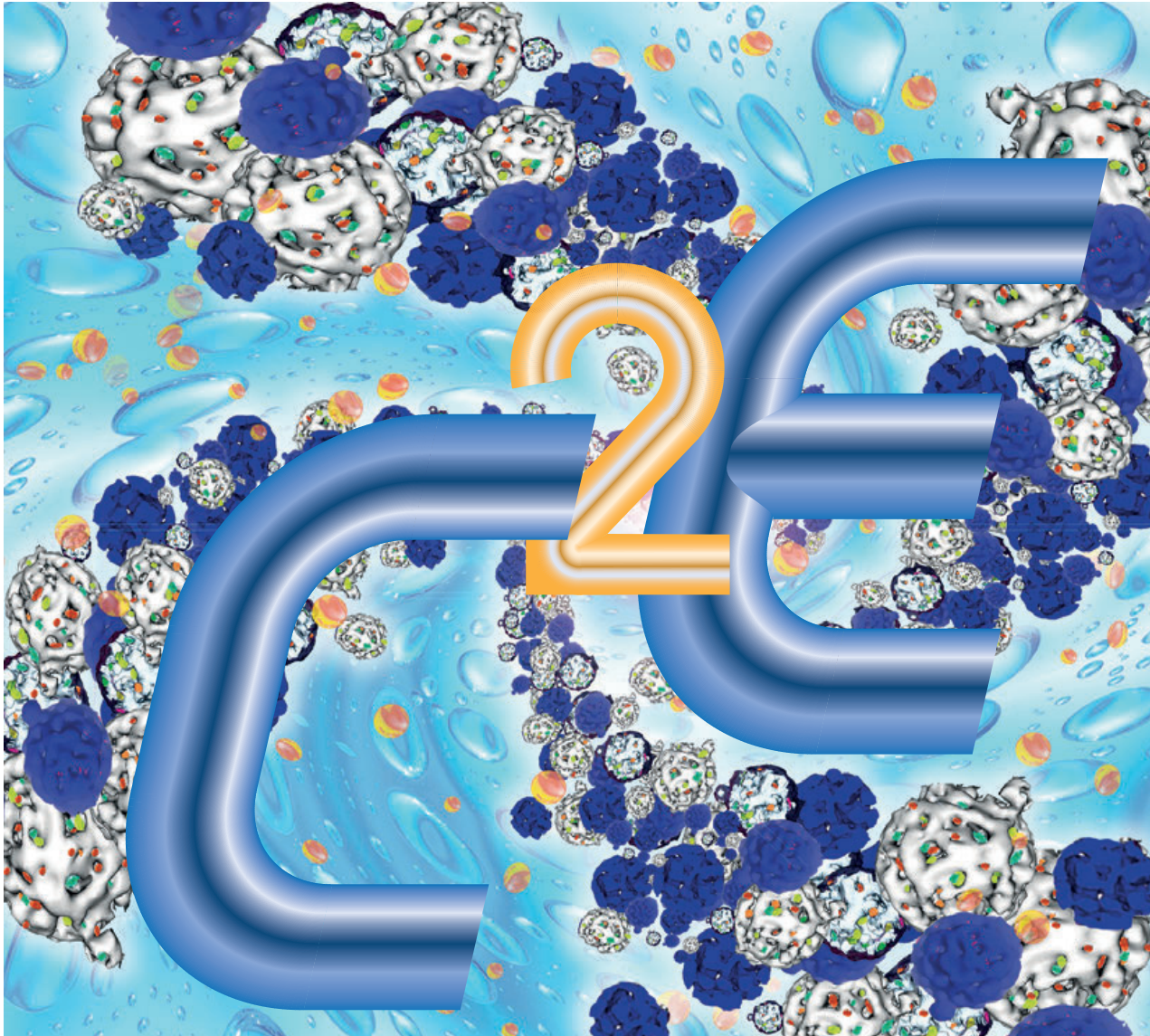
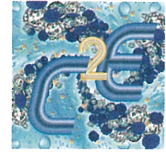


## Abstract volume



**C<sup>2</sup>E - Colloids and Complex fluids for Energies**  
Systems understanding: from preparation to process design  
Rueil-Malmaison, France ■ 4-6 December 2017

Partnership



## Context and Objective

Advances in the field of colloids and complex fluids sciences will lead to the development of new efficient and eco-friendly solutions designed to address some of the energy and environment-related challenges of the 21<sup>st</sup> century. The objectives of this international conference are to share scientific/technical advances in this field and discuss their potential to address new challenges related to oil & gas, nuclear and new energies sectors. In particular, progresses in system design, characterization, understanding and modeling will be highlighted.

The main scientific topic:

- *Nanoparticles synthesis, system nanostructuration, functionalization*
- *Dynamic interfacial phenomena understandings*
- *Rheology, flow and diffusion in confined systems (porous media, microfluidics)*
- *Stability, evolution and ageing of colloids and complex fluids*
- *In-situ characterization and behavior modelling*
- *Applications for energy, colloidal system processing, process design*

Among potential applications, we can list the enhanced oil recovery, water management, flow assurance, catalysis, energy storage, biomass transformation, nuclear fuel preparation and spent fuel treatment, cleanup and dismantling as well as radioactive waste management, storage and conditioning and any other application dedicated to the development of new energies.

The program of this international conference is structure to encourage interaction, stimulate exchange of ideas and debate still opened questions between players from the worlds of academic research, applied research and industry.



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