicularly to the field than parallel to it, which is in accordance with the results presented in ref [3]. For the system made of PS-grafted magnetic particles, we will show how we coat magnetic nanoparticles by a silica layer to graft PS chain from the nanoparticles surface in a controlled way as described in [2] on silica nanoparticles.

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SYNTHESIS OF SILICA MICROCAPSULES WITH EMBEDDED MAGNETIC NANOPARTICLES VIA MULTIPLE EMULSIONS

***N. Vilanova*, C. Solans, C. Rodríguez-Abreu**

Instituto de Química Avanzada de Cataluña (IQAC-CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain and CIBER de Bioingeniería, Biomateriales and Nanomedicina (CIBER-BBN), Spain

Microcapsules are vehicles for the encapsulation and sustained release of active substances, having important applications in pharmaceutical and cosmetic products. There is a growing interest on the fabrication of multifunctional, composite microcapsules, conferring different useful characteristics to the system, for instance the capacity of loading active ingredients and the possibility of guided delivery by embedded magnetic nanoparticles1. The first aim of this study was the synthesis of microcapsules using the so-called one step process, via the formulation of multiple water-in-oil-in-water emulsions (W1/O/W2) containing sodium silicate as a silica precursor 2,3. With this novel route, silica formation takes place at the oil-water interface of the multiple emulsion, so there is no need for the use of colloidal particles as templates and their subsequent removal by extreme conditions (acid, alkali or organic solvents, i.e. wet chemical etching, or high temperatures), which could affect or damage the encapsulated active ingredient during the synthesis4. The size of microcapsules and their morphology could be controlled by changing preparation and formulation variables. Moreover, the release of a model encapsulated substance was found to depend on the medium conditions (e.g. pH, temperature), so that the microcapsules could be stimuli responsive. Some preliminary studies were carried out on the incorporation of magnetic nanoparticles into the silica microcapsules during the synthesis.

Characterization of the obtained materials was carried out by several techniques.

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CONTROLLING THE SIZE, SHAPE, MAGNETIC PROPERTIES AND CRYSTAL MORPHOLOGY OF MAGNETIC NANOPARTICLES

***Vikash Malik**, Hervé Dietsch, Peter Schurtenberger*

Adolphe Merkle Institute (AMI) and Fribourg Center for Nanomaterials, University of Fribourg, CH-1723 Marly 1, Switzerland

Controlling the morphology of nanoparticles in terms of size, shape and crystallinity are important topics in colloidal science. The size and shape of nanoparticles can often be tuned through parameters such as precursor concentration, pH of the solution, temperature and/or time of reaction. Here we present data from an investigation of the synthesis of hematite nanoparticles with different final shapes such as cubical, spherical and spindles-type. The formation of hematite is a two-step process. In the first step, ferric hydroxides are formed, which subsequently transform into hematite through a nucleation and growth mechanism. We demonstrate that that we can control the size and the morphology (single crystal versus polycrystalline) of the final hematite particles through the concentration of the intermediate hydroxide particles (also called akaganeite). The controlled synthesis allows us to obtain hematite monocrystalline nanocubes of various cube sizes ranging from 40 nm to 180 nm. These hematite particles can then be further used as precursors for the synthesis of superparamagnetic particles. We also report on the preparation of silica-magnetite core shell nanoparticles whose surface can be easily functionalized via silane coupling agents and present potential applications in biomedicine, drug delivery, as MRI contrast enhancement agents and for protein separation. We use high-resolution Transmission Electron Microscope and single particle electron diffraction experiments to study the morphology of thus obtained particles. Crystalline structure and magnetic properties were measured using X-ray diffraction and SQUID measurements, respectively.

IONIC LIQUID-MODIFIED MICROEMULSIONS: A NEW TEMPLATE FOR THE SYNTHESIS OF GOLD NANOPARTICLES

***Oscar Rojas,* Joachim Koetz**

Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Strasse 24-25, Haus 25, 14476 Potsdam (Golm), Germany

By studying the influence of an ionic liquid (IL), i.e. ethyl-methylimidazolium hexylsulfate, on the spontaneous formation of microemulsions with ionic surfactants an optically clear phase region in water/toluene/pentanol mixtures in presence of the cationic surfactant CTAB can be observed. The characterisation of the isotropic phase channel by means of conductivity measurements, dynamic light scattering (DLS), ^{1}H NMR and cryo-scanning electron microscopy (SEM), allows the identification of a bicontinuous sponge phase between the oil-in-IL/water microemulsion (L_1) and the IL/water-in-oil microemulsion (L_2) [1].

Taken into account our knowledge about polyelectrolyte-modified microemulsions [2], poly(ethyleneimine) (PEI) was successfully incorporated into the reversed micelle. The given multi-component microemulsion system is used as a template phase for the synthesis of well designed gold nanoparticles, which are of special interest as bright agent for two-photon luminescence imaging of cancer cells and ultra-fine clusters for catalytic processes. Nanoparticles of about 10 nm in size were obtained in presence of the high molecular weight PEI. The particle formation is checked by mean of UV-vis spectroscopy and the particle size and size distribution are characterised by dynamic light scattering and transmission electron microscopy.

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Au@pNIPAM HYBRID PARTICLES: EFFECT OF THE CROSSLINKER ON THE SURFACE PLASMON RESONANCE

<u>Rafael Contreras-Cáceres</u>[a], Jorge Pérez-Juste[b], Isabel Pastoriza-Santos[b], Antonio Fernández-Barbero[a], Luis M. Liz-Marzán[b]

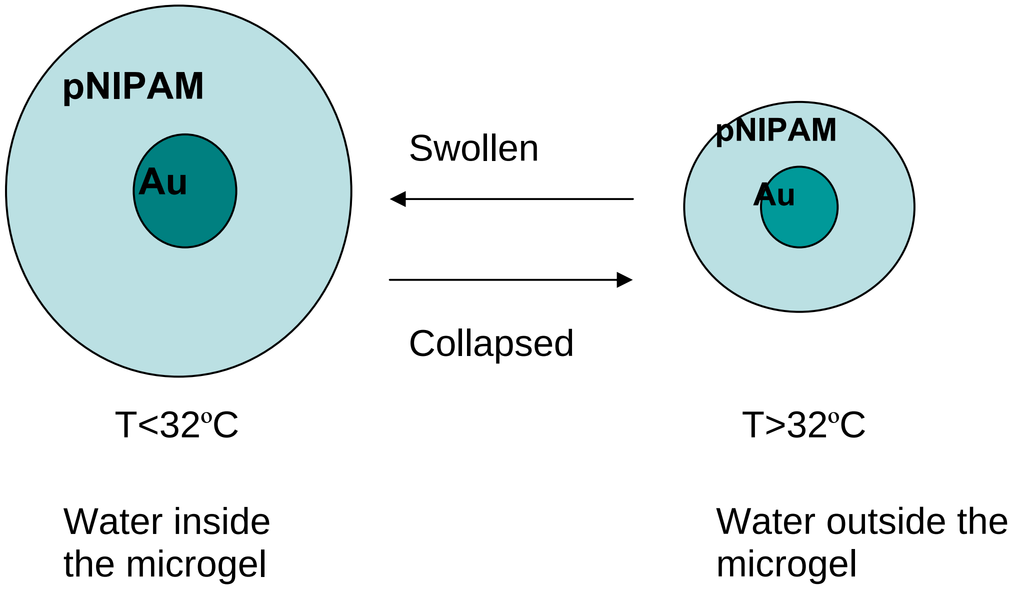
[a]Departament of Applied Physics. University of Almeria. 04120. Almeria. Spain
[b]Departament of Chemistry-Physics. University of Vigo.36310. Vigo. Spain

pNIPAM particles are formed by a monomer mixture, N-Isopropylacrylamide, and a crosslinker N,N`-methylenbisacrylamide (BA). Below 32ºC (LCST) this microgel remains in a swollen state. Above this temperature the microgel shows a collapsed phase, causing the migration of water molecules outside the polymer network.

The amount of water inside the microgel networks is controlled by the crosslinker concentration. On the other hand gold nanoparticles have a localized surface plasmon due to the deslocalization of conduction electrons. This plasmon use to exhibit a maximum in the absorbance spectrum at a well defined wavelength. The position of the peak depends among other factors on the refrax index around the gold nanoparticles.

A facile method to prepare a core-shell nanocomposite Au@pNIPAM system is achieved providing a terminal double bond over the gold core surface. Afterwards a pNIPAM polymerization is developed to obtain a core-shell Au@pNIPAM nanocomposite.

In this work we present the influence of the crosslinker concentration on the position of the plasmon peak for Au@pNIPAM hybrid particle.



FLUORESCEIN RELEASE FROM THERMORESPONSIVE MICROGEL - CELLULOSE FIBER THIN FILMS

Roberta Acciaro

Eotvos Lorand University (Hungary)

Negatively charged thermoresponsive poly(N-isopropylacrylamide-*co*-acrylic acid) (p-NIPAm-co-AAc) microgel particles and positively charged microfibrillated cellulose fibers (MFC) were used to build up polyelectrolyte multilayers on polyethilenimine coated quartz and silica substrates. The microgel particle, cellulose fiber thin films were build up by the traditional layer by layer deposition technique. Quartz Crystal Microbalance (QCM-D) and Ellipsometry measurements were used to monitor the polyelectrolyte adsorption. Both techniques indicated a steady state build up of the multilayer. Atomic Force Microscopy (AFM) was applied to image the structure of the formed composite films.

The prepared multilayers were loaded with fluorescein isothio-cyanate isomer I at room temperature. The release characteristics were then examined using UV-VIS spectroscopy. These measurements revealed slow release characteristics at room temperature and enhanced release when the temperature was cycled between 50 and 25 ^{o}C.

EFFECT OF COIL TO GLOBULE TRANSITION ON THE ELECTROSTATIC REPULSION OF PNIPAM-MICROGELS

M.Braibanti[1] *, C.Haro-Perez* [2]*, L.Rojas-Ochoa*[3] *and V.Trappe*[1]

1.Dept. Phys., University of Fribourg, Switzerland, 2. Dept. Phys., University of San Luis Potosí, Mexico, 3.Dept. Phys.,Cinvestav Mexico City, Mexico

Poly-N-isopropylacrylamide (PNiPAM) is an amphiphilic polymer that dissolves in cold water, but has a lower critical solution temperature (LCST) of ~ 33°C. Below the LCST, the hydrophilic character of the polymer dominates such that it is fully swollen; above the LCST the hydrophobic character dominates, which leads to a complete collapse of the polymer. Although PNiPAM is a neutral polymer, PNiPAM microgels are negatively charged because of the use of an ionic initiator in the synthesis of these systems; the charges are believed to be mainly located in the outer shell of the microgel [Daly, E., and Saunders, B. R. Phys. Chem. Chem. Phys **2** (2000) 3187; Sierra-Martin, B.et al. Langmuir **22** (2006) 3586].

In this contribution we explore the effect of the coil to globule transition on the electrostatic interactions between PNiPAM microgels, which we evaluate from the static structure factor $S(q)$. Our investigations reveal that the electrostatic interactions decrease as the solubility of our microgels decreases with increasing temperature. Moreover, we find that the temporal evolution of the electrostatic interactions sensitively depends on whether a temperature quench is performed from a low temperature to a temperature, which is still below the LCST, or to a temperature above the LCST. While the electrostatics adapts instantaneously when the temperature is increased to a temperature below the LCST, it exhibits a very slow evolution when the temperature is increased above the LCST. We attribute this behaviour as being due to a very slow rearrangement of the surface charge once the particle becomes hydrophobic at high temperatures.

THE AQUEOUS PHASE BEHAVIOR OF POLYION-SURFACTANT ION COMPLEX SALTS MIXED WITH NONIONIC SURFACTANTS

***John Janiak**, Salomé Santos, Lennart Piculell and Karin Schillén*

Division of Physical Chemistry , Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

The aim of this project is to understand the phase and association behavior of soluble complex salts in aqueous solution. They consist of poly(acrylates) (PA^-) and a cationic surfactant ion of C_xTA^+ and are denoted C_xTAPA_y, where x is the number of carbons in the surfactant chain and y is the number of monomer units (or degree of polymerization) in the polyacrylate [1]. The solubility of the C_xTAPA_y complex salts in water varies and it increases when the complex salt is composed of a surfactant with short alkyl chain and a longer polyion [2]. In order to make the complex salts soluble, forming a composite self-assembled macromolecular aggregate, nonionic surfactants of the type C_iE_j (where E stands for poly(ethylene oxide), PEO) are added.

The project is divided into two parts: a) initial phase studies of ternary mixtures of $C_{16}TAPA_y$, nonionic C_iE_j surfactants and water, b) investigation (main part) of the dilute solution properties of these new composite self-assembled structures at different temperatures are investigated by using dynamic and static light scattering, small-angle X-ray scattering, cryo-transmission electron microscopy and isothermal titration calorimetry. Both the PEO-length of the surfactant ($C_{12}E_5$, $C_{12}E_8$) and the length of the polyion in the complex salt are varied, keeping the alkyl chain length of the surfactant ion constant (i.e. $x = 16$). The degree of polymerization of the polyacrylate is either $y = 25$ or 6000.

This contribution will present the results from the ongoing phase studies and from dynamic light scattering measurements.

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COLLOIDAL FUMED SILICA IN ELECTROLYTES – AGING AND TRANSPORT PROPERTIES IN A SURFACE MODIFIED SYSTEM

***Jonas Nordström* and Aleksandar Matic**

Department of Applied Physics, Chalmers University of Technology,
412 96 Göteborg, Sweden

Incorporation of nanosized particles in polymer and gel electrolytes has proven to enhance both the mechanical stability and the ion transport of these systems [1]. By surface modification of the particles they can act as active fillers in the sense that they are necessary for any ion transport to take place. In these electrolytes the anions are chemically bonded to the colloidal particle and the major part of the conductivity will therefore be attributed to the cation, most often a lithium ion.

In this contribution we present results on a system where the surface of fumed silica has been modified with a lithium propanesulfonate group to enable lithium ion conductivity, in a gel type electrolyte [2]. By modification of the silica surface the interaction between particles is altered. As a result, these colloidal systems exhibit a strong aging behaviour and, for high concentration, go from a low viscosity dispersion to a self-standing gel. These gels have a conductivity of more than 10^{-3} S/cm. We use photon correlation spectroscopy as well as conductivity measurements to investigate the sol-gel transition and the lithium ion transport and compare this to the behaviour of dispersions and gels of non-modified fumed silica. Understanding the structure and interactions in these kind of systems is essential for an increased understanding of the ion transport and to further improve the mechanical properties of electrolytes based on surface modified colloidal particles.

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SELF-ASSEMBLING AMPHIPHILIC DIBLOCK COPOLYMERS: A DYNAMIC BEHAVIOUR?

Elise Lejeune[1]***, Christophe Chassenieux***[1]***, Olivier Colombani***[1]

[1] *Université du Maine – UMR 6120 – Polymères, Colloïdes et Interfaces*
Avenue Olivier Messiaen – 72000 Le Mans – France

e-mail : elise.lejeune.etu@univ-lemans.fr

We report on the structuration of a serie of amphiphilic diblock copolymers based on poly(n-butyl acrylate) (hydrophobic) and poly(acrylic acid) (hydrophilic) blocks where hydrophilic units have been incorporated on purpose in the hydrophobic block.

Despite the low T_g value ($T_g \sim 55°C$) of their hydrophobic block, the dispersion of pure diblock leads to frozen aggregates[1,2] displaying a behaviour similar to what is observed for molecular surfactants. These out-of-equilibrium aggregates result from the strong incompatibility ($X_{PnBA/PAA}$) between the two constituting blocks and are unable to reorganise through external stimuli (pH, salt, dilution). The incompatibility between both blocks can be decreased by incorporating growing amount of AA with the hydrophobic block as reported previously in the literature for styrene/acrylic acid-based systems[3]. We are systematically studying the influence of various ratio of acrylic acid in the hydrophobic block on the ability of the systems to form equilibrium aggregates. Controlled radical polymerization (ATRP) has been used to synthesize well-defined diblock copolymers; a prerequisite for this study. Light and neutrons scattering has been used to understand the behaviour of the polymers in aqueous solution (sizes, molar masses and interaction).

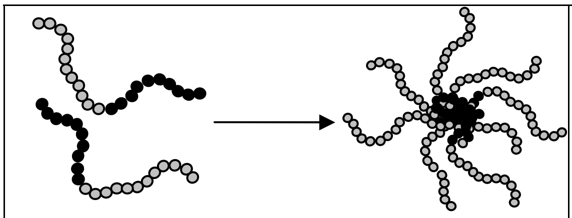	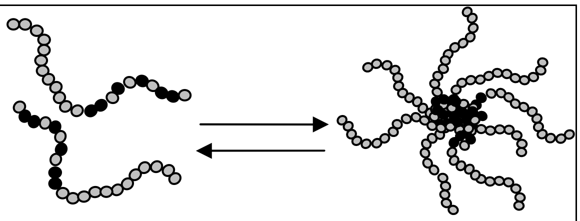
Figure 1 : Aggregation of the pure amphiphilic diblock copolymer P*n*BA-*b*-PAA *which drives to frozen aggregates*	*Figure 2 : Aggregation of the amphiphilic diblock copolymer* P(*n*BA-*co*-AA)-*b*-PAA *which drives to dynamic aggregates*

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HEXAGONALLY CLOSE-PACKED BUBBLE STRUCTURES IN CHITOSAN GELS

A.Testouri[1], D. Langevin[1], A. Ponton[2], V. Leroy[2], W. Drenckhan

Laboratoire de physique des solides, UMR 8502-Université Paris Sud, Orsay, France

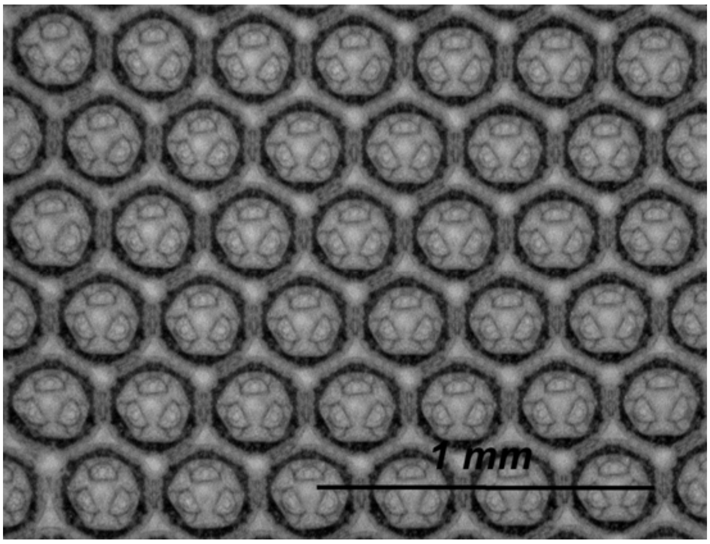
2 Matière et Systèmes Complexes UMR 7057 CNRS & Université Denis Diderot Paris, 7 MSC- Case 7056

75205 Paris Cedex 13, France

We investigate monodisperse wet foams, which consist of equal-volume, spherical bubbles in an aqueous solution that auto-organise under gravity or confinement to form hexagonally close-packed structures. We generate these “bubble colloids” using micro-fluidic flow-focussing techniques.

The aim of our work is generate ordered foam structures in a highly controllable manner and to solidify them, in order to study and compare their mechanical/acoustic properties in the liquid and solid state. For this purpose, we exploit the gelation of aqueous solutions of chitosan, a biodegradable polysaccharide, known for its ability to form stable hydrogels which have multiple applications (drug delivery, wound bandage, encapsulation of cells, waste water treatment, etc…). It is obtained by deacetylation of chitin which is the main component of the exoskeleton of crustaceans, such as shrimps and crabs.

We present here our first results obtained concerning the structure, stability and acoustic properties of our bubble colloids in the solid and liquid state.

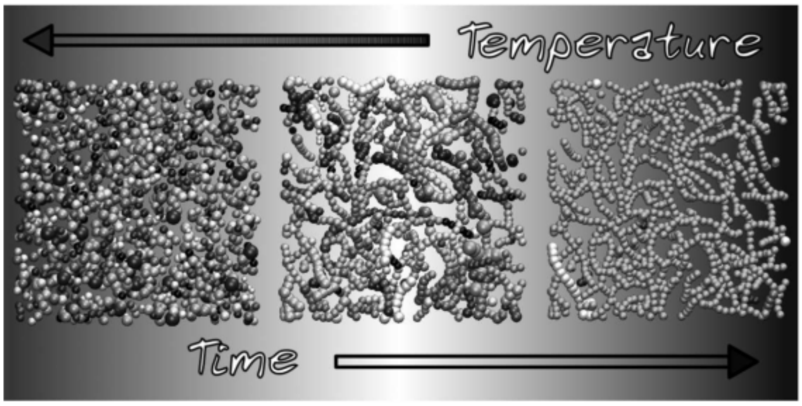


Example of hexagonally close-packed foam

REVERSIBLE GELS OF PATCHY PARTICLES: ROLE OF THE VALENCE

***John Russo**'[1] ,Piero Tartaglia,[2] and Francesco Sciortino[1]*

*1Dipartimento di Fisica and INFM-CNR-SOFT, Universit`a di Roma La Sapienza, Piazzale
A. Moro 2, 00185 Roma, Italy
2 Dipartimento di Fisica and INFM-CNR-SMC,Universit`a di Roma La Sapienza, Piazzale
A. Moro 2, 00185 Roma, Italy*



Gels are important materials both for their interesting and useful physical properties and also because they are representative of a remarkable class of systems which go under the name of arrested states.

Patchy colloids [1–3] represent a very promising tool for the study of gel static and dynamic properties. They consist of colloids decorated with short-range attractive spots. In this way they ensure a low coordination number for aggregation, enhancing the formations of networks while suppressing the formation of the bulk liquid (which would cause the phase separation). In this way it is possible to obtain a gel only through equilibrium states. Here we simulate a binary mixture of colloidal patchy particles with two and three patches respectively, for several relative concentrations and hence relative average valences. For these limited-valence systems, it is possible to reach low temperatures, where the lifetime of the patch-patch interactions becomes longer than the observation time without encountering phase-separation in a colloid-poor (gas) and a colloid rich (liquid) phase. The resulting arrested state is a fully connected long-lived network where particles with three patches provide the branching points connecting chains of two-patches particles. We investigate the effect of the valence on the structural and dynamic properties of the resulting gel and attempt to provide a theoretical description of the formation and of the resulting gel structure based on a combination of the Wertheim theory[4] for associated liquids and the Flory-Stockmayer approach for modeling chemical gelation.

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FLUORESCENT INTERPENETRATED PNIPAM-POLYTHIOPHENE MICROGELS

***Marco Laurenti,* E.López Cabarcos, F.García Blanco, B.Frick and J.Rubio-Retama**

Physical Chemistry Department, Faculty of Pharmacy, Complutense University,
Madrid 28040, Spain, and
Institut Laue Langevin, Grenoble, France

In this work, we present a facile and reproducible method to obtain thermally responsive, monodisperse, fluorescent microgels with diameters smaller than 700 nm based on poly(*N*-isopropyl acrylamide) (PNIPAM) interpenetrated with poly(thiophene-ethoxy butyl sulfonate) (PTEBS). Changing the temperature and inducing the microgel volume phase transition, it is possible to modify the photoluminescence (PL) properties of the microgels. Thus, when the temperature was below the low critical solution temperature (LCST) of PNIPAM, the PL intensity was higher than that above the LCST.

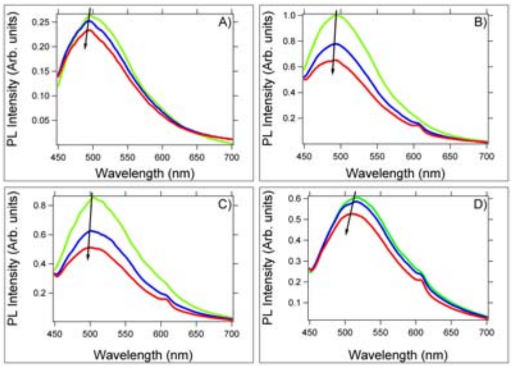


Fig.1.a

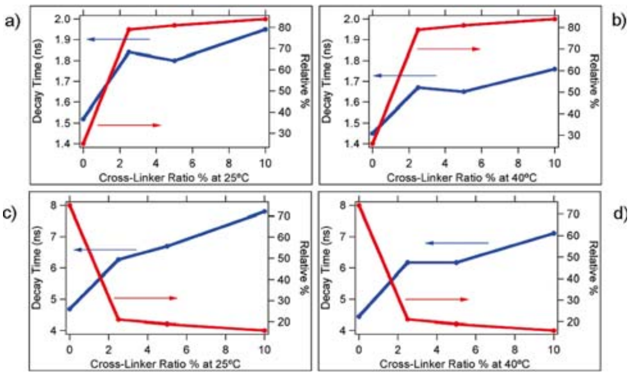


Fig.1.b

Figure 1.a Emission spectra of PTEBS and microgels at different temperatures (green line 25ºC, blue line 35ºC and red line 45ºC) measured at 0.02% (w/w) concentration: A) pure PTEBS at concentration $4.3\cdot10^{-4}$M; B) PTEBS-PNIPAM microgels with 2.5% cross-linker; C) PTEBS-PNIPAM microgels with 5% cross-linker, and D) PTEBS-PNIPAM microgels with 10% cross-linker.

Figure 1.b Two fluorescence decay times (blue) and percentage contribution to the steady state intensity (red) as a function of cross-linker content of PTEBS-PNIPAM microgels in the swollen (a, c) and collapsed states (b, d).The fast component is shown in the upper panel, and the slow one in the bottom panel.

Time-resolved fluorescence measurements indicate that, in the swollen state, the increment of cross-linking increases the fluorescence decay time of PTEBS. By contrast, in the collapsed state, variations in the decay time were attributed to higher rigidity of the PNIPAM−PTEBS system, which was confirmed by neutron scattering measurements. Moreover, the shift in the wavelength of the fluorescence emission peak observed above the LCST indicates that the collapsed PNIPAM matrix was able to interact with the PTEBS chains hindering the formation of π−π interactions.

The present work shows an easy way for the synthesis of fluorescence microgels based on PNIPAM and PTEBS. The PL properties of the interpenetrated microgels were studied as a function of cross-linking degree, temperature, and rigidity of the polymer matrix. The results confirmed the close relationship between the environment and the PL emission of the encapsulated π-conjugated polymer.

THE INTERACTION BETWEEN MULTI-CHARGED ORGANIC SALT AND POLY VINYL PYRIDINE MICROGEL PARTICLES

***Kaizhong Fan,* Melanie Bradley, Brian Vincent**

School of Chemistry, University of Bristol,
Cantock's Close, Bristol, BS8 1TS, United Kingdom

The interaction between three organic salts, Tropaeolin O, Sunset Yellow FCF and Sulfanilic acid azochromotrop, with poly(2-vinylpyridine) (PVP) microgel particles has been investigated. The three organic salts differ in the number of sulfuric ions present in their molecules. This is significant since the uptake of dye into the PVP microgels was investigated in relation to the ionic interaction between the organic salts and the positively charged microgel network. For all the three organic salts, the particle size and electrophoretic mobility decrease with the organic salt concentration, and the concentration of dye required to cause this decease is reduced upon increasing the number of sulfuric ions present in the organic salt molecule. The absorbed amount of organic salt into the microgel particles also decreased with increasing number of sulfuric ions. The addition of background electrolyte to the system decreased the interaction between the organic salts and the microgel particles. These results suggest that the uptake of the organic salt into the microgel particles is through an electrostatic interaction and increasing the number of charged groups present in the organic salts results in physical cross-linking of the microgel network.

MICRORHEOLOGY OF DROPLETS OF PNIPAM MICROGEL DISPERSIONS

Simon Wongsuwarn

Biological and Soft Systems Group. Cavendish Laboratory. University of Cambridge. (United Kingdom)

Microgel dispersions are colloids of cross-linked polymers. Aqueous poly(n-isopropylacrylamide) (PNIPAM) microgels are often labelled 'smart' materials due to the fact that they exhibit a sharp change in solvency in response to environmental stimuli. The bulk complex modulus of such a material is simply measurable via traditional rheometry. However, to know the rheological changes as a function of position in a droplet, as well as the developing rheological changes upon drying, a non-contact method is required in order to access traditional rheometric parameters. We explore the use of passive particle tracking microrheology (PPTM) for this purpose. PPTM is a non-contact method for determining the complex moduli of materials from the thermal motion of embedded tracer particles.

SYNTHESIS OF GELES USING WATER SOLUBLE $Cp(CONHCMe_3)_2$ CONTAINIGN ALLENYLIDENE RUTHENIUM COMPLEXES

***Mery Mallqui Ayala*[a], *Antonio Romerosa*[a]*, *Manuel Serrano Ruiz*[a],**
***Maurizio Peruzzini*[b] and *Luca Gonsalvi*[b]**
[a]*Área de Química Inorgánica, Universidad de Almería, 04120, Almería(Spain);*
[b]*Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), 50019, Sesto Fiorentino (Italy)*

Catalytic synthesis of water soluble polymer offers an adequate way for developing functional gels. Large open network structures including groups located in selected positions could give rise to new gels with special properties useful in areas such as catalysis, sensor technology, and materials science.[1] Traditional synthetic procedures are not normally eco-benign producing a large variety of possible contaminant sub-products. These problems could be solved partially by using catalytic synthetic processes in water and water soluble metal complexes as catalysts. Water is cheap and environmentally benign and the catalytic process have to lead to the synthesis of the desiderate polymer in high purity. We have demonstrated that ruthenium vinylidenes and allenylidenes complexes stabilized by water soluble phosphine m-TPPMS (m-TPPMS=metal-mono-sulphonatedtriphenylphosphine) catalyzes efficiently the ring opening metathesis polymerization (ROMP) of cyclic alkenes.[2] As a further step, we report here the synthesis and characterization of a family of water soluble metal complexes of formula $[Ru\{Cp(CONC(CH_3)_3)_2\}(X)LL']_n$ (Cp = cyclopentadienyl; X = halogen, allenylidene ligands (figure1); L = PPh_3, PTA, mPTA, mTPPMS; L' = PTA, mPTA, mTPPMS) (mPTA = methyl – 1,3,5-triaza-7-phosphaadamantane) which are efficient catalysts for synthesizing polymers in water (scheme 2).

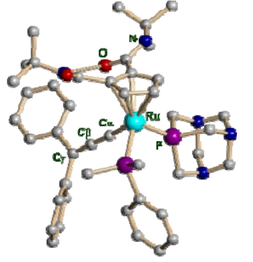
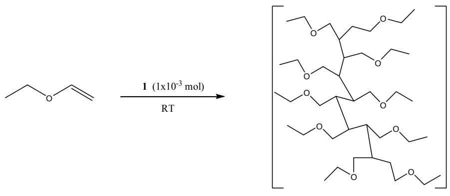


Figure 1. Crystal structure of allenylidene complex $[RuCl\{Cp(CONHCMe_3)_2\}(PPh_3)(PTA)]$(**1**)



Scheme 1. Synthesis of vinylethers polymers.

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Acknowledgements. Funding is provided by Junta de Andalucía through PAI (research team FQM-317) and Excellence Project FQM-03092, the COST Action CM0802, the MCYT (Spain) projects CTQ2006-06552/BQU and the AQUACHEM project.

ORGANOMETALLIC GELS CONTAINING $[(PTA)_2CpRu{-}X{-}RuCp(PTA)_2{-}Au(CN)_4{-}]_n$ FRAMEWORK (PTA=1,3,5-triaza-7-phosphaadamantane; $X=NCS^-$, N_3^-)

<u>Nazira Jadagayeva</u>, Antonio Romerosa*, Manuel Serrano Ruiz

Área de Química Inorgánica, Universidad de Almería, 04120, Almería (Spain)
njn642@ual.es, romerosa@ual.es, mserrano@ual.es

Metal-polymeric systems find practical applications in an extremely wide variety of scientific and technical areas[1] such as microelectronic, medicine, solar sensible devices, etc. Despite of the importance of this kind of compound few examples are known and only a reduce number of water soluble metal-polymer have been described. Since several years we are involved in obtaining new water soluble poly-metal-polymer.[2,3] The first step to the synthesis of a new metal-polymer is the choice of adequate metals and ligands that lead to the desiderated compound but the selection of reproducible methods for its synthesis is also of paramount importance. Achieving a selected self-organization by rearrangements of the different metal-polymer parts could give rise to the synthesis of a vast variety of different metal-polymeric compounds.

Herein we present the synthesis of new water-soluble air stable heterobimetallic complexes containing the frameworks $[CpRu{-}X{-}RuCp]^+$, $[Au(CN)_4]^-$ ($X = SCN^-$, N_3^-) which are connected by molecules of PTA (PTA =1,3,5-triaza-7-phosphaadamantane) through P and N coordination modes.

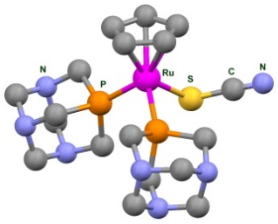
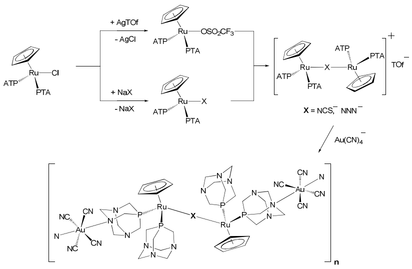


Figure 1. Crystal structure of $CpRu(NCS\text{-}\kappa S)(PTA)_2$.



Scheme 1. Synthesis of $[(PTA)_2CpRu{-}X{-}RuCp(PTA)_2{-}Au(CN)_4{-}]_n$

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Acknowledgements. Funding is provided by Junta de Andalucía through PAI (research team FQM-317) and Excellence Project FQM-03092, the COST Action CM0802 and the MCYT (Spain) projects CTQ2006-06552/BQU.

WATER SOLUBLE ORGANOMETALLIC MICROGELS WITH A NON LINEAL STRUCTURE

***Manuel Serrano-Ruiz*[a], *Antonio Romerosa*[a]**, Benjamín Sierra-Martín, and Antonio Fernandez-Barbero*[b]**

[a]*Área de Química Inorgánica,* [b]*Departamento de Física Aplicada, Universidad de Almería, 04120, Almería (Spain).*

The self-assembly and self-organization of small molecules to supramolecular agregates displays an intense research activity and in particular for obtaining gels.[1] Although important advances have already been made, few metallopolymers are soluble in water. The unique air-stable water-soluble multimetallic polymers describe until now have been reported by us. These metal-polymers display a lineal (1D) structure and include mixed P,N ligands as metal-coordinating spacers.[2,3] Herein, we presented the first example of an air–stable water-soluble heterobimetallic complex containing $[(PTA)_2CpRu\text{-}CN\text{-}CpRu(PTA)_2]^+$ moieties (Cp=cyclopentadienyl, PTA = fosfaadamantane) and $[Au(CN)_4]^-$ which displays a non linear structure (figure 1).

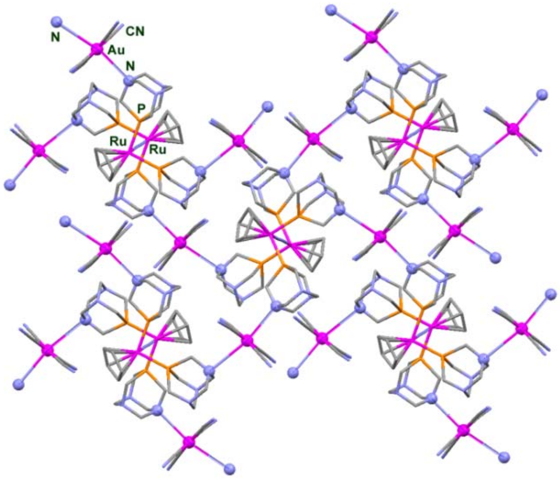

Figure 1.

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Acknowledgements. Funding is provided by Junta de Andalucía through PAI (research teams FQM-317 and FQM-230) and Excellence Projects: FQM-02353 and FQM-03092, the COST Action CM0802, the MCYT (Spain) projects CTQ2006-06552/BQU and MAT2006-13646-C03-02.

INFLUENCE OF ORGANIC SOLVENTS ON THE HYDRODYNAMIC DIAMETER OF HYDROPHOBICALLY-MODIFIED POLY(*N*-ISOPROPYLACRYLAMIDE)-BASED MICROGELS

***J.B. Thorne**, L.S. Benée, M.J. Snowden*

Medway Sciences, School of Science, University of Greenwich at Medway, Central Avenue, Chatham Maritime, Kent ME4 4TB

Several studies have investigated the swelling behaviour of poly(*N*-isopropylacrylamide) (NIPAM) microgel particles in short-chain alcohol-water solutions, observing particle collapse at low volume fractions of alcohol and re-entrant swelling at higher volume fractions.[1,2] This investigation focused on the effect of increasing the hydrophobic nature of the microgel upon particle collapse/re-entrant swelling behaviour in aqueous dispersions in the presence of a range of increasingly hydrophobic organic (but water-miscible) solvents.

A range of poly(NIPAM)-based copolymers, incorporating hydrophobic co-monomers such as vinyl laurate (C_{14}) and vinyl stearate (C_{20}) (at 10 % w/w of NIPAM monomer), were prepared by a surfactant-free emulsion polymerisation reaction. Dynamic light scattering was used to measure the particle size (hydrodynamic diameter) variation of each aqueous microgel dispersion in the presence of increasing mole fractions (0–100 %) of co-solvents of varying polarity. The solvents selected had varying dielectric constants and included methanol (ε = 32.63), ethanol (ε = 24.3) and formic acid (ε =58.5).[3] The hydrodynamic diameters were measured at 25 and 50 °C, i.e. above and below the volume phase transition temperature of each microgel dispersion. It has been proposed that chain collapse is a consequence of the effect of added alcohol molecules on the environment of the poly(NIPAM) chains, with water molecules removed from the particle interior to form clathrate structures around the alcohol molecules,[4] thereby promoting hydrophobic bonding between poly(NIPAM) chains and followed by chain collapse.[2] However, re-entrant chain swelling is thought to result from direct interaction of alcohol molecules with hydrophobic groups within the poly(NIPAM) macromolecular structure, once the higher alcohol mole fractions disrupt the clathrate structures.[2] As the hydrophobic nature of poly(NIPAM)-based copolymer microgels and/or the added co-solvents were increased, changes in particle sizes occurred Different trends were observed depending on the hydrophobic nature of the microgels/co-solvents. These results suggest that such microgels may have future applications, for example in the removal of hydrophobic materials/solvents from water.

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PHYSICOCHEMICAL CHARACTERIZATION OF STIMULI RESPONSIVE “SMART” POLYMERS

***Abdulhakim Jangher*[1], *Johannes Pall Magnusson*[1], *Cameron Alexander*[2], *Pete Griffiths*[1], *and Renuka Nilmini*[1]**

1. School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK

2. School of Pharmacy, Nottingham University, Nottingham, NG7 2RD, UK

Responsive “smart” materials have been an increasing focus for chemists in the pharmaceutical and biomedical sectors. Until recently, however most responsive polymers have been based on poly(N-isopropylacrylamide). Recently, the physicochemical characteristics of some new biocompatible responsive polymers with potential biomedical applications have been explored. These polymers are synthesised from the commercially available monomers poly(ethylene glycol) ethyl ether methacrylate (M_n 246, PEGMA-EE 246), and poly(ethylene glycol) methyl ether methacrylate (Mn 475, PEGMA-ME 475).We prepared two polymers from a series reported previously, i.e. polymer P6 (PEGMA-EE 246_{85}: PEGMA-ME 475_{15}: PEGMA-ME $475_{6;}$ M_n = 26 KDa) and P7 (PEGMA-EE 246_{89}: PEGMA-ME 475_{11}: PEGMA-ME 475_{17}; M_n = 26 KDa) and studied their solution properties via Pulsed-Gradient Spin-Echo NMR (PGSE-NMR) and Small-Angle Neutron Scattering (SANS). All samples exhibited a similar pattern in that, with increasing temperature, the self-diffusion coefficient increased, associated with a decrease in the hydrodynamic radius. According to the SANS data, both polymers, P6 and P7 scattered in same way at low temperature and data were fitted to polydispersed Gaussian coil. However, from SANS and PGSE-NMR data it was shown that P6 exhibited a smaller hydrodynamic radius than P7.

INTERFACIAL TENSION, INTERFACIAL RHEOLOGY AND CHEMICAL CROSSLINKING OF CATIONIC THERMOSENSITIVE MICROGELS AT THE OIL / WATER INTERFACE

***Tingting Liu* and Walter Richtering**

Institute of Physical Chemistry, RWTH Aachen University
Landoltweg 2, 52056 Aachen, Germany

Charged poly(N-isopropylacrylamide) (PNiPAM) microgels[1] have been proven to be able to stabilize Pickering emulsions with robust stability and responsiveness to temperature and pH changes.[2] Cationic imidazole- and amine-containing PNiPAM microgels are prepared via precipitation polymerization. The adsorption of the microgels to the oil/ water interface changes the oil / water interfacial tension and the mechanical modulus of the interfacial layer. In this work, this effect studied by a pendent drop tensiometer with an interfacial dilatational rheometry module will be presented. In the case of amine-containing microgels, glutaraldehyde was introduced to study the chemical crosslinking of the microgels at the oil-water interface. The crosslinking in an emulsion provides a way to prepare microgel capsules. The size and charges of the microgels are characterized by Dynamic Light Scattering (DLS) and zeta potential measurements, respectively. The emulsions are prepared using Ultra-Turrax. The droplet size distributions of the emulsions are evaluated by optical and fluorescent microscope and the droplet size distribution is monitored by Flow Image Particle Analyzer (FPIA). The capsules are visualized in a fluorescent microscope.

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ADSORPTION FROM POLYMER/SURFACTANT MIXTURES AT AN EXPANDING LIQUID INTERFACE

Anna Angus-Smyth* **[a,b], *R.A.Campbell*[a], *and C.D. Bain*[b]**

(a)Instiut Laue-Langevin, BP 156, 6 rue Jules Horowitz, Grenoble 38042, France.
(b)Department of Chemistry, University of Durham, South Road, Durham, DH1 1LE, UK.

Mixtures of oppositely charged polymers and surfactants are widely used in industrial applications as detergents, foam stabilisers, wetting agents, emulsifiers, and rheology modifiers. The extent to which polymers and surfactants interact in solution can determine both the bulk and interfacial properties of the system. Our interest is in the dynamics of such systems, rather than their traditionally studied equilibrium properties, as many applications of polymer/surfactant mixtures are employed under conditions far from equilibrium. The Overflowing Cylinder is an established platform for the study of adsorption dynamics from surfactant solutions, as it is based on the creation of a stable continuously expanding interface which can be studied using different techniques and for long time periods. Thus far, our studies of adsorption from polymer/surfactant systems have been restricted to ellipsometry measurements, but Neutron Reflectometry will also be employed.

Different combinations of polymers and surfactants exhibit very different adsorption behaviour on the overflowing cylinder. Interfacial adsorption has been shown to increase with surfactant concentration at low surfactant concentrations, for combinations of charged surfactants and polymers. At higher surfactant concentrations, several systems show a large decrease in the adsorbed amount, material appears to desorb from the interface. However, this behaviour does not necessarily correspond to the charge equivalence point as may be expected.

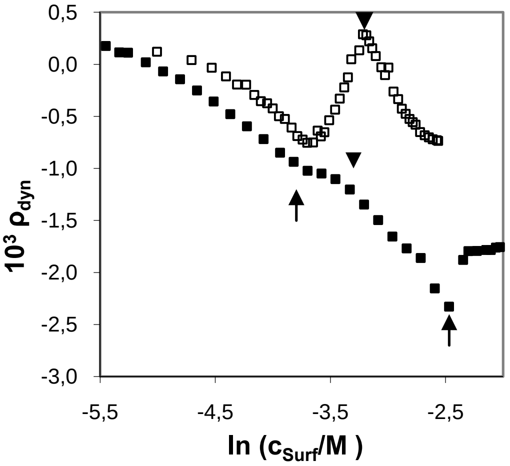

Figure 1 Ellipsometry data of C_{12}TAB/PSS[17k] [open squares] and PDMDAAC [100-200k]/SDS [closed squares], both at 100ppm. Downward pointing arrows indicate the charge equivalence points for the two solutions.

Different combinations of polymer and surfactant show quite different adsorption behaviour, even if they are expected to behave similarly as a consequence of the extent of their charge. For example, figure 1 displays the contrasting behaviour seen for the systems C_{12}TAB/PSS and PDMDAAC/SDS, which are both strongly interacting systems, although the former is anionic surfactant/cationic polymer and the latter is anionic polymer/cationic surfactant. This data shows there is more to the adsorption behaviour of these systems than simply the extent of charge. We intend to study these systems using Neutron Reflectometry and Ellipsometry, as well as other complimentary techniques, in order to examine their characteristic adsorption behaviour and the reasons behind it.

INTERACTIONS BETWEEN SURFACES IMMERSED IN MULTIVALENT OR MACROIONIC SALT SOLUTIONS

***Martin Trulsson*, Bo Jönsson, and Jan Forsman**

Theoretical Chemistry, Lund University

Using grand canonical Monte Carlo simulations in the primitive model we analyze the force between two macroscopic surfaces, both uncharged and charged, immersed in multivalent salt or macroionic solutions at various separations. These macroionic solutions can either be charged dendrimer or charge micellar solutions, where the macrion is either the dendrimer or micell. We first show, in good agreement with experiments, that multivalent salt adsorbs strongly to oppositely charged surfaces and can easily overcharge the surface. For the case of having two oppositely charged surfaces interacting with eachother one can thereby easily turn the interaction between them from attractive to repulsive, while increasing the concentration of the multivalent salt. We also find the amount of multivalent salt needed to overcharge to be highly dependent on the valency of the salt, in agreement with both theory and experiments. The force between neutral surfaces in a macroionic solution displays the well-known depletion attraction at short separations, but can be preceded by a stabilizing repulsive force at slightly larger separations at high concentrations of macroionic solution. Charged surfaces with opposite sign of the macroion adsorbs and orders the macroions, both along as well in between the surfaces. The nominal charge of the surfaces are easily overcompensated by the macroions. The apparent surface charge density do however change sign more than once, with a oscillatory decaying behavior. In these cases the force also displays a weak tendency to similar behavior. Having the same sign of the charge of the surfaces and the macroion also shows a non-monotonic behavior in the force. The force is dominated by the bare interaction of the surfaces (bare surfaces plus it's counterions), but shows a weak attraction due to depletion of the macroionic solution at intermediate separation.

ELECTRIC MULTIPOLE MOMENT FLUCTUATIONS IN POLAR LIQUIDS

Joakim Stenhammar[1], Per Linse1 and Gunnar Karlström[2]

[1]*Division of Physical Chemistry,* [2]*Division of Theoretical Chemistry*
Lund University, Sweden

E-mail: joakim.stenhammar@fkem1.lu.se

A general assumption in dielectric theory as well as in the different techniques used to simulate dipolar liquids is that the effect of higher order moments (quadrupole, octupole etc.) on the structure and energetics of the medium is negligible. In the present work, we have derived a general formula for the functional form of the probability distribution function P(μl) for a sphere of dielectric material, where μl represents one component of the fluctuating 2l-pole moment of the dielectric sphere. It turns out that the probability distribution is given by the Gaussian function exp(−αμ2), where α is a constant which depends on the dielectric permittivity ε of both the dielectric sphere and its surrounding.

The main focus of the work has been to identify how the value of the exponent α, and therefore the width of the multipole moment distributions, is affected when the dielectric sphere is brought from vacuum into a dielectric continuum of the same dielectric constant as that of the sphere. Our results show that there is a significant widening of the distributions for all the moments as the sphere becomes solvated. Furthermore, by calculating the free energy related to the interaction between the fluctuating 2l-pole and its surroundings we can partition the electrostatic part of the solvation free energy A^{solv}_{tot} of the sphere into separate parts originating from all the individual moments, according to

$$A_{tot}^{sol} = \sum_{l=1}^{\infty}(2l+1)A_l^{sol} \quad (1)$$

It turns out that the terms A^{solv}_{tot} are nearly constant as l become large, meaning that the sum of equation (1) is formally divergent, giving an infinite free energy salvation. Even though this result is true for a system exhibiting dielectric properties on all length term of equation (1) become effectively suppressed, leading to that the sum become convergent. Our results gain support by simulations, where we have calculated the exponent α from simulations of dipolar particles. The values of α agree well with the theoretical predictions for l = 1, 2, 3, 4 for different sizes of the dielectric sphere. Our results indicate that the higher order moments of the system by no means can be ignored in a molecular simulation. This should have a profound impact on, for example reaction field simulations, where the long range part of the interaction is approximated by the reaction field due to the dipole moment of the primary system, leading to that a significant part of the free energy of solvation is lost.

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EFFECT OF IONIC LIQUIDS ON ASPHALTENES PRECIPITATION FROM PETROLEUM FLUIDS

M. Boukherissa [1,2], M. Rogalski [1] , A.Diko [1]

[1] *Université Paul Verlaine, 1, Boulevard Arago, 57078, Metz*
[1,2] *Centre de Recherche et Développement CRD SONATRACH Boumerdès*
Université Paul Verlaine, 1, Boulevard Arago, 57078, Metz

Petroleum fluid can be divided into three parts: oil, resins and asphaltenes. This partition is very broad; every part of the petroleum fluid consists of a wide range of molecules with varying structures and properties. Asphaltenes are part of the heavy and polar fractions of crude oils defined as insoluble in the alkenes. One of properties of asphaltenes is to flocculate and precipitate in function of thermodynamic conditions and chemical composition of solvent. Asphaltenes self associates to form aggregates that flocculate in the well. This precipitation decreases the productivity of oil. In particular, asphaltenes containing crude oils are especially difficult to stabilize, but the increasing number of technical problems resulting from asphaltenes flocculation makes it necessary to develop new dispersing additives. Ionic liquids (IL) are a new class of ordered fluids having potentially dispersing capacity. In this work, we compare the performance of this additives with a resin model compound 4-nonylphénol. The length of the alkyl group gives to the ionic liquid amphiphilic, surfact-like character; chemical properties of the cation were modulated by introducing boronopropyl or allyl moieties. The anions were selected to give a suitable acidity and hydrophobicity. Therefore, ionic liquids considered may have a wide range of physical and chemical properties. Based on a single cation one obtains compounds having a different dispersing potential. Efficient dispersants should either delay the flocculation process or modify the thermodynamics or the mechanism of flocculation. In the second case, the physical properties of the precipitate are modified in a way to diminish harmful effects of the flocculation. Generally ILs accelerate flocculation kinetics. The flocculation becomes very rapid but only a part of asphaltenes precipitates. Moreover the granulometry of the precipitate was quite different; In this case very fine, crystal-like grains were obtained. We note that small quantities of water increase stability of asphaltenes in presence of IL.

RELEASE KINETICS AND MECHANISM OF A DISPERSED SPECIES IN WATER-IN-OIL EMULSIONS.

***C. Villatte*, JF Argillier, F. Leal Calderon**

IFP (Rueil-Malmaison, FR)
ISTAB - TREFLE (Bordeaux, FR)

We studied the release of a water-soluble dye dissolved in droplets of a water-in-oil emulsion (W/O). The oil phase was dodecane, the surfactant was sorbitan monooleate (Span 80) and the aqueous dispersed phase was a 0.5M NaCl solution (Φ_d=17%) containing the water-soluble dye Tartrazine E102. Two configurations were adopted in order to measure the release kinetics of the dye from the internal droplets to an external water phase:

- the W/O emulsion was introduced in a dialysis bag, this latter being immersed in a large aqueous reservoir containing NaCl.
- the W/O emulsion was in direct contact with the aqueous reservoir.

The NaCl concentration in the reservoir was varied to probe the influence of an osmotic pressure mismatch between the droplets and the reservoir. The release of the dye in the reservoir phase was followed using UV/Visible spectroscopy.

We found that the emulsions were very stable and that the rate of release of the dye was extremely slow, even in the presence osmotic mismatch (fig. 1).

The rate of release was faster when the emulsion contained in the dialysis bag was mechanically agitated because of coalescence events occurring between the droplets and the dialysis bag (fig. 2).

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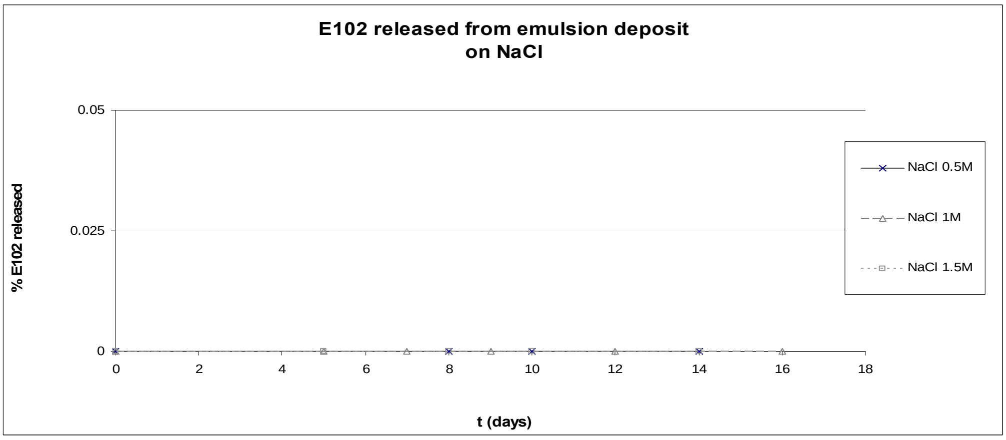

Fig. 1

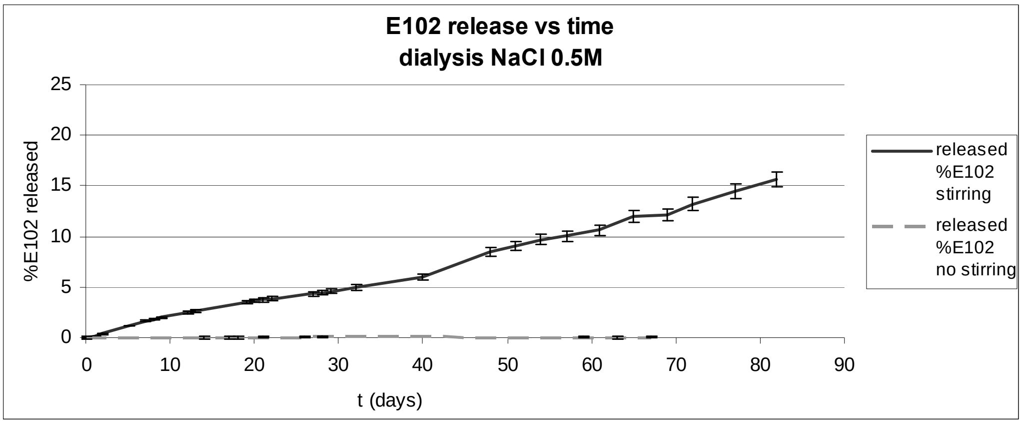

Fig 2

COMPARISON OF AQUEOUS CLAY SUSPENSIONS

Yannan Cui

School of Chemistry, Cantock's Close, Bristol BS8 1TS, UK

The behaviour of smectite clay particles is sensitive to particle concentration, ionic strength and presence of surfactants and polymers. In principle, these platelike clay particles could spontaneously form an aligned (nematic) state on increase of concentration. However this isotropic-nematic transition is not observed in most aqueous clay systems. Instead a gel tends to be formed before the nematic phase is reached. Four smectite clays were dispersed into water, dialysed and fractionated. Birefringence was only observed in aqueous nontronite suspensions. This nematic phase spontaneously aligned when places in thin flat capillaries. Adding amine-functionalised stabilisers resulted in increased platelet spacings.

PRODUCTION OF JANUS PARTICLES USING PARTICLE-STABILISED EMULSIONS

Karl M. Reed ***and Tommy S. Horozov***

Surfactant & Colloid Group, Department of Chemistry, University of Hull, Hull, England

It has been suggested that anisotropic particles which are non-spherical in shape and/or possess inhomogeneous surface composition (Janus particles) show potential for advantageous use in many applications. The fine tuning of their properties enable control over the behaviour of the particles and the particle interactions at either liquid interfaces or in bulk phases. For example, it has been shown that charged particles with opposite charge on each hemisphere can self assemble in a bulk liquid phase to form interesting structures[1], thus suggesting that such particles are promising building blocks for novel materials.

We explore particle-stabilised emulsions for the fabrication of Janus particles. Polymerisable oil-in-water emulsions stabilised by micrometer or submicrometer monodisperse silica particles have been used for this purpose. The advantages and drawbacks of this approach are discussed and compared to other methods for the preparation of Janus particles.

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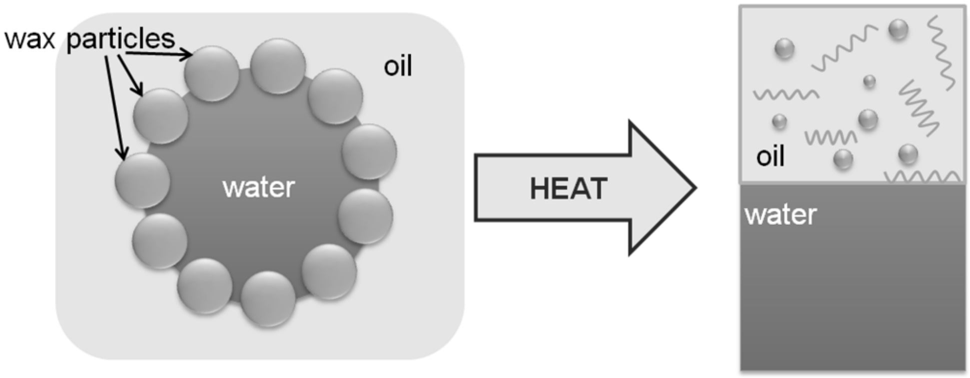
EFFECTS OF TEMPERATURE ON WATER-IN-OIL EMULSIONS STABILISED SOLELY BY WAX MICROPARTICLES

Bernard P. Binks and Anaïs Rocher

Surfactant & Colloid Group, Department of Chemistry,
University of Hull, Hull, HU6 7RX, U.K.;
b.p.binks@hull.ac.uk; www.hull.ac.uk/scg
E-mail: a.rocher@2006.hull.ac.uk

Particle-stabilised emulsions, well known as "Pickering emulsions", have been intensively studied these last years. Stability and type of emulsion can be controlled by changing the particle wettability, the pH or the salt concentration in the system, to cite a few examples. In this work, emulsions stabilised by micro-wax particles (7 to 10 µm) alone were investigated, and the temperature influence on the emulsion stability was described. Since particles are hydrophobic at the oil-water interface, as judged from the contact angle measurement, they act as effective emulsifiers of water-in-oil emulsions. The stability of these emulsions at different temperatures to both sedimentation and coalescence was studied in this work. It was found that it depends on whether particles are adsorbed to drop interfaces or not prior to temperature change. If drops are formed at room temperature, increasing the temperature of the emulsion subsequently leads to a progressive increase in the extent of coalescence as particles melt and cannot provide a sufficient barrier to drop fusion. This phenomenon occurs in the same range as that of the melting range of the particles alone. By contrast, emulsions prepared and stored at elevated temperatures are particularly stable in respect to coalescence. It is suggested that surface-active molecules, arising from the melting wax, adsorb to freshly created interfaces in these emulsions. The temperature effect may provide a means to control the coalescence tendency of wax-particle stabilised emulsions.



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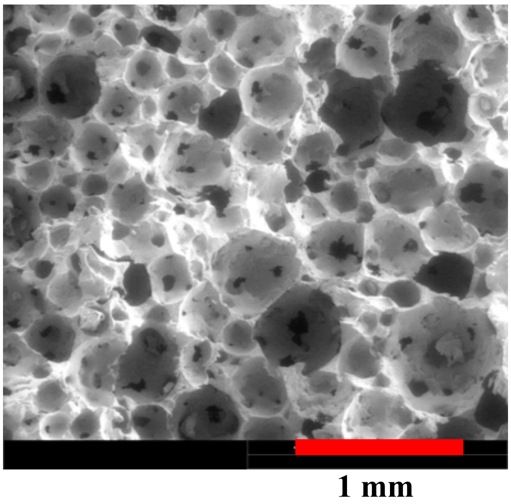
CONTROLLING MICROSTRUCTURE OF CERAMIC PARTICLE STABILIZED FOAMS

Chayuda Chuanuwatanakul**, **Carolina Tallon, David E. Dunstan and George V. Franks

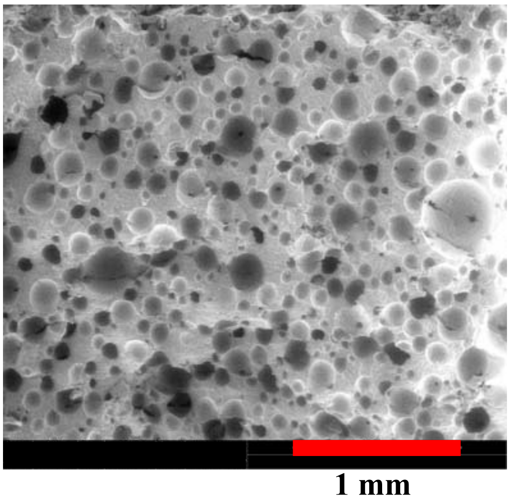
Chemical and Biomolecular Engineering, University of Melbourne, Vic, 3010, Australia

The microstructure of gelled ceramic foams is the most important factor which influences their properties such as the mechanical strength, the permeability, and the temperature resistance. The present work studies the microstructure, such as the amount of porosity, pore size and its distribution and the morphology of alumina (Al_2O_3) gelled ceramic foams. The microstructure of the gelled ceramic foams is affected by the surfactant concentration and type which is added to the ceramic suspension to cause the particles to become hydrophobic so that they stabilize air bubbles introduced by beating. It was found that the microstructure is changed from closed pore (bubble) morphology at the low surfactant concentration to opened pored (granular) morphology at the high surfactant concentration. (See the figures below.) The viscosity of the suspension before foaming points out that there is aggregation of the alumina particles at the higher surfactant concentrations. Moreover, the same trend of microstructure is obtained when the amount of carbon in the tail of surfactants is increased, but at the lower surfactant concentration.

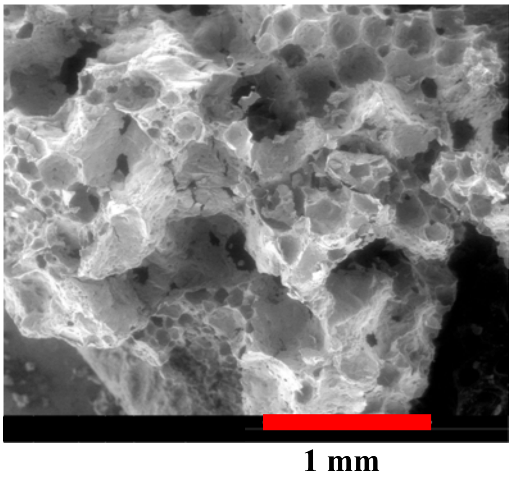
0.1 wt% of 1-butane sulfonate at pH 2.0



0.7 wt% of 1-butane sulfonate at pH 2.0



1.1 wt% of 1-butane sulfonate at pH 2.0



EFFECT OF SOLVENT QUALITY ON RHEOLOGY OF MICELLES OF MODIFIED TRIBLOCK COPOLYMER

Jorge Rodrigues Jr*, *Regina S. Nascimento

Instituto de Química, Universidade Federal do Rio de Janeiro, Brazil

Triblock copolymers that present two hydrophilic blocks of poly(ethylene oxide) and a hydrophobic one of poly(propylene oxide), PEO-PPO-PEO, behave as macromolecular surfactants. In water, these molecules usually tend to associate forming spherical micelles, due to the high hydration of the hydrophilic segments. However, the presence of salt and co-solvents changes the solvation of the polymer segments, and consequently its critical packing parameter (CPP). This effect leads, in some cases, to the formation of wormlike micelles that are flexible nanostructures. These systems can be applied in drug delivery systems, oil recovery and drilling fluids. In this work it was evaluated the effect of co-solvents and salt in micellar growth of modified triblock copolymers.

Two different products were synthesized through esterification of a commercial triblock copolymer, Pluronic P123, with lauric (C12) and oleic (C18.1) acids. Rotational and oscillatory rheological measurements of aqueous solutions containing the products were performed. Different co-solvents such as glycerin, ethylene glycol and poly(ethylene glycol) were used in order to evaluate their effect on micellar growth, inferred through the rheological results.

Aqueous solutions of P123 with co-solvents and in the absence of KCl had Newtonian behavior, suggesting the formation of spherical micelles. In the presence of KCl the system presented a significant shear thinning and viscoelastic behavior, suggesting the formation of wormlike micelles. However, in systems containing the modified copolymers this effect was observed even in the absence of KCl.

The growth of P123 micelles required both dehydration of PEO segments and swelling of PPO segment, promoted by KCl and co-solvent addition, respectively. However, the growth of the micelles of synthesized products just required the addition of an adequate co-solvent, suggesting a different micellar structure.

WATER-FUEL-MICROEMULSIONS

***P. Wulff*, L. Bemert, S. Engelskirchen, R. Strey**

Department Chemistry, University of Cologne,
D - 50939 Cologne

Pollution combusting fossil as well as biogenic fuels is still an unsolved problem. Addition of water in emulsified form showed by *Schwab et al.* [1,2] can reduce emissions. However, thermodynamicaly emulsions are not stable. Emulsions can not be stored for longer times impending simple appliance. The best way achieving thermodynamic stable mixtures of water and oil are microemulsions. So we developed water-fuel-microemulsion. Our microemulsions allow a drastic reduction of raw emissions in diesel engines [3]. The emission reduction using microemulsions proves to be higher than using emulsions. An explanation accompanies the better dispersion of water in oil with domain sizes about 10 nm, as we assume. The soot-nitrogen oxide-trade off (diesel dilemma) can be avoided. Engine tests using water-diesel-microemulsions showed a soot reduction of about 80 %, while nitrogen oxide emissions were reduced simultaneously by about 30 %. In this contribution we will present the development as well as combustion tests of water-fuel-microemulsions.

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HETEROGENEOUS POLYCONDENSATION REACTION IN AQUEOUS ENVIRONMENT

Johanna Bailey[1], Malin Christensen, Lennart Piculell[1], Ola J Karlsson[1,2]

[1]*Department of Physical Chemistry, Lund University, P.O Box 124, S-22100 Lund, Sweden*
[2]*MIP Technologies AB, Box 737, S-22007 Lund, Sweden*

Polycondensation reactions are traditionally carried out with solvents present at high temperature to drive off water and thereby increase the overall conversion. Recently it has been shown that it is possible to carry out polycondensation reactions in presence of water as suspension polymerizations o/w and w/o [1] or as miniemulsion polymerizations [2]. Various catalysts have been tried but the most successful ones have been surfactants with built in acidic catalytic functions (so called "Catasurf"). Enzymatic controlled miniemulsion reactions have also been reported [3].

In the present study polycondensation reactions have been performed as o/w suspensions using an acidic Catasurf. The reactions were carried out either in a glass reactor or a CPA202 calorimetric reactor (ChemiSens AB, Sweden) that enabled control of the reactions in real time. Solids content, Catasurf concentration, temperature (95 °C – 150 °C) and stirring rates were varied. Conversion, determined by titration, and the calorimetric data were used for kinetic evaluation and the resulting conversions varied between 75-95%.

The results from the calorimetric reactor showed a very fast initial reaction rate at high temperatures, i.e. an initial higher conversion, whereas lower reaction temperatures resulted in lower reaction rates but higher final conversions. The initial reaction scheme is dominated by the forward esterification reaction, but at longer times the deesterification backwards reaction becomes important and the polycondensation reaction reaches an equilibrium at a temperature dependent level of conversion. The conversion results were interpreted using a kinetic model taking interfacial catalytic activity into account.

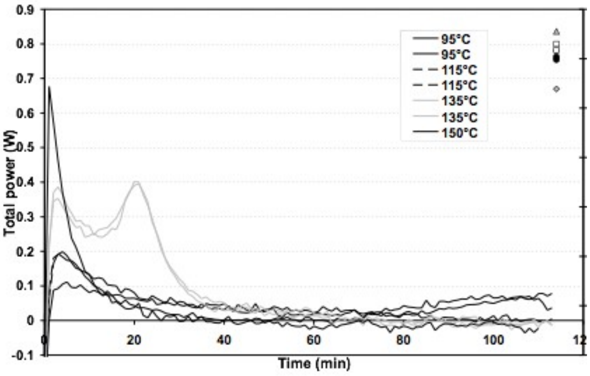

Figure: Lines show energy generated by the polycondensation reactions performed at 150, 135, 115 and 95°C. The conversion after two hours of reaction is shown in the upper right corner, ♦ 95°C,▲ 115°C, □ 135°C, ● 150°C.

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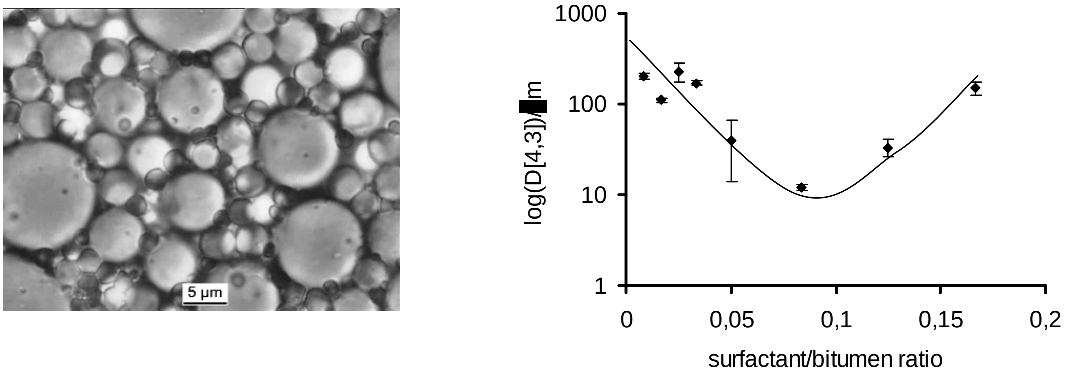
STUDY OF PREPARATION AND STABILIZATION OF O/W BITUMEN EMULSIONS

M. Martínez-Rodríguez[a,*], *J.M. Vilasau*[a], *C. Solans*[a], *F. Valor*[b], *J. Esquena*[a]

[a] *Instituto de Química Avanzada de Cataluña (IQAC),*
Consejo Superior de Investigaciones Científicas (CSIC), Barcelona, Spain,
[b] *Centro de Investigación Elpidio Sánchez Marcos (CIESM), Madrid, Spain*

Bitumen has important technological applications in the road construction due to its low water permeability, pronounced adhesion and good cohesive properties [1-3]. The temperature of application in road pavements can be greatly reduced by the use of O/W bitumen emulsions, allowing its application at low temperature [4]. However, the use of bitumen emulsions is restricted because these emulsions are generally not very stable. The high viscosity of bitumen leads to inefficient emulsification and big droplets are formed, which show fast sedimentation. In the present work, the main objectives are the preparation of bitumen emulsions and the study of emulsion stability. The bitumens were characterized by means of Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Electrophoretic Mobility and Small-Wide Angle X-Ray Scattering (SWAXS). Bitumen oil-in-water emulsions were prepared by Ultra Turrax agitation, using various cationic surfactants. The stability of the emulsions was assessed by direct visual observation, droplet size determinations and electrophoretic mobility measurements. The results obtained by thermal analysis and SWAXS confirmed that the bitumen samples are mainly amorphous, with a small fraction of crystalline components. The droplet size of O/W emulsions was studied as a function of surfactant concentration. The stability has been related to the particle size, greatly reducing the sedimentation by decreasing the particle size. The zeta potential of emulsion droplets is rather high, above +50 mV, which stabilizes against flocculation. The presence of positive charges, many of them attributed to the chemical nature of bitumen, plays an important role in emulsion stability.



A B

Fig 1. Examples of emulsions containing 60wt% bitumen. A) Optical microscopy image, B) Droplet size as a function of surfactant concentration.

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Acknowledgements

The authors greatly appreciate the finantial support from CDTI (CENIT 2007 – 1014 project).

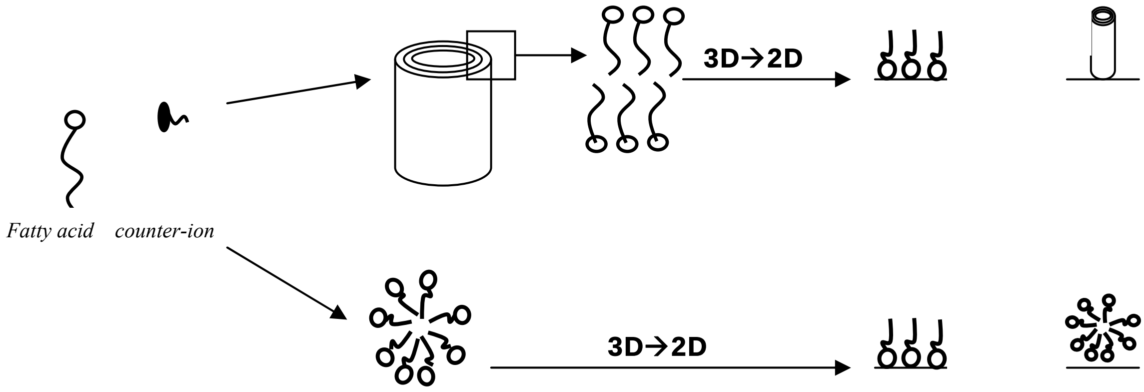
SELF ASSEMBLY OF HYDROXYLATED FATTY ACIDS IN SOLUTION: FROM VOLUME TO THE INTERFACE.

A-L.Fameau [1,2], B. Novales [1], B. Houinsou-Houssou [1], F. Cousin [2], F. Boue [2] and J-P. Douliez[1]

[1] *UR1268 Biopolymères Interactions Assemblages Inra,*
rue de la Géraudière, 44316 Nantes, France.
[2] *Laboratoire Léon Brillouin, CEA Saclay, 91191 Gif sur Yvette Cedex, France.*

The use of agricultural resources for industrial purposes will undoubtedly be one of the major challenges of the 21st century, both from the energy point of view (by contributing to the replacement of fossil fuels) and with respect to non-energy uses, resulting from the availability of organic "biosynthons" to the chemicals industry. This work on dispersions of fatty acids and hydroxylated derivatives forms part of these efforts in that it seeks to demonstrate the potential contribution these biological compounds of plant origin could make as a new class of surface active agents. The aim of the present work is to determine the impact of the structure of the fatty acid supramolecular assemblies on the interfacial properties, the formation and the stabilization of foams and emulsions. It is known that fatty acids and their hydroxylated derivatives are insoluble in water. The utilization of counter-ions allowed us to fully disperse the fatty acids, forming various supramolecular architectures from cones to tubes and twisted ribbons. We produced ethanolamine, arginine, guanidium chloride and tetrabutyl-ammonium salts of fatty acids. The interfacial, foam and emulsion properties of those systems vary with the polymorphism. For instance, the ethanolamine salt of fatty acids yielded incredibly stable foams whereas in the case of tetrabutyl ammonium, the foams rapidly collapsed. This was in agreement with dynamic surface tension measurements which showed that the adsorption rate and the surface tension at equilibrium were very different according to the fatty acid and counter-ion mixtures. Preliminary studies using neutron reflectivity allowed to obtain information on the thickness of the fatty acid layer at the Si/D_2O interface and at the air/ D_2O interface for some fatty acid/counter-ion mixtures. We are performing Langmuir monolayer experiments for studying the effect of the counter-ion on the fatty acid monolayers.

Those results show that the interfacial behaviour depends on the fatty acid/counter-ion system and should help us to further design generic rules for understanding the relation between the supramolecular assemblies and their properties at the interface.



CONTROL OVER MICROEMULSIONS WITH SOLVENT BLENDS

Olesya Myakonkaya*

School of Chemistry, University of Bristol
Cantock's Close BS8 1TS
E-mail: Olesya.Myakonkaya@bristol.ac.uk

It is known that AOT (sodium bis(2-ethylhexyl)sulfosuccinate) stabilized microemulsions, formulated in decane, display critical-type phase separation (T_{crit}) above a characteristic critical temperature.[1, 2] The phase separation manifests as two coexisting water-in-oil (w/o) microemulsion phases, which have essentially the same droplet size, but different volume fractions, as shown by small-angle neutron scattering (SANS).[2] At other temperatures a cloud-point separation (T_{cloud}) of a water-rich phase is more commonly observed, where a viscous, opaque surfactant-rich phase eventually separates from an oily phase.[3]

In this work the effect of solvent mixtures on phase behaviour of AOT - stabilized water-in-oil microemulsions has been studied by using heptane/dodecane, decane/dodecane, octane/dodecane and nonane/undecane blends. Small-angle neutron scattering was employed to explore the effect of changing the solvent composition on the microemulsion properties, especially near the cloud point (T_{cloud}) and the liquid-liquid critical separation (T_{crit}). It is shown that droplet interactions can be strongly influenced by changing the solvent blend compostion, which has implications for the locations of observed phase boundaries. Of particular interest is the use of carefully selected solvent blends, which have the effect of lowering T_{crit} by up to 6 º C from the value found in pure decane.

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DEVELOPMENT AND PHYSICO-CHEMICAL PROPERTIES OF "BALANCED CATALYTIC SURFACTANTS"

***Marion Collinet-Fressancourt**, Véronique Nardello-Rataj, Jean-Marie Aubry*

Université Lille 1, Sciences et Technologies, LCOM, UMR CNRS 8009,
Equipe « Oxydation & Physico-Chimie de la Formulation », Cité Scientifique, Bât C6,
59655 Villeneuve d'Ascq, France.
E-mail: m.fressancourt@free.fr

The concept of Balanced Catalytic Surfactants (BCS) has been developed to answer the problem of substrate-oxidant incompatibility met in catalytic H_2O_2-based oxidations of organic compounds. This new class of surfactants has been designed according to two essential properties: i) they result from the electrostatic association of a catalytic ion able to interact with H_2O_2 and an ionic surfactant; ii) they are "balanced", that is to say they provide "optimal" three-liquid-phase microemulsions (µems) in simple water-oil-surfactant systems.

If the first feature can easily be achieved, the second one requires resorting to physico-chemical considerations for the experimental development of the process. According to the Hydrophilic Lipophilic Deviation (HLD) concept,[1] optimal three-phase µems, whose main properties are a maximum cosolubilization of water and oil due to an ultra-low water/oil interfacial tension and a zero-curvature interface, are obtained for HLD = 0 (see eq. 1).

$$\mathbf{HLD = \sigma + Ln[salt] - kEACN + t\Delta T + a[coSurfactant]} \qquad \textbf{eq. 1}$$

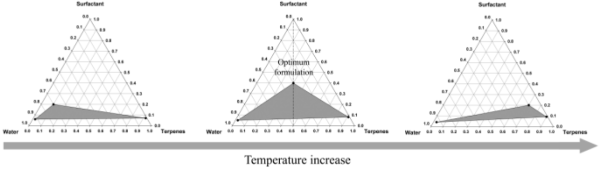
Thus catalytic surfactants are said balanced when their chemical structure allows providing spontaneous three-phase µems without addition of salt or co-surfactant at room temperature. Such chemical structures are characterized by an effective packing parameter (P_{eff}) equal to 1 and correspond to an amphiphilic molecule with similar affinity for water and oil. We present here how dimethyldioctylammonium molybdate have been designed as a BCS on the basis of physico-chemical investigations. The aqueous phase behavior (T_{Krafft}, cmc, liquid crystals formation) have been determined for a series of quaternary ammonium molybdate with various chain lengths and numbers of long alkyl chains. In the same way, behavior in water-oil-surfactant mixtures have been investigated thanks to the elaboration of optimization phase diagrams with oil as a scan variable. These diagrams could be compared in terms of surfactant efficiency, i.e. the minimal amount to form a single-phase µem, and surfactant PACN value (Preferred Alkane Carbon Number), i.e. the EACN of the oil providing the optimal formulation at 25 °C. Finally, effect of H_2O_2 addition on self-aggregation and behaviour in water-oil-surfactant mixtures of dimethyldioctylammonium molybdate has been evaluated since H_2O_2 addition modifies the packing parameter of the surfactant as peroxomolybdate species are formed. This aspect was examined through the elaboration of ternary phase diagrams. This usefulness of such systems is finally demonstrated through the "dark singlet oxidation" of several hydrophobic substrates.

FROM MICRO TO MACROEMULSION FORMULATION: THREE-PHASE BEHAVIOUR OF TERPENE / NON-IONIC SURFACTANT / WATER SYSTEMS

***M. Durand*, F. Bouton, V. Nardello-Rataj, J-M. Aubry**

LCOM, Equipe Oxydation et Formulation, UMR CNRS 8009, ENSCL,
BP 90108 F-59652 Villeneuve d'Ascq, France, *jean-marie.aubry@univ-lille1.fr*

In order to provide a pleasant smell and to fulfil consumer needs, perfumes are added to numerous end-use products. The composition of such systems is always a challenge for the formulator as fragrance raw materials tend to destabilize emulsions and other delivery systems. Moreover fragrance or essential oil based microemulsions are still a hot field for fragrance companies, the formulation of alcohol-free perfumes or disinfecting microemulsions based on essential oils being still under research. To be commercially valuable, microemulsions have to be achieved with low surfactant contents. In order to understand the key mechanisms involved in the formulation of such systems and consequently to minimise the proportion of surfactants, phase behaviour of several terpene / water / surfactant systems have been determined. Terpenes and terpenoids have been preferred as they constitute one of the widest families among fragrance raw materials, which can be ranked from low to relatively high polar oils. Amphiphilic species, such as some terpenoid alcohols, may even be preferentially adsorbed at the interface and act as lipophilic linkers, increasing surfactant efficiency. Ethoxylated alcohol surfactants (CiEj) have been used as they do not require the addition of any further components (salt or co surfactant) to exhibit three phase behaviour. Results have been described according to Winsor's classification and quantitatively expressed by the HLD (Hydrophilic Lipophilic Deviation) concept. The optimum formulation, which corresponds to the maximum solubilization of oil and water in the microemulsion phase, has been accurately determined by modelling the Gibbs triangle as a function of the temperature. This unusual approach is particularly valuable as it allows the determination of temperature/surfactant concentration section of the Gibbs prism, also named fish diagram, at any Water to Oil Ratio (WOR).



At the optimum formulation, the HLD equation can be expressed as:

$$HLD = Cst + c.T^{*} - k.EACN = 0$$

where EACN stands for Equivalent Alcane Carbon Number, and T* the optimum temperature. The EACN has been used to characterise and classify terpenes. By comparing the EACNs of oils exhibiting a more or less complex chemical structure, some general tendencies were drawn with regard to the structural effect (unsaturation, cyclisation, branching) [1]. Finally a prediction model of EACN is proposed based on two theoretical descriptors.

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INTERACTION STUDIES OF SYNTHETIC POLYMERS WITHIN MUCIN SOLUTIONS: USE OF PULSED-GRADIENT SPIN-ECHO NMR AND SMALL ANGLE NEUTRON SCATTERING

Paola Occhipinti[1,2]***, Peter Griffiths***[2] ***and Mark Gumbleton***[1]

Welsh School of Pharmacy, Cardiff University, King Edward VII Avenue Cardiff, CF10 3XF, Wales, UK.School of Chemistry, Cardiff University, Main College, Park Place, Cardiff, CF10 3AT, Wales, UK.

Polymers with a linear, branched or dendritic architecture are being exploited as nano-sized hybrid therapeutics and nano-sized drug delivery systems with the purpose of improving the delivery and targeting of pharmaceutical agents[1]. However, these 'polymer therapeutics' must overcome many biological barriers to reach the target site. Epithelial surfaces are coated in a mucosal bio-gel which has a fundamental role in limiting the exposure of human tissues to external particles. As such, this mucus layer potentially represents a barrier to the efficient delivery of therapeutics to mucosal epithelium and beyond[2, 3]. Mucin glycoproteins are the main organic component of mucus and are responsible for the gel-like character of this bio-polymer[4]. Therefore, understanding the interaction and/or diffusion of macromolecules with this mucosal media is fundamental. Small-angle neutron scattering (SANS) has been used to examine the structure of mucin and changes in its structure induced by the addition of the synthetic polymers. In a SANS experiment, a neutron beam is elastically scattered by a sample and the resulting pattern is analysed to provide information about size and shape of the scattering centres. Also, pulsed-gradient spin-echo NMR (PGSE-NMR) experiments have been performed to investigate the diffusion of probe polymers in mucin media. PGSE-NMR is non-invasive, non-destructive but most importantly the chemical specificity of NMR enables the behaviour of each component within the mixture to be identified and analysed in a single experiment. Scattering data are reported as the intensity of the scattering, I(Q), against the wavevector, Q, a function of the scattered angle. Scattering from porcine gastric mucin (PGM) solutions were treated most appropriately by a model in which the scattering intensity, I(Q), was considered as a contribution of three terms: $I(Q) = I(Q)_{Lorentzian} + I(Q)_{monomer} + I(Q)_{Q^{-4}}$. The fitting model describes the mucin as a gel network with a long correlation length (ζ) of 665 nm in which the polyelectrolyte side chains of the mucin are considered as polydisperse spheres with a radius of 10 nm. No change in scattering occurred when linear PEG 10K g mol^{-1} and 100K g mol^{-1} were added to mucin solutions, indicating no significant interaction between the PEG and mucin. By contrast, the addition of PAMAM dendrimer G2 (MW=3.26K g mol^{-1}) and G4 (Mw= 14.21K g mol^{-1}) induced pH dependent changes in the mucin scattering and by inference, conformation, suggesting an electrostatic interaction with the mucin glycoproteins. Diffusion studies indicated that the PAMAMs experienced a greater decrease in the rate of diffusion through mucin when compared to PEG.The scattering data from mucin solutions in the presence of PEG polymers supported the restricted diffusion of these probe polymers observed in the bio-gel by PGSE-NMR. In fact, the hindered diffusion of the PEGs in the mucin gel network was mainly due to the physical obstruction of the polymer by the mucin network. The greater delay in the diffusion rate of PAMAM dendrimers in mucin solutions observed indicated a specific interaction between the dendrimers and the mucin polyelectrolyte, as anticipated from the scattering data. However, the interaction between the dendrimers and the mucin resulted pH-dependent as it is function of the charge that the dendrimers and the mucin exhibit at the different pHs.

The combination of SANS and PGSE-NMR enables us differentiate specific and non-specific interaction between polymers and bio-polymer.

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SQUEEZING F-ACTIN: A MICROSCOPY STUDY

***Angeliki Tsigkri**, Pavlik Lettinga and Zvonimir Dogic*

Research Center Jülich –Instiut of Solid State Research - Soft Matter
Jülich D-52425 Germany
Department of Physics, Brandeis University, Waltham 02454 Massachusetts USA

We study the interaction of F-actin which is a semiflexible biopolymer, with a wall, as induced by the addition of small Dextran polymers. In this way we address the competition between the excluded volume and the conformational entropy. By changing the dextran concentration we are able to define different regimes with respect to the presence of the F-actin at the surface. These regimes are probed by direct observation of the fluorescently labeled F-actin with total internal reflection microscopy, a technique which allows measuring the distance of the filaments from the glass surface.

At low dextran concentration, i.e below $\varphi = 0.088$ is the 'free' regime. At this low volume fraction, the osmotic pressure by the dextran is not enough to push the F-actin to the surface so in this case only few filaments appear shortly at the surface. As the dextran concentration is increased up to $\varphi = 0.094$, the 'short-residence' regime is found. Now the filaments stay at the surface for over 60% of the recording time and by more than 50% of their total contour. The chain ends though, remain free to dangle away from the surface. At higher dextran, up to $\varphi = 0.100$ we find the regime of almost 100% residence of the filaments at the surface. The chain ends desorb now less but a profound 'looping' activity is observed. This means that the central parts of the filament are lifting up from the surface forming the so-called 'loops' that can appear for one or more images in a row. At even higher $\varphi > 0.100$ the filaments stay constantly at the surface without desorbing in the ends or looping in the middle. This is the so-called 'push-down' regime.

X-RAY REFLECTOMETRY OF SEMI-FLUORINATED AND HYDROGENATED SURFACTANTS ON MICA

Francesca Speranza,[1] ***Kashif Hussain,***[1] ***Peixun Li,***[2] ***Laurence Bouchenoire,***[3] ***Robert M.J. Jacobs,***[2] ***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
3. ESRF, 6 Rue Jules Horowitz, 38043 Grenoble, France

Semi-fluorinated surfactants (semiF's) are an especially interesting class of compound and, thanks to their unusual characteristics, they can be found in numerous industrial applications. Many of these applications rely on the interfacial activity of these semiF's. Over the past decades, grazing angle incidence X-ray reflectometry (XRR) has been applied effectively to obtain structural information on surfactants adsorption at the solid-liquid interface, and in this study we apply XRR to mica due to X-ray's insensitivity to mica's birefringence.

Due to its readily achievable molecular smoothness, mica is a preferred model substrate in many imaging and force measurement techniques such as AFM, SFA and electron microscopy (EM)[1]. Our XRR measurements will provide unique complementary structural characterisation for these techniques. Using a unique homemade liquid cell, we have performed synchrotron XRR measurements of semiF and hydrogenated surfactants on mica at the European Synchrotron Radiation Facility (ESRF) beamline BM28 in Grenoble. Three different systems have been studied: 1). Salt ($NaNO_3$) effect on the adsorption of three surfactants on mica: one hydrogenated Gemini surfactant ($(C12TAB)_2$-H12) and two semiF Gemini surfactants with fluorinated spacers, ($(C12TAB)_2$-H4F4H4 and $(C12TAB)_2$-H3F6H3). 2). Competitive adsorption between hydrogenated and semiF single-chained surfactants from three surfactants mixtures: C16TAB-F4H11(d)TAB, C16TAB-F5H10TAB and C18TAB-F8H6(d)TAB). 3). Interactions at the mica-water interface between a semiF surfactant, CsPFN, and a polyelectrolyte, poly(ethyleneimine) (or PEI). From the experimental results, the adsorption behaviour of these surfactants and PEI-CsPFN complexes on mica can be obtained and the thickness, density and roughness of the self-assembled surface structures can be calculated.

Acknowledgement: Financial support from the EPSRC and ESRF is acknowledged.

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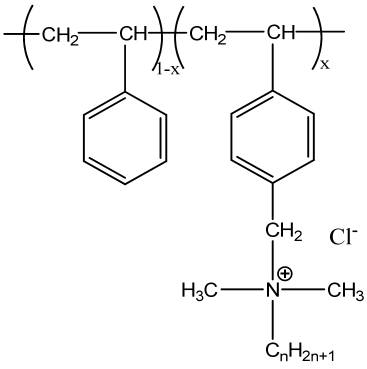
STRUCTURATION OF AMPHIPHILIC COMB-LIKE COPOLYMERS BASED ON STYRENE IN AQUEOUS SOLUTION STUDIED BY SCATTERING TECHNIQUES

***Wissam Moussa*, Christophe Chassenieux and Olivier Colombani**

Polymères, Colloïdes, Interfaces UMR CNRS 6120
Université du Maine, Avenue O. Messiaen, 72085 Le Mans cedex 09, France

e-mail: wissam.moussa.etu@univ-lemans.fr

Amphiphilic polymers are increasingly used as additives in aqueous formulations. Their role is to control the rheology and the colloidal stability in such complex fluids. Their properties are directly related to their self-organization capacity and have stimulated an increased number of studies in the past decade [1–5]. Of course, the self-organization capacity is related to the molecular architecture of the amphiphilic polymer, i.e. the nature and the distribution of the hydrophilic and hydrophobic units along the polymer backbone. In aqueous solution, the hydrophobic units associate leading to an increase of the viscosity of the solution, due to this property they are referred to as Associative Polymers or also Hydrophobically Modified Water Soluble Polymers. We will report on the behavior of a series of copolymers that we have synthesized by free radicalar polymerization a family of amphiphilic polymers (figure 1) based on both hydrophobic (styrene) and amphiphilic units (chloromethylstyrene modified with a long tertiary amine) where the content of each comonomer (x) and the size of the alkyl side chains (n) can be varied. We will focus on a copolymer with $x = 0.45$ and $n = 12$. At relatively low concentration, they form of highly viscous solutions in water. Moreover, the solutions show birefringence that is an indication of the formation of liquid crystalline mesophases. A Small Angle Neutrons Scattering study helped us in concluding that such a mesophase is lamellar.



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WHY DOES CONTACT ANGLE DEPEND ON THE METHOD OF MEASUREMENT?

Carmen Lucía Moraila Martínez, Miguel Cabrerizo Vílchez, Miguel Ángel Rodríguez-Valverde

Biocolloid and Fluid Physics Group,
Department of Applied Physics, University of Granada,
Campus of Fuentenueva, Granada, E-18071, Spain.

Just recently some underlying principles of the dynamic process of colloidal drying have been published. Contact line pinning is usually observed in evaporating drops of colloidal suspensions. Hence, the measurement of meaningful values of receding contact angle is a priority task.

In this work, we measured low-rate dynamic contact angles using a non-linear variation of drop volume in order to force the uniform motion of the three-phase contact line over a wide region of the solid sample. At constant speed, the balance of interfacial forces along the contact line is hold. This dynamic state is theoretically equivalent to the impending drop motion where in fact the advancing and receding contact angles are referred to.

Commonly, the low-rate dynamic contact angle measurements are achieved with a continuous linear variation of drop volume. However, this way, the contact line is continuously accelerated. This kinetic energy change can relax the system to other metastates different to the advancing and receding ones.

Due to the limitations of stepper-motor–driven syringe pumps, our strategy is based on the discontinuous variation of drop volume in time at increasing/decreasing motor speeds. We assured that the capillary number of the contact line was small enough (≈10^{-6}). Moreover, the time between each addition/removal of liquid was intentionally chosen greater than the interfacial relaxing time of drop. Hence, the growing/shrinking drop was not altered by Hydrodynamics.

We measured the low-rate dynamic contact angles of distilled water on different polymer surfaces with uncontrolled roughness (as provided by the supplier), using the conventional method of volume variation and our proposal at different contact line speeds. We applied the technique Axisymmetric Drop Shape Analysis-Profile using a microinjector Hamilton ML500.

The non-linear volume variation provided values of advancing and receding angle more representative of the system, with minor error and averaged over a greater area of the solid surfaces (see Fig 1.).

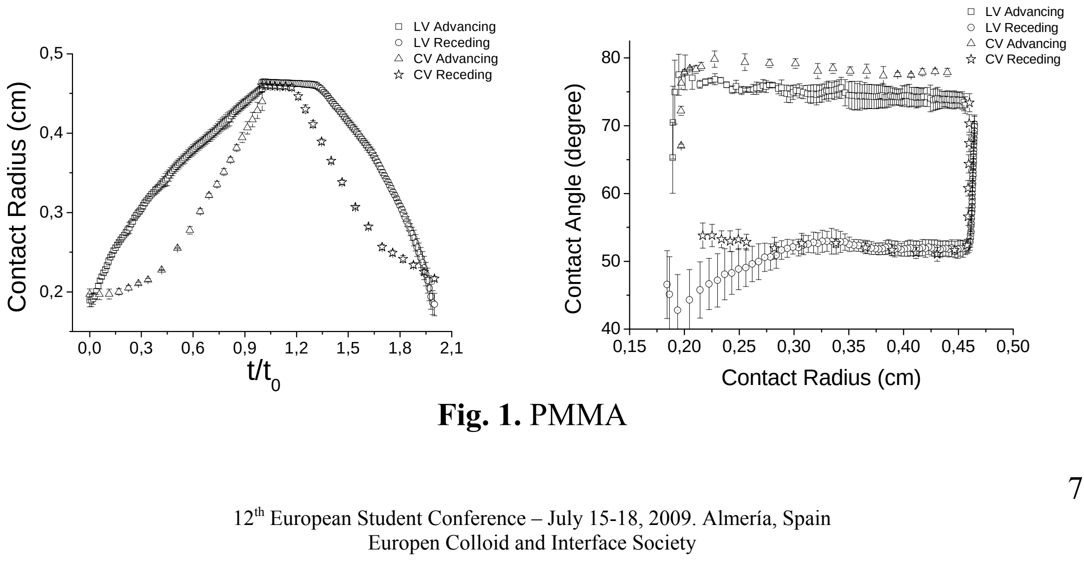


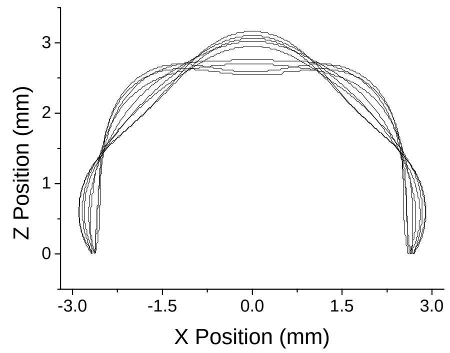
Fig. 1. PMMA

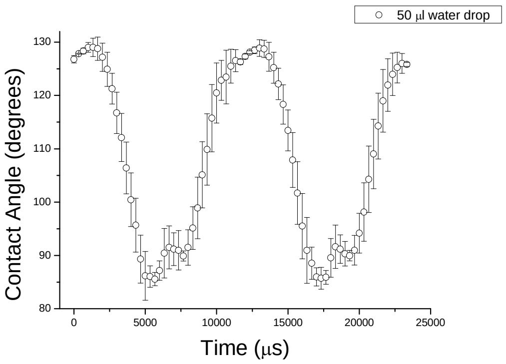
DESIGN OF AN EXPERIMENTAL APPARATUS TO MEASURE EQUILIBRIUM CONTACT ANGLE OF LIQUID DROPS PLACED ON SOLID SURFACES (WETTABILITY) USING CONTROLLED VIBRATION

Felipe II Guerrero-Barba, Carmen Lucía Moraila-Martínez, Miguel Ángel Rodríguez-Valverde and Miguel Ángel Cabrerizo-Vílchez

Department of Applied Physics, University of Granada,
Campus of Fuentenueva, Granada, E-18071, Spain.

The equilibrium contact angle of real solid surfaces is the thermodynamically meaningful experimental angle. This angle represents the true thermodynamic equilibrium configuration of the system (i.e. the global energy minimum) and so, it is directly related to the concerning specific interfacial energies. However, the equilibrium contact angle is hardly observable since the system can occupy different metastable states. Recently, inspired in the work of Andrieu et al. [1], several authors reported that equilibrium contact angle can be experimentally accessible through the vibration-induced relaxation of the solid-liquid-vapor system. Following this strategy, we designed a set up which allows observation of a drop placed on a vibrating surface with a high speed digital camera (Phantom Miro 4). The camera acquires side-view images of the vibrating drop at 3000 fps. The substrate is vibrated with a mechanical vibrator (SF-9324 Pasco). The input signal (frequency, amplitude) is generated by a sound-card (SoundMAX HD Audio) and amplified accordingly. These components are controlled by a PC. The test surfaces are easily interchangeable. In this work, we present preliminary results of water drops on Teflon in order to visualize the resonance for different drop volumes.





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SURFACE SPECTROSCOPY OF SERIES OF UNSATURATED FATTY ACIDS AT LIQUID – AIR INTERFACE

***Petru Niga*, Eric Tyrode and Mark W.Rutland**

School of Chemical Science and Engineering, Royal Institute of Technology, Sweden.

Vibrational Sum Frequency Spectroscopy (VSFS) employed to study the interfacial behavior of fatty acids films at liquid – air interface. The vibrational spectra of the fatty acids films were investigated at different surface pressures on a Langmuir through device. The degradation of the vinyl stretch was studied spectroscopically for the first time with VSFS for a series of unsaturated fatty acids with increasing number of unstaurations per alkyl chain. Monitoring the change in the relative intensity of vinyl vibrational mode we have followed the degradation process for different periods of time. The more unstaurations per alkyl chain the faster the oxidation process goes. We have found that under humid Nitrogen atmosphere the unsaturated fatty acid monolayer are stable for longer time. We have also established that the degradation process is not driven by atmospheric molecular Oxygen and we believe that the oxidation reaction is triggered tiny amounts of atmospheric Ozone. An important parameter of the degradation process is the surface pressure at which the fatty acid monolayer is compressed. The slope of the degradation process is increasing with increasing the surface pressure of the fatty acid film. The change into conformation of the alkyl chain under different surface pressures was also followed spectroscopically. We have found that the fatty acids molecules undertake a more upright configuration with increasing the surface pressure in the monolayer.

ORDERING OF NANO FIBRILLATED CELLULOSE (NFC)

Andreas Fall[1], Magnus Norgren[1], Janne Ruokolinen[2], Emily Cranston[3] Lars Wågberg[1]

[1] Fibre and polymer technology, Royal Institute of Technology, KTH Stockholm, Sweden
[2] Applied Physics, Helsinki University of Technology, Espoo, Finland
[3] Surface and Corrosion Science, Royal Institute of Technology, KTH Stockholm, Sweden

Individual fibrils and fibrillar networks of NFC have been studied with atomic force microscopy (AFM), cryo transmission electron microscopy (Cryo-TEM), scanning electron microscopy (SEM) and polarized optical microscopy (POM). From image analysis the NFC fibrils where found to have dimensions of diameter around 5nm and length 100 – 1000nm, see figure 1 and 2. Another goal with the study has been to investigate what effect change in ionic strength and/or pH of the NFC solution has on network formation and on fibrillar form. This was shown to affect NFC network formation and under the right circumstances it induces string like network formation. The string networks could be up to hundreds of micrometers long. No effect on individual fibrillar form was seen from changes in ionic strength or pH. Instead the fibrillar form was shown to be affected of the structure of the anchoring polymeric layer when absorbed on a surface. The effects were compared against prediction of effects from theoretical models with good consistency. To conclude the results of the study shows that it is possible to create order networks of NFC fibrils and that surfaces with controlled NFC form can be created. This can be used to create hierarchically ordered materials from nanometre up to micrometre level. Possible usages are within light weight materials and membrane materials.

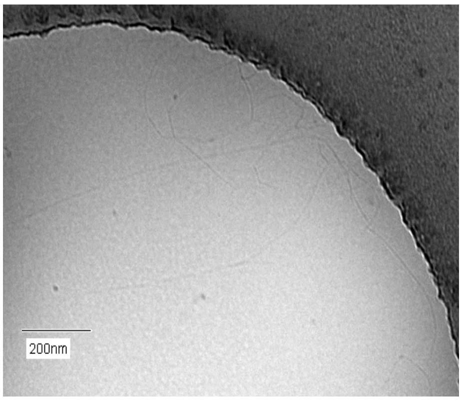


Figure 1: Cryo-TEM image of NFC

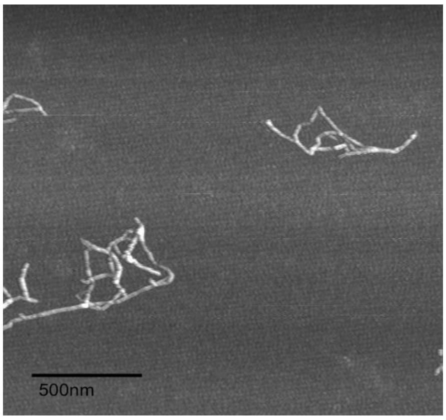


Figure 2: AFM image of NFC

DYNAMIC ELECTRON MICROSCOPY STUDIES OF SUPRAMOLECULAR BIOMATERIALS

Anna Jansson

Division of Microscopy and Microanalysis, Department of Applied Physics, Chalmers University of Technology, Gothenburg, Sweden

The transport of water and other soluble compounds is important in applications such as controlled release of drugs in pharmaceuticals, release of flavour and vitamins in foods and water management in personal care products. Therefore, there is a demand for improved control of the mass transport properties of materials. Such properties are governed by morphology and interactions with the transported substance. Supramolecular materials in particular tend to be structurally heterogeneous at a range of different size scales, and as such possess a hierarchy of structures that govern the overall rate of transport. While the diffusion rate will depend on the structure at the nanometre scale, the extent of convective flow through the material will depend on the micro- and mesoscale heterogeneity and the occurrence of structural gradients. Upon wetting and subsequent swelling, the structure of the material will change and the mass transport properties will be affected. Studies of the transient structures created by these dynamic events may yield information useful for predicting the mass transport as a function of structure, and may ultimately help in the design of new materials tailored for specific applications.

The present project focuses on the characterisation of supramolecular biomaterials and the investigation of the transient structures formed during dynamic hydrating or dehydrating experiments. Two materials will be evaluated during the initial stages of the project, namely a two-component polymer film for controlled drug release and a system of cellulose fibres. The analysis methods used are environmental scanning electron microscopy (ESEM) and transmission electron microscopy (TEM). Over the past decade, ESEM has been increasingly used to characterise soft materials, particularly under hydrating conditions, both due to its compatibility with non-conducting materials and its ability to stabilise water-containing samples. By varying the gas pressure inside the sample chamber and the temperature of the sample, a specimen may be kept at equilibrium with its surroundings, or may be subjected to controlled evaporation or condensation of water. Furthermore, TEM provides the possibility of reconstructing the three-dimensional structure of the materials through electron tomography, as well as performing dynamic experiments by means of a newly developed sample holder.

MECHANICAL PROPERTIES OF SELF-ASSEMBLED MESOSCALE FIBERS

Daniel Kluge[a], Frank Abraham[b], Stephan Schmidt[a], Hans-Werner Schmidt[b], Andreas Fery[a]

[a]Department of Physical Chemistry II, University of Bayreuth, Universitätsstraße 30, 95444 Bayreuth, Germany

[b]Department of Macromolecular Chemistry I, University of Bayreuth, Universitätsstraße 30, 95444 Bayreuth, Germany

Fibers with diameters in the range of nm to µm have a large field of applications, mainly for tissue engineering and composite materials. The mechanical properties of the fibers are crucial for all possible applications and therefore there is a need for suitable characterization methods. We performed AFM (atomic force microscopy) based bending experiments to investigate fibrillar self-assemblies of aromatic benzene trisamides. Our approach on this technique uses the force mapping mode of the AFM to enhance the reliability of the measurements. With models of beam theory we were able to show that a clamped configuration was valid for our experiments. We successfully determined the flexural rigidity of the self-assemblies. The obtained value of their elastic modulus is comparable to semi-crystalline polymers. The presented approach can be applied for other fibrillar systems and marks a starting point for further modeling and a more detailed understanding of fiber deformation on the nanoscale.

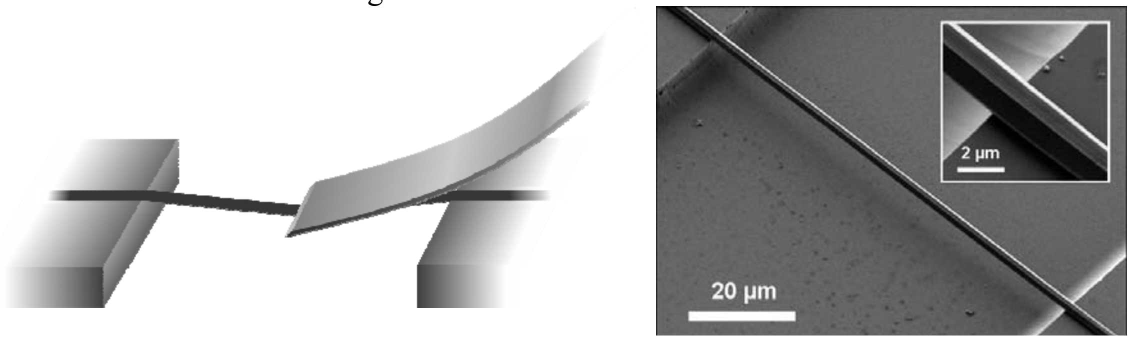


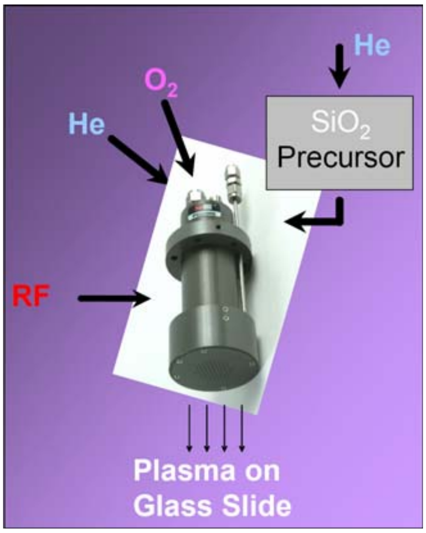
Figure 1: Schematic setup of the bending experiments and SEM image of a fiber stretched over a channel of the structured substrate.

MULTILAYER SILICA DEPOSITION BY ATMOSPHERIC PLASMA

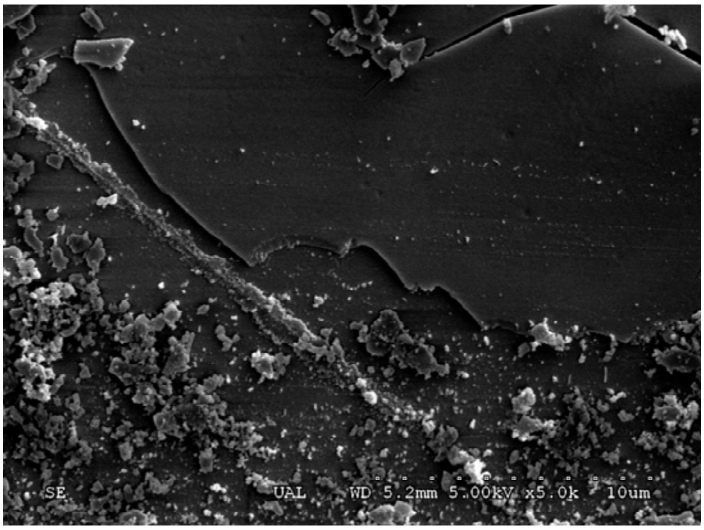
Andrés Granados del Águila*, *Iván J. Suárez*, *A. Fernández Barbero

Group of Complex Fluid Physics, Department Applied Physics
University of Almería

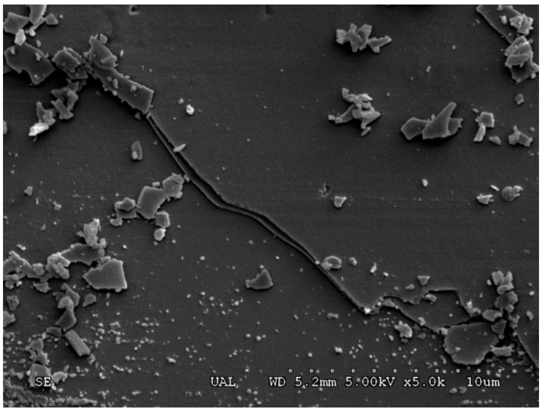
Atmospheric plasma has been used to deposit thin layers of SiO_2. Surface deposition is performed though a nozzle in which gases (Helium and Oxigen) and a volatile precursor are injected. Plasma is produced after RF application. Finally, the scramble is projected on a glass slide using a 3D robot. The speed deposition and distance between the nozzle and the target surface are critical parameters to be controlled. A change of the standard conditions provoke important variations on the final geometry, thickness and layers properties. Using this technique, we have improved a method to grow multilayer packs from hexamethyldisilazane $(CH_3)_3SiNHSi(CH_3)_3$ as precursor with the aim of modifying the optical properties. Multilayer formation is monitored by SEM (Scanning Electronic Microscopy) and AFM (Atomic Forces Microscopy). In this poster we show several multi-layers composed by 15-20 nm thick single layers.



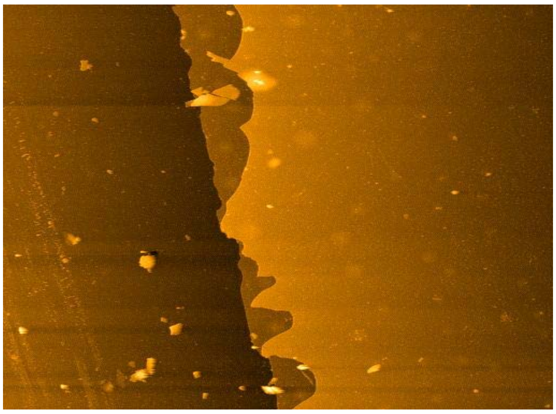
Experimental setup



Silica single layer (SEM)



Silica multilayer (SEM)



(AFM)

AFM SINGLE-HAIR-FORCE SPECTROSCOPY: “IN-SITU” MEASUREMENTS

***Eva Max*[1], *Claudia Wood*[2], *Frank Bartels*[3], *Albert Sugiharto*[3], *Andreas Fery*[1]**

[1]*Department of Physical Chemistry II, University of Bayreuth, Germany*

[2]*Care Chemicals, BASF SE, Ludwigshafen, Germany*

[3]*Polymer Physics, BASF SE, Ludwigshafen, Germany*

e-mail: eva.max@uni-bayreuth.de

Hair Care products like shampoos and conditioner play an important role for our health and wellbeing. Our aim is to provide methods that allow quantifying friction and interactions as a consequence of hair treatment on the single-hair level. We have developed an approach in which hair-hair interactions can be detected using Atomic Force Microscopy (AFM) force spectroscopy. We are using hair fragments for our measurements, which were cut from so called standard Caucasian hair and immobilized on tipless AFM cantilevers. Our technique allows “in-situ” friction force measurements in a closed liquid cell to quantify hair’s friction properties. For this the torsion of the modified cantilevers is monitored in aqueous environment (see Fig.1). Different active agents of hair-care products can be added in situ, rinsing cycles can be performed and the resulting changes in friction and interactions can be monitored. As well, parameters like salt concentration or temperature can be controlled.

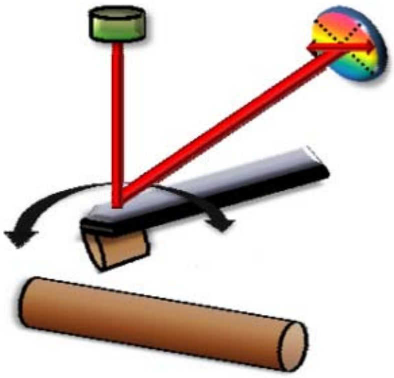


Fig.1. Scheme of the set-up for measuring AFM single-hair-hair interactions

SURFACE INTERACTIONS BETWEEN FUNCTIONAL BIOMIMETIC THIN FILMS

***Niklas Nordgren* and Mark W. Rutland**

Department of Chemistry, Surface and Corrosion Science,
Royal Institute of Technology,
Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden

The growing interest of miniaturising different applications in the fields of biotechnology and electronics has led to issues concerning surface force interactions and tribology. In order to study how these nano-regime phenomena depends on changes in the surrounding environment techniques such as the AFM colloidal probe (Ducker et al., 1991) and QCM-D (quartz crystal microbalance with dissipation) (Rodahl et al., 1997; Plunkett et al., 2003; Nordgren et al.,2008) can be employed on polymer grafted model surfaces.

In this study quartz crystal microbalance with dissipation (QCM-D) was utilized to monitor the grafting of end functionalised poly-dimethylaminoethyl methacrylate (pDMAEMA) to gold forming a brush-like layer. The dual-responsive nature of the brush was further investigated using atomic force microscopy in colloidal probe mode between two such polymer bearing surfaces. Force and friction measurements were carried out at various pH and Temperatures. It was shown that the different solvent conditions induced significant changes in the conformation of the grafted polymer chains. At low pH long-range electrosteric repulsion was present resulting in high lubrication at the interface. Deswelling of the layer was observed with increasing pH yielding higher friction. When raising the temperature above the critical solution temperature (LCST) the system turned attractive with a small friction reduction interpreted as being due to a lowering of the surface roughness.

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Nordgren, N., J. Eklöf, Q. Zhou, H. Brumer and M. W. Rutland (2008). Top-Down Grafting of Xyloglucan to Gold Monitored by QCM-D and AFM: Enzymatic Activity and Interactions with Cellulose. Biomacromolecules. 9, 942-948.

Plunkett, M. A., Z. Wang, M. W. Rutland and D. Johannsmann (2003). Adsorption of pNIPAM Layers on Hydrophobic Gold Surfaces, Measured in Situ by QCM and SPR. Langmuir. 19, 6837-6844.

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MICROMECHANICS AND ADHESION PROPERTIES AND OF SMART POLYMERIC MICROBALLOONS STUDIED BY COLLOIDAL PROBE AFM AND MICROINTERFEROMETRY

Melanie Pretzl[1*], *Paulo Fernandes*[1], *Andreas Fery*[1]

1) University of Bayreuth, Department of Physical Chemistry II, 95440 Bayreuth , Germany

email: melanie.pretzl@uni-bayreuth.de

Gas filled polymer microballoons represent novel mesoscopic devices with high potential use as multifunctional agents for enhanced ultrasound imaging and controlled drug delivery [1-3]. These soft colloidal hollow particles consist of telechelic polyvinylalcohol and show a remarkable shell life, a variety of functionalizations of their surface and diverse loading possibilities of the core.

For their medical application micromechanics and adhesion are the key properties to understand and control the microcontainers stability and its behavior in contact with surfaces. To study how mechanic and adhesion properties are affected by functionalizations, temperature, external forces and pH we used a colloidal probe AFM in combination with microinterferometry under controlled conditions (temperature, solvent, pH). This set-up is a powerful tool to identify qualitatively adhesive surfaces and to analyze quantitatively in detail the microballoons deformation behavior, contact area, adhesion forces and the shape of deformed and undeformed microballoons.

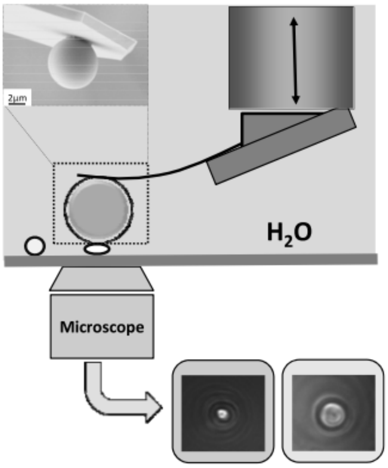

Figure 1 Scheme of colloidal probe AFM combined with optical inverted microscope.

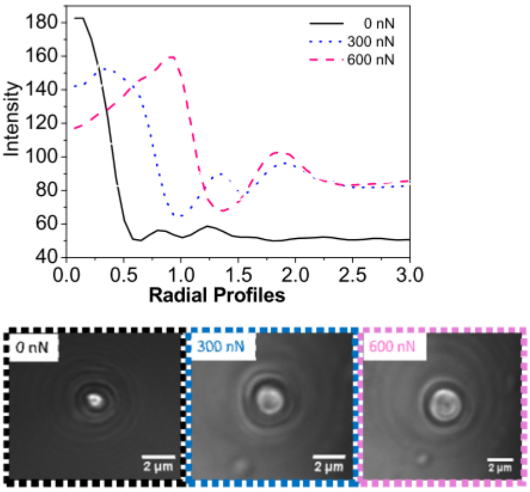

Figure 2 Radial profiles of a typical interference pattern of undeformed and deformed microballoons.

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INVESTIGATION OF MULTIVALENT INTERACTIONS BETWEEN HOST-GUEST MOLECULES BY COLLOIDAL PROBE FORCE SPECTROSCOPY

***Öznur Kaftan**, Andreas Fery*

University of Bayreuth, Department of Physical Chemistry II, Germany

Atomic force microscopy (AFM) is a useful tool for studying surface interactions by means of force-distance curves. Such curves can provide valuable information on local material properties and almost all kind of forces, such as capillary, Coulomb, Van der Waals, double layer, solvation, and hydration, hydrophobic, specific and steric forces can be investigated.[1] Among them specific forces has wide application in biological systems. Those specific interactions are non-covalent forces that generate very strong adhesion between molecular groups. In such specific interactions the molecular geometry plays an important role, like “lock and key” model the molecules fit together in a precise stoichiometry. In order to measure specific forces with AFM, it is necessary to functionalize the tips by covering them with one of the two molecules under study. If a spherical particle of typically 2-20 µm diameter is attached to the end of the cantilever instead of a sharp tip[2] the technique is called colloidal probe technique.

Measurement of single molecule specific interaction using force microscopy is extensively studied in last decades. However, multivalency phenomena is getting attractive currently as a powerful and versatile self-assembly pathway especially in biochemistry.[3] Self-assembled structures based on many cooperative weak, reversible, and sometimes short-lived interactions, can be thermodynamically stable or may even become kinetically stable, depending on the number of interactions. To enlighten the mechanism of these types of interactions can provide more understanding on natural systems. Because they govern many interactions between proteins and small molecules, between proteins or antibodies and cell membranes, between viruses and cells, etc.[4]

In this study we have chosen the host-guest interaction between small molecules to investigate the multivalent specific interaction. Among the numerous host-guest complex types, those formed by β-cyclodextrin (B-CD) and hydrophobic adamantane (AD) moieties present the advantage to have a high binding energy and steric selectivity with regard to the size of the host-guest moieties. The host B-CD and the guest AD molecules are grafted on a positively charged natural polyelectrolyte, namely chitosan, in various degree of substitution to vary the number of molecules. These modified chitosans are attached to the flat and colloid probe surface to study the specific interaction. Due to strong interaction between B-CD and AD peeling-off event has been observed in mild binding conditions. Various surface chemistry techniques were applied to have stronger binding of the macromolecules on both surfaces and obtained force curves were evaluated to calculate the adhesion forces and energies of host-guest molecules.

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TEMPERATURE RESPONSIVE CELLULOSE DERIVATIVES

***Rasmus Bodvik* and Per Claesson**

Department of Chemistry, Surface & Corrosion Science, KTH, Royal Institute of Technology, Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden

This project aims at understanding the temperature-responsive properties of cellulose derivatives, in particular methyl cellulose (MC) and hydroxypropyl methyl cellulose (HPMC). For these polymers, small structural changes result in markedly different solution properties at elevated temperatures. Some polymers show a decreased solubility with increasing temperature. Such negative temperature response can be achieved by grafting various types of groups to cellulose. The phase separation, which occurs upon heating, results in markedly changed solution viscosities. The transition from viscosity increase on heating to viscosity decrease at elevated temperatures can be induced by very small changes in the polymer architecture. We want to understand why.

We have been studying methyl cellulose and hydroxypropyl methyl cellulose. The bulk properties of these polymers in aqueous solution were investigated at different temperatures. A comparison between small-angle X-ray scattering (SAXS) and rheology measurements indicated a very good correlation between an increase in aggregation and changes in viscosity for all three celluloses. For MC a sudden increase in viscosity was seen at 45 °C. HPMC first underwent a drop in viscosity (at 65-75 °C) and then a rise shortly after. The size of the polymer aggregates at different temperatures was investigated using light scattering. HPMC formed large aggregates at a well defined temperature. In contrast, the size of MC rose continuously. Cryo-TEM imaging showed a change from small particles to larger aggregates for both MC and HPMC. In the case of MC, the aggregates grew to a certain point, where a network rapidly started to form.

MOVE IT, SHAKE IT, ANYWAY YOU WANT IT: BUILDING OPTICAL TWEEZERS TO INITIATE NUCLEATION IN COLLOIDS

Richard Hanes

Heinrich-Heine Universität, Düsseldorf (Germany)

e-mail Richard.hanes@uni-duesseldorf.de

We have combined a spatial light modulator (SLM) and galvanometer-mounted mirrors into an optical tweezers set-up. This provides great flexibility by allowing us to create an array of traps which can be moved in a smooth and fast way. To optimise the performance we investigated the effect of incidence angle on the SLM with respect to phase and intensity response. Although it is possible to use the SLM at an incidence of 45 degrees, smaller angles give a more constant response with a full 2pi phase shift. We calibrate the traps using an active oscillatory technique and a passive probability distribution technique.

HUMECTANTS IN HYDRATION OF LIPID MEMBRANES

Agnieszka Nowacka[1]***, Stéphane Douezan***[1,2]***, Daniel Topgaard***[1]***, Emma Sparr***[1]

[1]*Physical Chemistry, P.O.B. 124, Lund University, SE-221 00 Lund, Sweden*
[2]*ESPCI, 10 rue Vauquelin, 75231 Paris, France*

In skin products, urea and glycerol are used as moisturizers. The aim of this work was to see how those solutes affect lipid membranes under dehydration. As a model membrane system a simple system of dimyristoyl-phosphatidylcholine (DMPC) at low water content was used and investigated with the use of Nuclear Magnetic Resonance (NMR). The system was studied both without the "moisturizers" and in presence of various amounts of either urea or glycerol. The technique used was solid state NMR under the conditions of Magic Angle Spinning (MAS). Three types of experiments were performed: insensitive nuclei enhanced by polarization transfer (INEPT), cross polarization (CP) and direct polarization (DP) experiments[3]. These measurements give information on the more fluid parts of the phospholipid chain, more solid parts of the phospholipid chain and the quantitative relations of carbons respectively. Results show that the presence of urea or glycerol in the system enables the lipid bilayers to maintain in a more fluid lamellar phase down to much lower relative humidities compared to the pure lipid system. Results from sorption microbalance and DSC experiments are consistent with the ones obtained by NMR, proving that the phase transition from liquid crystalline to gel lamellar phase occurs at lower relative humidity for the systems with urea or glycerol[4].

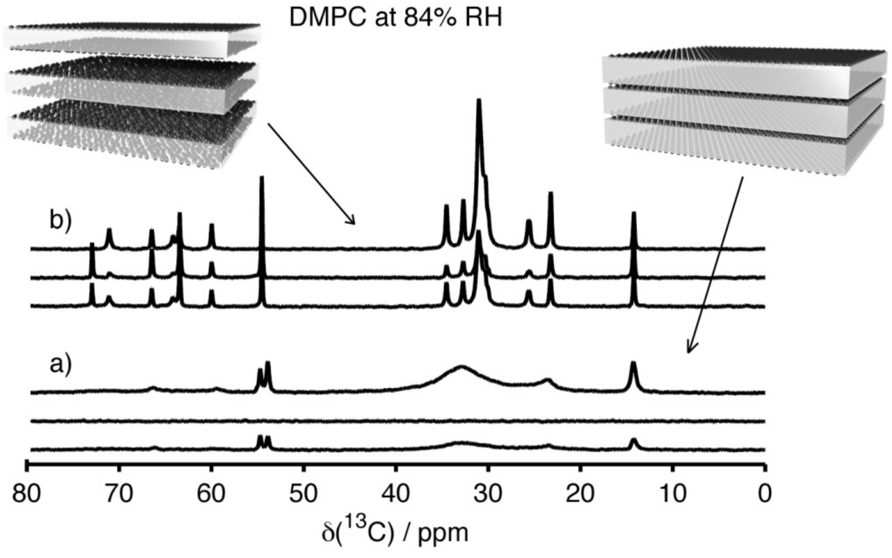

Figure 3 The spectra of DMPC at Relative Humidity of 84%: a) pure DMPC – spectra of a crystalline sample, b) 10% of glycerol – spectra of a sample in liquid crystalline phase. Bottom – DP, middle – INEPT, top – CP. By comparing the intensities and peak positions it is possible to determine the phase.

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[3] A. Nowacka, R. W. Martin, D. Topgaard, *Manuscript in preparation*
[4] A. Nowacka, S. Douezan, D. Topgaard, E. Sparr, *Manuscript in preparation*

THE PHYSICOCHEMICAL CHARACTERISATION OF POLYMER THERAPEUTICS- SOLUTION CONFORMATION OF HYDROPHOBICALLY MODIFIED HPMA COPOLYMERS

Craig James ***and Alison Paul***

School of Chemistry, Cardiff University, Cardiff, UK;

The term polymer therapeutics is used to describe a series of nano-sized medicines in which a therapeutic agent such as a drug or a protein has been chemically bound (such as in polymer-drug conjugates and polymer-protein conjugates) or physicochemically associated (such as in polymeric micelles and polyplexes) to a biocompatible, water-soluble polymer in order to enhance the solubility of the drug whilst reducing toxicity [1]. Of these systems, polymer-drug conjugates have found particular clinical success as anti-cancer therapeutics, enabling targeted delivery and controlled release of drugs to sites of disease within the body. There is increasing recognition that the conformation adopted by these conjugates during transport and delivery processes can significantly influence therapeutic performance [2][3].

Using the clinically relevant copolymer hydroxypropyl methacrylamide (HPMA) containing either 5 or 10 mol % of Gly-Phe-Leu-Gly peptidyl side-chains as our starting point, we are systematically investigating the influence of drug chemistry on HPMA-drug conjugate solution conformation. Here we present data where these peptidyl side chains are either end-capped with amino propanol, or have been conjugated to either the simple aromatic nitrophenol or the simple hydrocarbon dodecylamine. This group of systems allows us to investigate the influence that factors such as hydrophobicity and π-π stacking have on conformation of these model polymer-drug conjugates. Small-angle neutron scattering (SANS) has been used to characterise the size and shape of these conjugates in solution and evidence of uni-molecular, core-shell morphology obtained using contrast variation SANS experiments.

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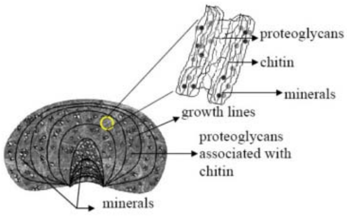
SULPHATED PROTEOGLYCANS ARE RESPONSIBLE FOR THE SACRIFICIAL BONDS IN RED CLAW LOBSTER (CHERAX QUADRICARINATUS) GASTROLITHS

Ranjith Krishna Pai†, Kjell Jansson†, Hiroyasu Mizuno‡, Niklas Hedin†, M. Soledad Fernández§, José LuisArias§, Mark Rutland‡ and Lennart Bergström†

Material Chemistry Research Group, Department of Physical Inorganic and Structural Chemistry, Arrhenius; Laboratory, Stockholm University, Stockholm, Sweden. ‡Division of Surface Chemistry, School of Chemical; Science and Engineering, Royal Institute of Technology, Stockholm, Sweden. §Faculty of Veterinary Sciences and CIMAT, University of Chile, Santiago.

The unusually high fracture energy of many biomaterials is related to the microstructure of the inorganic-organic composites and their ability to dissipate energy. Recent work has shown that the interface between the inorganic and organic components and the formation and sequential breakage of sacrificial bonds is of pivotal importance1. In this study we focused on gastrolith in red claw lobster which is a composite of calcium carbonate and organic materials, including proteoglycans associated with chitins2. A systematic study of adhesion for the gastroliths was performed by pull-off measurements using an atomic force microscope as a function of the amount of calcium carbonate in gastroliths. The relative amount of the inorganic phase was systematically varied by a demineralisation procedure and the chemical composition and microstructure was analysed by scanning electron microscopy (SEM) and EDS. Proteoglycans associated with chitin were also purified from the gastrolith and the adhesion force was investigated. The magnitude of the adhesion force and the adhesion energy was analysed quantitatively and related to a formation of elongated strands of the proteoglycans. This study gives clear evidence that the sulphated proteoglycans are responsible for the sacrificial bonds in red lobster gastroliths.



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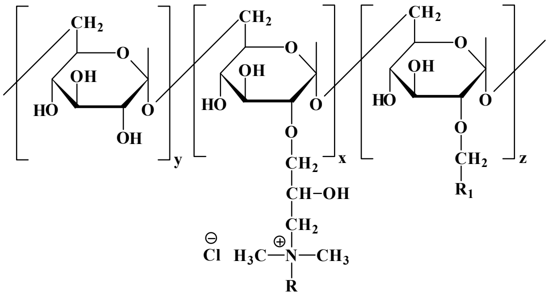
VISCOSITY AND FLUORESCENCE STUDIES OF SOME CATIONIC AMPHIPHILIC POLYSACCHARIDES

Magdalena C. Stanciu*, Marieta Nichifor, Luminita Ghimici, Bogdan C. Simionescu
”Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania

**Corresponding author: e-mail: cstanciu@icmpp.ro*

A series of cationic amphiphilic polysaccharides (Scheme 1) has been synthesized and the balance between electrostatic and hydrophobic intra- or/and intermolecular interactions occurring in salt free aqueous solutions was investigated by means of capillary viscometry and fluorescence techniques, as a function of polymer characteristics (DS, length of the substituent R, M_W and nature of polysaccharide backbone). Huggins plots of viscometric experimental data had a more or less parabolic profile, with a minimum in semi-dilute domain, indicating the predominance of one of interactions for each concentration regimes. Intrinsic viscosities ([η]) were calculated by fitting the viscometric experimental data obtained in dilute regime (C_p < 1g %) to Rao and Heller equations. Critical association concentrations (***C****cr*) for hydrophobically modified polymers were determined from viscometric data obtained in concentrated regimen by Utracki-Simha method. The examination of fluorescence excimer emission for Py-labeled dextran and nonradiative energy transfer process between Np to Py chromophores attached to separate dextran chains, confirmed the existence of intermolecular associations between polymer hydrophobic groups at C_p much lower than ***C****cr*, showing that the fluorescence techniques are more sensitive tools and allow to detect hydrophobic associations and conformational changes in the amphiphilic polymers at microscopic level, while viscosity reflects only global changes in the polymer dimensions. According to these results, all the interactions can be found in each concentration domain irrespective of chemical composition, but we could establish chemical structures (DS, R length) for which a predominance of one interaction can be observed over the entire concentration range: electrostatic (pure polyelectrolytes), hydrophobic intra-molecular (polysoaps) hydrophobic inter-molecular (associative polymers).



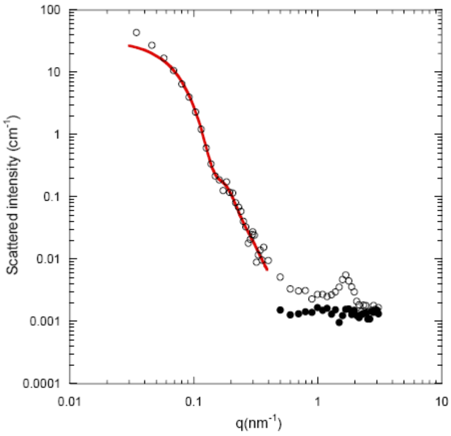
Scheme 1. Chemical Structure of Cationic Amphiphilic Dextrans
R = Et (C_2), Bu (C_4), Octyl (C_8), Dodecyl (C_{12}) or Cetyl (C_{16});
R_1 = pyrene (Py) or naphtalene (Np);
Polymers used in viscometric studies : z = 0 ; DS = $100x/(x + y)$, mol %
Polymers used for fluorescence measurements: z = 0.1-0.5 mol%

POLYELECTROLYTES/SURFACTANT COMPLEXATION IN BULK AND AT THE AIR-WATER INTERFACE: CASE OF DNA AND CARBOXYMETHYLCELLULOSE

Gabriel Espinosa-Pérez**, **Armando Maestro-Martín**, **Samuel Guillot***, **Eric Raspaud**,*
François Boué*, **Dominique Langevin***

Laboratoire de Physique des Solides UMR 8502, Université Paris Sud Bât 510, 91405 Orsay Cedex, France (espinosa@lps.u-psud.fr, raspaud@lps.u-psud.fr, langevin@lps.u-psud.fr)
**CRMD-UMR 6619, CNRS-Université d'Orléans, 1B, rue de la Férollerie, 45071 Orléans Cedex 2, France (samuel.guillot@cnrs-orleans.fr)*
*** Laboratoire Léon Brillouin, CNRS/CEA, CE Saclay 91191 Gif-sur-Yvette Cedex, France (francois.boue@cea.fr)*
**** Departamento de Química Física, Universidad Complutense de Madrid, 28040 Madrid, Spain (armanmaestro@quim.ucm.es)*

Studies of aqueous solutions of a cationic surfactant (dodecyltrimetylammonium bromide) and polyelectrolytes of opposite charge (DNA, carboxymethylcellulose) will be presented. Various techniques have been used: optical microscopy, scattering of light and neutrons for the bulk studies, surface tension and surface rheology for the surface studies. The bulk aggregates grow with increasing surfactant concentration. The aggregates are rod-like in the case of DNA, and their growth has been analysed after neutron scattering experiments. At large surfactant concentrations, micron-sized aggregates are formed and the aggregation kinetics has been followed and observed to be extremely fast. The influence of the mixing procedure on the aggregate size will be described. The corresponding mixed layers at the air-water interface are strongly viscoelastic. Their rheological properties have been studied using a rheometer equipped with a biconical disk in a wide range of frequencies and amplitude of deformation. The data will be presented and discussed in relation with the bulk properties.



Left figure: Typical SANS spectrum of aggregates. The solid line is a fit. Closer to the precipitation boundary, the aggregates can be observed by optical microscopy (right figure).

EFFECT OF α-HELICAL PEPTIDES ON LIPOSOME STRUCTURE AND LEAKAGE

Karin Reijmar

Department of Physical and Analytical Chemistry, Uppsala University, Box 579, SE-751 23 Uppsala, Sweden, Fax +46(0)18-471 36 54

karin.reijmar@fki.uu.se

We have studied the effect of the antibacterial peptides melittin, alamethicin and magainin II on different POPC-based liposomes.

The affinity of melittin for the lipid membranes was estimated using a fluorescent based binding assay. The emission spectrum of melittin is sensitive to the polarity of the environment of the melittin trypthophan residue. When melittin associates to lipid bilayers the less polar environment of the bilayers leads to a shift of the melittin emission spectrum to lower wavelengths as compared to the spectrum of melittin free in water. The shift was used to construct association isotherms describing the affinity of melittin to lipid membranes. Alamethicin does not possess any thrypthophan residue and can therefore not be investigated using the fluorescence-based method. Instead we used CD measurements for this peptide. In this technique the helical content of the peptide is measured. When the peptide is free in solution the helicity is low, but when it is attached to the liposome the helical content is enhanced. Peptide induced leakage was measured by adding the peptides to liposomes loaded with the fluorescent dye carboxyfluorescein.

Investigations using cryo-transmission electron microscopy (cryo-TEM) were made to observe the structural effect on the liposome dispersions upon addition of the peptides. Melittin and alamethicin both induce liposome rapture and formation of open bilayers. The binding assays were used to correlate the structural effects observed with cryo-TEM to the leakage of carboxyfluorescein.We can see from our investigations that cholesterol, as well as negatively charged lipids, have a large influence on both the binding and the leakage.

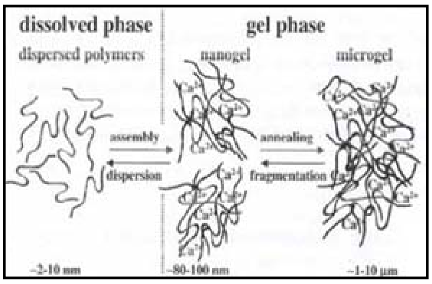
MICROGEL IN AQUATIC ECOSYSTEMS

Ignacio P. Mazuecos ***[1,2], A. Granados del Águila[1],***
Isabel Reche[2], Antonio Fernández-Barbero[1]

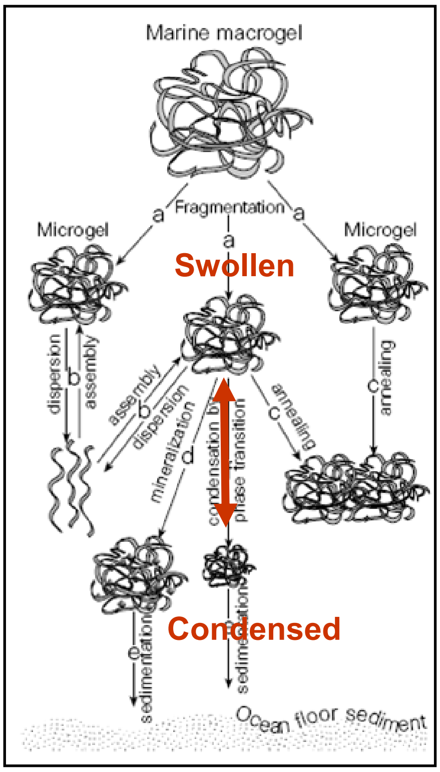
[1]Group of Complex Fluid Physics, Department Applied Physics, University of Almería
[2]Department of Ecology, University of Granada

Dissolved organic matter (DOM) can assemble to form microgel particles, which evolves in the time to form macro-structures, such as TEPs (Transparent Exopolymer Particles) or marine snow. All of these gels are of high ecological importance, especially in the carbon cycle, since they show a phase transition from collapsed to swollen states. These natural gels (in condensed phase) sink and sediment into the water column. This fact is of special relevance since it is one of the most important mechanisms for carbon removing in aquatic ecosystems.

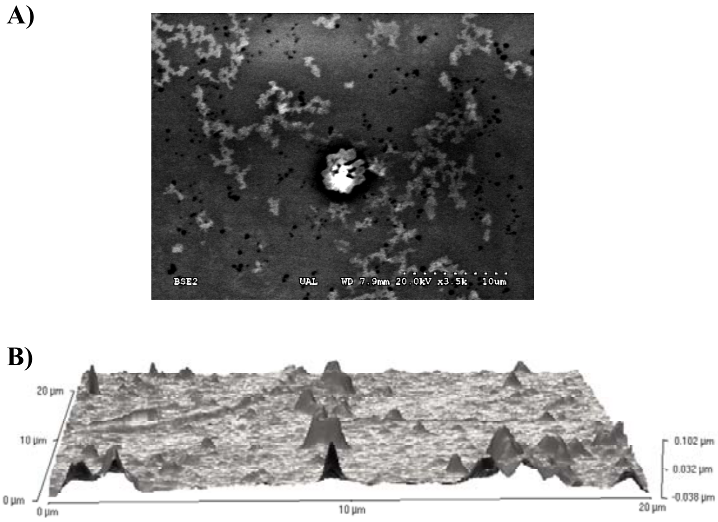
In this work we show the influence of ph on the dynamics of DOM microgels. Variations in the mean particle size have been monitored by dynamic light scattering (dls), atomic force microscopy (AFM) and scanning electron microscopy (SEM). We observed that the ph is critical for the microgel transition, which would cause a deviation in the fate of carbon in real aquatic ecosystems.



Self-assembling of DOM microgels. [1]



Mechanisms of assembling. [2]



Microgels photographs at different pH
A) pH 8.22, microscopy electron scanning (SEM).
B) pH 5.59, atoic force microscopy (AFM)

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Acknowledgements:

Projects MAT2009-14234-C03-02 and (FQM-230, RNM-125) Andalusian Excellence Project.

NANO-FIBRIL REINFORCED FOOD GRADE MICROCAPSULES

***Francisco J. Rossier-Miranda*, Karin Schroën, Leonard Sagis, Remko Boom**

Food Process Engineering Group and Food Physics Group, Wageningen University,
Bomenweg 2, 6703HD Wageningen, The Netherlands, fax +31 317 482237,

francisco.rossier@wur.nl

Targeted and controlled delivery of drugs or probiotics is a major goal for the pharmaceutical and food industry. For efficient smart delivery, microcapsules should have sufficient (mechanical) stability, a well defined permeability to the encapsulated material, present a release trigger mechanism, and ideally be monodisperse. Also, especially for food applications, its shell has to be food-grade and inexpensive.

We investigated the production of microcapsules using layer-by-layer adsorption of oppositely charged polysaccharides, proteins, and proteins fibrils (Figure 1a) or colloidal particles (Figure 1b) under acidic conditions. While the size of the microcapsule is determined by the template droplet (which is tuned by membrane emulsification), its mechanical strength, and possibly its permeability, is controlled by the number and composition of the adsorbed layers. During the presentation, we will present details on the production and characterization of these novel microcapsules in relation to the various building blocks that were used.

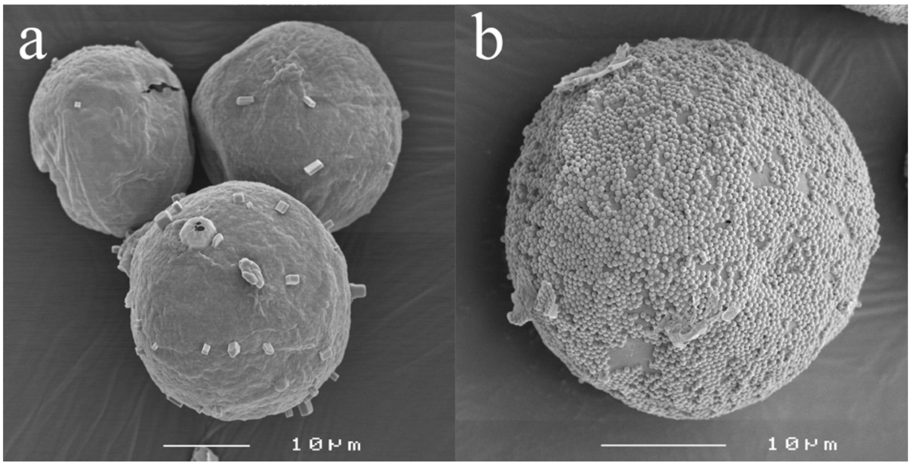

Figure 1: SEM pictures of the microcapsules obtained by the electrostatic layer-by-layer adsorption. a) protein/pectin/protein fibril system, b) protein/pectin/colloidal particle system

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CHARACTERIZATION OF HUMIC SUBSTANCES BY PARTICLE SIZE DISTRIBUTION AND ZETA-POTENTIAL MEASUREMENT

***Szilvia Joó*[1], Judit Tóth[2], Rita Földenyi[1]**

[1]*Institute of Analytics, Environmental Sciences and Limnology,*
University of Pannonia, Hungary
[2]*Institute of Materials and Environmental Chemistry,*
Chemical Research Center HAS, Hungary

Corresponding author: [1] jooszilvi@gmail.com

One of the main problems in drinking water treatment is caused by humic materials. If disinfection is carried out by chlorine, then humic materials may become dangerous, carcinogen materials, like trihalomethanes. Removing humic materials from drinking water and analysing their solubility properties have an obvious importance. The way of humic materials getting into waters has been analysed. One of their sources is the soil, so particle size distribution of different soil suspensions which are typical in Carpathian Basin – sandy soil, chernozem, brown forest soil – were measured by laser diffraction. The behaviour of soils is basically determined by its particle size distribution fundamentally. Particle size distribution influences the specific surface of material hereby capacity of adsorption. Adsorption processes have determinative importance about chemicals further fate that enters into the environment. Different aqueous media can influence particle size distribution of soil and transport processes.

The aim of present work was to determine the effect of the composition of different aqueous media on particle size distribution of soil suspensions. Sandy soil suspensions with different aqueous media – salts, tensides – were also analysed detailed.

The investigated surfactants are used as detergent in cosmetics (sodium dodecylsulphate: SDS) or in industry (alkyltrimethylammonium bromide: Cetrimide) furthermore as forming agents with pesticides (Supragil WP). Surfactants influence the particle size distribution, sodium dodecylsulphate, a widely used detergent was especially significant. According to measurements SDS adsorbs on sandy soil in more layer, and shows an L-type of isotherm.

The presence of humic materials was measured by UV-VIS spectroscopy at 254 nm. Solutions of fulvic acid, sodium salt of humic acid and suspensions of sandy soil were examined according zeta-potential at different pH values (pH=5; 6; 7; 8). Zeta-potential let us conclude the stability of solution or suspension, which affects the fate of the suspension in natural waters. We could conclude how pH and the c.m.c of tensides affect zeta potential and the stability of the suspension. If the tenside concentration is higher than c.m.c, the suspension is stable, if concentration is lower, the suspension is instable. Dependence on pH value is related on the type of the humic substances.

CYCLODEXTRINS IN DNA-CTAB COMPLEX DECOMPACTION

Jonas Carlstedt[a]***, Rita S. Dias***[b]***, Alfredo González-Pérez***[c]***, Björn Lindman***[a,b]

[a]*Physical Chemistry 1,Center of chemistry and chemical engineering, Lund University, P. O. Box 124, 221 00 Lund, Sweden* [b]*Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal* [c]*MEMPHYS – Center for Biomembrane Physics, Dept. for Physics and Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark*

Control of the conformational state of large DNA molecules is believed to play a key role in non-viral gene delivery. Various strategies have been used to compact DNA, such as addition of cationic surfactants, polyamines, dendrimers and also by changing the solvent properties.[1] The decompaction strategy is, naturally, dependent on the method used for the compaction. Addition of anionic or nonionic surfactants has been used to decompact DNA-cationic surfactant complexes. DNA compacted by polyamines and dendrimers can be decompacted by addition of heparin. Recently, a paper introducing β-cyclodextrin (β-CD) as a decompacting agent for DNA previously compacted by the cationic surfactant cetyltrimethylammonium bromide (CTAB) was published.[2] Cyclodextrins are cyclic oligomers of glucose and are used to encapsulate and solubilize various hydrophobic molecules in aqueous solution by forming host-guest complexes by association of the hydrophobic parts into the hydrophobic cavity of the cyclodextrin. Cyclodextrins are resistant to degradation of human enzymes and do not produce an immune response in mammals. They are therefore of interest in therapeutical applications. The inclusion complexes formed by β-CD and CTAB were investigated by Cabaleiro-Lago and coworkers[3] and a high association constant was found. Both 1:1 and 2:1 β-CD-CTAB complexes were found.

In this work, various aspects of cyclodextrin induced DNA-CTAB decompaction are being addressed. Fluorescence microscopy, steady state fluorescence spectroscopy, and precipitation diagrams were used, among other techniques, to study the dissociation of DNA-CTAB complexes and the decompaction and release of DNA into solution, both on microscopic and macroscopic viewpoints. Thermal melting and circular dichroism were used to look into direct DNA-CD interactions.

Interestingly, the cyclodextrin induced decompaction was shown to be a non first-order transition, as opposed to the CTAB induced DNA compaction and the DNA-CTAB dissociation induced by anionic surfactants.

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EFFECT OF BICELLAR SYSTEMS IN STRATUM CORNEUM LIPIDS

Gelen Rodríguez*[*1], Lucyanna Barbosa-Barros[1], Avencia Díez[2], Joan Estelrich[3], Alfonso De la Maza[1] & Olga López[1].

[1]Dpto. de Tecnologia Química i de Tensioactius, I.Q.A.C- C.S.I.C., Barcelona, Spain.
[2]Servicio de Espectrofotometría, I.Q.A.C-C.S.I.C, Barcelona, Spain.
[3]Dpto. de Fisicoquímica, Facultad de Farmacia, Universidad de Barcelona, Barcelona, Spain.

**Present author:* gelen.rodriguez@iiqab.csic.es

Bicellar systems constitute a new nanostructure with discoidal morphology. These systems are composed by a phospholipid of long hydrocarbon chain in a bilaminar flat center and a phospholipid of short chain in the edges [1]. These aggregates are used as membrane models providing an excellent support to study membrane associated proteins. Additionally, in recent works we have proposed the use of phospholipid bicelles for dermatological applications owing to their small size, enough for passing through the skin and, their composition, consisting completely of lipids. These studies demonstrated that the effect of bicelles on the skin barrier depend on different compositional variables, working as permeabilizing agents of the skin or as reinforcing agents of the lipid structures present in this tissue [2, 3]. Despite of the potencial applicability of former results, knowledge about the mechanism that induces these specific effects is still lacking. The main function of the skin is to serve as a physical barrier at the interface between the body and the environment. This barrier is provided by the outermost layer of the epidermis, the stratum corneum (SC), which consists in anucleated cells (corneocytes) surrounded by lipid layers formed mainly of ceramides, cholesterol, and fatty acids. Hence, ATR-FTIR (attenuated total reflectance-Fourier transform infrared) spectroscopy was applied to study the effects of the bicelles formed by dimyristoyl-glycero-phosphocholine (DMPC) and dihexanoyl-glycero-phosphocholine (DHPC) in porcine stratum corneum (SC) in vitro. A comparison of skin samples treated and untreated with bicelles at different temperatures was carried out. The analysis of variations after treatment in the position of the symmetric CH_2 stretching, CH_2 scissoring and CH_2 rocking vibrations reported important information about the effect of bicelles on the skin. Part of the bicelles remained probably adhered to the skin surface after washing with water. The washing with a surfactant solution after treatment with bicelles allowed to remove the adhered bicelles and to detect the interaction of these nanostructures with the SC lipids. This interaction caused a phase transition from the gel or solid state to the liquid crystalline state in the lipid conformation, reflecting the major order-disorder transition from hexagonally packed to disordered chains. These results are probably related with the permeabilizing effect previously described for the DMPC/DHPC bicelles.

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MICROCAPSULES USED AS A COMPONENT OF DENTAL COMPOSITES

***Agnieszka M. Cwalińska* [1], *Paul Reynolds* [1], *Anthony Ireland* [2]**

[1] *Bristol Colloid Centre, School of Chemistry,*
University of Bristol, Bristol, United Kingdom

[2] *Department of Child Dental Health, Bristol Dental School,*
University of Bristol, Bristol, United Kingdom

Dentistry is a dynamic field determined by the increasing expectations of patients. Intensive research has been conducted to develop ever more advanced dental composites.

In this poster, the types of current dental composite materials are presented in brief, with their advantages and disadvantages. In this research a modification of the chemically cured composites is proposed in order to create a new single component restorative material. The intention is to achieve this by the addition of microcapsules containing the activator or initiator into the composite resin. These capsules would be broken with mechanical stimulus to begin curing of the composite.

ASSESSMENT OF GEMINI SURFACTANTS AS SKIN PENETRATION ENHANCERS

***J. A. S. Almeida*[(a)], *E. F. Marques*[(b)], *A. S. Jurado*[(c, d)] and *A. A. C. C. Pais*[(a)]**

[(a)] *Chemistry Department, University of Coimbra, Portugal*
[(b)] *Chemistry Department, Oporto University, Portugal*
[(c)] *Biochemistry Department, University of Coimbra, Portugal*
[(d)] *Center for Neurosciences and Cell Biology, Coimbra, Portugal*

Surfactants are known to influence lipid membrane organization [1], and most ionic surfactants have been shown to enhance permeation through biological membranes [2]. Their ability to solubilise lipids within the stratum corneum and improve skin permeation have also been noted [3].

With the purpose of studying the enhancing effect of cationic gemini surfactants on skin permeation, we analyze the impact of these surfactants upon dipalmitoylphosphatidylcholine liposomes.

A systematic assessment on the effect of tail and spacer length of gemini surfactants upon the organization of lipid membranes was carried out resorting to a differential scanning calorimetry and a fluorescence anisotropy study. Results suggest that the type and degree of perturbation clearly depend on the respective structural features and concentration. The potential skin toxicity/irritancy was concomitantly assessed on cultured human keratinocyte cells (NCTC 2544) by a modified Alamar Blue assay.

Additionally, molecular dynamics simulation results provide significant insight into the molecular interaction mechanism of these surfactants with DPPC bilayers.

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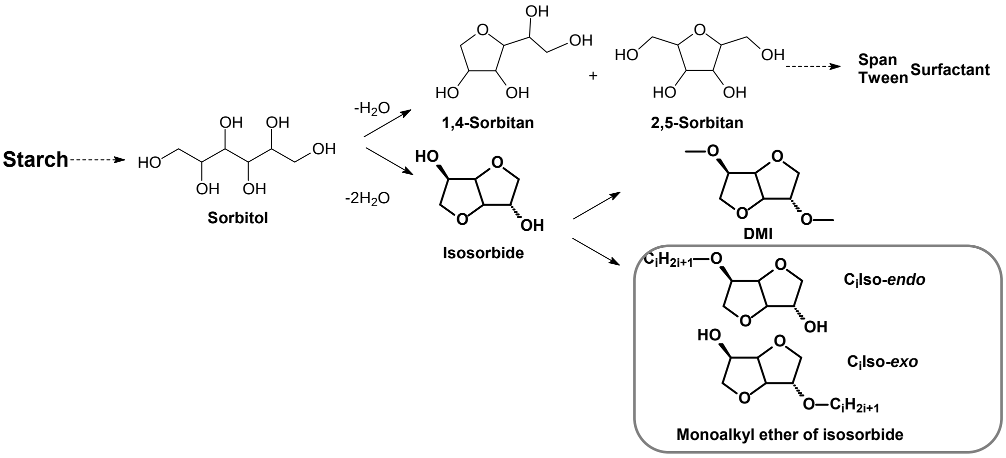
NEW FAMILY OF “GREEN” HYDROTROPES DERIVED FROM ISOSORBIDE: REGIO-ISOMERIC EFFETS ON THE AMPHIPHILIC BEHAVIOURS

Ying Zhu**, **Valérie Molinier, Morgan Durand, Jean-Marie Aubry

LCOM, Equipe « Oxydation et Formulation », UMR CNRS 8009,
ENSCL BP 90108, 59652 Villeneuve d’Ascq Cedex, France

In the search for environmentally-friendly products for the surfactant industry, interest has been paid to the carbohydrate-based molecules derived from renewable resources. Isosorbide is a product of the starch industry, obtained by dehydration of sorbitol at moderate temperature. This molecule is non-toxic and thermally stable up to 280°C. A new family of isosorbide derivatives, the short-chain monoalkylethers (C_iIso, i = 4 and 5), have been synthesized and assessed as “green” hydrotropes.[1]



We describe firstly the synthesis of the short-chain monoalkyl ethers of isosorbide. Two series of isomers have been obtained: the *endo*-orientation and the *exo*-orientation ethers. Their amphiphilic behaviours have been studied in the monomeric state as regards to the partitioning in water/cyclohexane and then in the aggregated state by determining the optimal formulation in C_iIso/oil/water systems when changing the oil polarity. In both alkyl chain lengths (4 or 5 carbons), C_iIso-*exo* appear to be less polar. The contribution of the isosorbide polar head for the *exo*-ethers has been evaluated to one ethyleneglycol whereas for the *endo*-ethers is closer to two ethyleneglycols. This difference has been attributed to the existence of an intramolecular hydrogen bond between the OH-*endo* and the oxygen atom in the tetrahydrofuran ring of isosorbide which is maintained only in the *exo*-ethers.

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LIPID-MEMBRANE PERMEATION MEASURED WITH SURFACE PLASMON RESONANCE

***Seyed Tabaei*, Magnus Brändén and Fredrik Höök**

Div. of Biological Physics, Dept. of Applied Physics, Chalmers University of Technology, Göteborg, Sweden

Lipid bilayer membranes define the boundary of cells and act as hydrophobic barriers preventing solutes from freely diffusing in and out of cells. A living cell, however, is critically dependent on molecules, ions and signals being continuously transported across the membrane in order to maintain its biosynthesis, energy production and communication with the surrounding environment. Hence, transport across biological membranes, which is strictly controlled by specialized membrane proteins, has been, and is, extensively studied, not only because it increases our knowledge of the fundamental biochemical processes of life, but also because several common diseases are caused by deficient transport of essential molecules across cellular membranes. In drug discovery, therefore, a lot of effort is directed towards functional analysis of membrane proteins and half of the 100-best selling drugs are targeted against these proteins. We present a new method to study cell-membrane permeation, unique in the sense that it provides direct measurements and rapid screening of the transfer rate of both uncharged and charged solutes across biological membranes. To the best of our knowledge this is the first study illustrating the use of surface plasmon resonance (SPR) for direct and time-resolved measurements of biomolecular transfer across a lipid bilayer membrane. In addition we report a new self-assembly route for formation of multiple macroscopically homogenous and highly fluid tethered lipid bilayers using bicellar solution.

SELF ASSEMBLY BOVINE LACTOFERRINE

***B.A. Persson**, J. Forsman, M. Lund, T. Akesson*

Departament of Theorical Chemistry, Lund University

The whey protein Lactoferrin is considered important in many biological events and has useful properties for technical applications. On several occasions it has been noted that the protein appears to form aggregates in biological fluids. While most of the major protein components in whey have received much theoretical attention. Lactoferrin remains an unexplored subject.

In this work the pair interaction of Bovine Lactoferrin has been characterized by means of Monte Carlo simulations. A mesoscale description has been used to obtain a simplified, while rational represenation of the rather large protein. The model uses crystallographic data to generate an approximate structure that preserves the charge distribution, caused by titrating amino acids. Electrostatic interactions are treated explicitly in the primitive model or on a Debye-H¨uckel level. Augmented hard sphere or Lennard-Jones interactions are used to describe a homogeneous short range dvan der Waals attraction between amino acids. Starting from the augmented primitive model, results are presented that clearly testifies to the fundamental importence of including vdW interactions. It is also demonstrated that the problem can be simplified considerably using Debye-Hückel, while obtaining good agreement within the model. The twobody interaction gives rise to stable dimers over a range of solution conditions, i.e. a few pH units around pI and low to intermediate ionic strength. The results show how a intimate interplay between the geometry of the protein and its charge distribution is responsible for the self assembly and - even though the model is simple as such - we can demonstrate untrivial effects due to the non-linear nature of the free energy. The dimer is found to have a stereo specific and well defined structure due to a complementarity in the charge distribution and contact surface. Probing thecomplementarityofthechargedistributionbypointmutationsofchargedamino acids reveal how different amino acids in the protein are responsible for attraction and sterospecificityinthe self assemblingprocess.

THE LINOLEIC ACID INFLUENCE ON MOLECULAR INTERACTIONS IN CHOLESTEROL/PHOSPHOLIPID MEMBRANES

***Katarzyna Makyła*, Maria Paluch**

Department of Physical Chemistry and Electrochemistry, Faculty of Chemistry,
Jagiellonian University, Ingardena 3, 30-060
Kraków, Poland,
Tel.: +48 12 6632079; Fax: +48 12 6340515; E-mail address: makyla@chemia.uj.edu.pl

Fatty acids (FAs) play an important role in maintaining the homeostasis of lipid membranes [1]. Their composition influences various physiological and biochemical processes including blood pressure regulation, glucose metabolism [2], lipid metabolism and erythrocyte deformability [3].

Therefore studies on the fatty acids monolayers play a crucial role in providing valuable information on properties of the natural bilayers. The present work explores the properties of binary mixed Langmuir monolayers consisted of cholesterol and 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), and also ternary mixed Langmuir monolayers consisted of Linoleic acid (LA), cholesterol and DPPC at the air/water interface, treated as the simplest models of a half of the biological membranes.

Our researches were conducted by using the Langmuir film balance, by means of which we registered the surface pressure (π) as a function of the area of water surface available to each molecule (A). It was found that cholesterol and DPPC are miscible in binary as well as LA, cholesterol and DPPC in ternary mixed monolayers, however in ternary mixed monolayers, at higher content of fatty acid (for molar fraction XLA = 0.6, 0.8) this components were miscible only at the surface pressure below approximately 27 mN/m. Furthermore the results of our measurements show that LA reveals very strong influence on the membrane composition. Depending on various amounts of this fatty acid within the models of biological membranes it seems to affect different stability of natural bilayer.

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THE TEMPERATURE INFLUENCE ON THE SURFACE PROPERTIES OF GALACTOLIPIDS OBTAINED FROM WHEAT CALLUS CULTURES

***Barbara Gzyl-Malcher*[a], *Katarzyna Makyła*[a], *Maria Filek*[b, c]**

[a]*Department of Physical Chemistry and Electrochemistry, Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland, E-mail address: makyla@chemia.uj.edu.pl*
[b]*Institute of Biology, Pedagogical University, Podbrzezie 3, 31-054 Kraków, Poland*
[c]*Institute of Plant Physiology, Polish Academy of Sciences, Niezapominajek 21, 30-239 Kraków, Poland*

Biological membranes are macromolecular arrangements of lipids and proteins. Chloroplast membranes contain only a small fraction of phosphatidylglycerol and mainly (to around 90%) are composed of galactolipids, which consist of galactose units and fatty acids linked to a glycerol backbone: monogalactosyldiacylglycerol (MGDG) and digalactosyldiacylglycerols (DGDG). The influence of temperature on surface properties of galactolipids was studied by Langmuir balance method. Galactolipids were isolated from plastids of winter wheat cells initiated from immature inflorescences and cultivated for 3 weeks on Murashige and Skoog (MS) medium.

Compression measurements were performed in a Langmuir trough (KSV 1000, Finland). It was found that MGDG and DGDG were miscible at the water surface and formed insoluble monolayers in liquid expanded state. The lowest average molecular area and collapse pressure values were recorded for MGDG. Temperature increase led to monolayer expansion and to lowering of monolayer stability against the collapse process, independly of the kind of galactolipid.

INVESTIGATING THE SOLUBILITY MECHANISM OF ETHYLENE OXIDE OLIGOMERS IN FLUORINATED LIQUIDS

Gemma Talbot[1], ***Alison Paul***[1], ***Peter C. Griffiths***[1] ***and Philippe G. A. Rogueda***[2]

[1]*School of Chemistry, Cardiff University, Cardiff, UK;*
[2]*Novartis Pharmaceuticals UK Limited, Frimley Business Park, Surrey, UK;*

Aerosol inhalation is an effective method of drug delivery for chronic pulmonary disorders including asthma. Pressurised metered dose inhalers (pMDIs) are cheap, reliable devices that provide a convenient method of drug delivery to the lungs, and contain a drug suspended or dissolved in a propellant usually with a surfactant or polymer excipient. Chlorofluorocarbon (CFC) propellants have now been replaced by non-ozone depleting hydrofluoroalkane (HFA) alternatives. However, the different physicochemical properties of HFAs, such as lower intermolecular attractive forces, mean that traditional excipients used in CFC formulations have low solubility in HFAs and significant reformulation is often required.

Low molecular weight poly(ethylene glycol)s (PEGs) may be incorporated into CFC-free formulations as excipients to enhance drug solubility or stabilise suspensions. Here, a series of HO- or CH_3- end-capped PEGs have been studied in mixtures of the model propellant 2H, 3H-decafluoropentane (HPFP) [1] and its fully fluorinated analogue perfluoropentane (PFP) in order to investigate the influence of solvent composition (hydrogen bonding ability), polymer end-group structure and molecular weight on the ternary phase behaviour in these systems. Building on previous work within the group [2-4] dry-weight analysis and ^{1}H NMR have been used to determine the polymer and solvent distributions at the phase boundaries, and thereby elucidate the driving force for the phase separation observed.

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SELF-ASSEMBLY OF ASYMMETRIC SINGLE-CHAIN BOLAPHOSPHOLIPIDS

G. Graf (1), A. Meister (1), S. Drescher (2), G. Hause (3), B. Dobner (2), A. Blume (1)

(1) Institute of Chemistry, Martin-Luther-University Halle-Wittenberg
(2) Institute of Pharmacy, Martin-Luther-University Halle-Wittenberg
(3) Biocenter, Martin-Luther-University Halle-Wittenberg

Long-chain bolaphospholipids with a single alkyl chain and two dimethylammonioethylphosphate headgroups (Me2PE-Cn-Me2PE, n = 24-32) self-assemble in water into fibers depending on the temperature and the pH of the suspension [1]. They gel water very efficiently by the formation of a three-dimensional network of nanofibers [2]. This type of nanofibers may serve as template for the fixation of gold nanoparticles (AuNPs) without prior functionalization [3].

The aim of this study was to investigate the aggregation behavior of asymmetric bolaphospholipids that are composed of a [hydroxy-(2-hydroxyethoxy)phosphinyl]oxy and a 2-[(3-dimethylaminopropyl)dimethylammonio]ethylphosphate headgroup. The self-assembly process of this new bolaphospholipid and the formed aggregates were investigated using differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and rheological measurements at different pH-values in aqueous suspensions.

The experiments show that the fiber structure is maintained regardless of the symmetry of the molecules, even in mixtures with symmetric molecules. The fibers were used as template for the one-dimensional organisation of gold nanoparticles.

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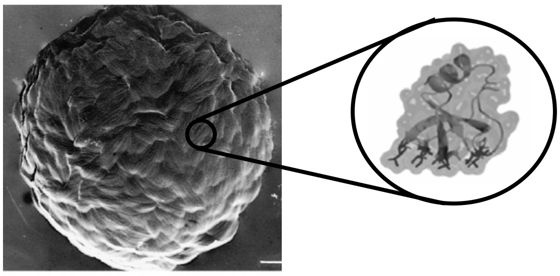
INTERFACIAL BEHAVIOUR OF SMALL AMPHIPHILIC PROTEINS (HYDROPHOBINS)

Olga Krivosheeva*, ***Eva Blomberg*, and Per Claesson****

**Department of Chemistry, Division of Surface Chemistry, KTH, Royal Institute of Technology, Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden*

Protein adsorption is a topic which has been interested for many years. A lot of researchers all over the world are working with it. When we are talking about protein adsorption first of all we are thinking about adsorption mechanism. How the protein behaves on the surface, which conformational changes occurs. In this work we tried to understand surface behaviour of rather newly discovered protein.



About 20 years ago Professor Joseph G. H. Wessels from the Netherlands discovered a new protein and named it "Hydrophobin". These proteins are produced by filamentous fungi and have a wide range of biological functions. They can act as coatings on spores, hyphae, and fruiting bodies. Hydrophobins also take part in the attachment of fungi to different surfaces and reducing the water surface tension to enable the formation of fungal aerial structures [1].

There are two major classes of Hydrophobins: Class I and Class II and the hydropathy patterns can be used to divide them into different classes. The main difference between Class I and Class II is the formation of different supramolecular assemblies. Proteins from the Class I form a "rodlet coating" and those of Class II ordered monolayer films [2]. Hydrophobins are rather small proteins with a diameter of about 2 nm. They consist of around 100 amino acid residues and have molecular mass approximately 10 kDa (HFBI = 7532 Da, HFBII = 7188 Da). Further, the protein molecule contains of 4 disulphide bridges which makes it globular and rather rigid. Hydrophobins are amphiphilic proteins having both hydrophilic and hydrophobic (around 12% of the total area) parts. By using the Langmuir-Blodgett technique (KSV Instruments) the behaviour of HFBI and HFBII at the air/liquid interface have been investigated. It was shown that both HFBI and HFBII formed rather condensed layer, so called "skin", at the interface resulting a steep surface pressure-area isotherm. The adsorption of HFBI ans HFBII on negatively charged hydrophilic silicon oxynitride was studied by using Dual Polarization Interferometer (DPI, Farfield Scientific). With this technique one can measure thickness and refractive index of adsorbed protein layers. This method helps us to understand the adsorption mechanism of hydrophobins. We can conclude that the adsorption of HFBI and HFBII is quite different. The former adsorbs weakly on the surface and can easily be removed by rinsing with water. The latter adsorbs more strongly on the surface and remains after rinsing.

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EFFECT OF Ca^{2+} AND pH ON FOAM BEHAVIOUR OF SODIUM ALKYL BENZENE SULPHONATE SOLUTIONS

***Li Ran*, Professor Peter Garrett**

School of Chemical Engineering and Analytical Science, The University of Manchester, UK

E-mail: Li.Ran@postgrad.manchester.ac.uk

Sodium linear alkylbenzene sulphonate (NaLAS) is the main foaming substance in detergents. The foam behaviour of NaLAS is significantly influenced by water hardness and soils from garments. Ca^{2+} in hard water causes precipitation of $Ca(LAS)_2$; and this reaction is determined by the solubility product $K_{sp} = [Ca^{2+}][LAS^-]^2$. The impact of soils on foamability is more complex, since antifoam mechanisms can be different with various types of triglyceride/fatty acid mixtures contained in soils. In addition, the presence of Ca^{2+} may cause the formation of calcium soap by reacting with the fatty acids, which may influence the effectiveness of soil antifoams. This reaction can however be controlled by varying the pH. The foaming behaviour of NaLAS at a concentration of 2×10^{-3} M with a Ca^{2+} concentration from 0 to 40×10^{-4} M under pH 3, 7 and 10.5 will be presented to illustrate the effect of pH, Ca^{2+} and the presence of mixed triglyceride/fatty acid antifoam. It has been found that in the absence of antifoam, foam behaviour is independent of pH and is dominated by the formation of $Ca(LAS)_2$ precipitate. Dynamic surface tension measurements confirm that low foamability in the $Ca(LAS)_2$ precipitate/micellar region of the Ca^{2+}/LAS^- phase diagram is due to low rates of transport of surfactant to the rapidly generated air-water surfaces. Antifoam effects with two types of triglyceride/fatty acid mixtures – triolein/oleic acid (liquid/liquid) and triolein/stearic acid (liquid/solid) have also been studied using techniques ranging from optical and electron microscopy to measurement of the critical capillary pressures for rupture of pseudoemulsion films by the film trapping technique[1]. Antifoam effects with triolein/oleic acid mixtures are only found at high pH and in the presence of calcium. Under these conditions calcium oleate particles form at the oil-water interface where they can rupture pseudoemulsion films, leading to emergence of the triolein into the air-water surfaces of foam films and therefore foam collapse[2, 3]. However triolein/stearic acid mixtures exhibit large defoaming effects at all pHs, even in the absence of calcium. This suggests an antifoam effect dominated, under certain conditions, by hydrophobic stearic acid particles rather than formation of calcium soaps.

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PEPTIDE-LIPID INTERACTION: COMPETITIVE BINDING TO LIPOSOMES AND POLYMER-STABILIZED DISKS

***Malin Morin**, Karin Reijmar, Per Wessman and Katarina Edwards*

Department of Physical and Analytical Chemistry, Uppsala University, Box 579, SE-751 23 Uppsala, Sweden, Fax +46(0)18-471 36 54

malin.morin@fki.uu.se

We have developed a protocol that offers a simple and convenient means to explore the potential influence of curvature on the interaction between peptides and lipid surfaces. We have studied the affinity of the amphiphilic peptides melittin, alamethicin and Magainin II for lipid surfaces with different curvature using a competitive approach. The peptides were added to a mixture of PEG-stabilized bilayer disks and liposomes encapsulating a self-quenching fluorescent dye. Leakage of the dye was then measured spectroscopically. The results were compared with the leakage obtained upon addition of peptide to solutions containing a mixture of empty and dye-filled liposomes.

Leakage from the dye encapsulating liposomes was considerably lower in the presence of disks, as compared to in the presence of empty liposomes, indicating that all three peptides have higher affinity for the disks than for the liposomes. This behaviour is most likely explained by preferential binding of the peptides to the highly curved rim of the disks. Another indication of this propensity to accumulate at curved surfaces comes from the structural change that occurs in liposome dispersions upon the addition of peptides. We have seen using cryo-TEM that melittin and alamethicin can induce liposome breakage and formation of open bilayer structures when added to liposomes. It is likely that the peptides reside at and stabilize the curved rims of these open structures.

Because of their ability to carry large amounts of peptides the PEG-stabilized bilayer disks constitute interesting structures for formulation and delivery of pharmaceutically interesting peptides.

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Zhu	*Ying*	*New Family Of “Green” Hydrotropes Derived From Isosorbide: Regio-Isomeric Effets On The Amphiphilic Behaviours*

NOTES

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Consejería de Innovación, Ciencia y Empresa

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Group of Complex Fluid Physics

Rafael Contreras Cáceres
Ignacio Pérez Mazuecos
Andrés Granados del Águila
Sergio Martínez Escobar
Iván José Suárez Suárez
Alejandro Cuetos Menéndez
Antonio Fernández Barbero

IN LUMINE SAPIENTIA · UNIVERSITAS ALMERIENSIS

Group of Photo-Coordination Chemistry

Manuel Serrano Ruiz
Mery Mallqui Ayala
Mounia Chaara
Nazira Jadagayeva
Antonio Romerosa Nievas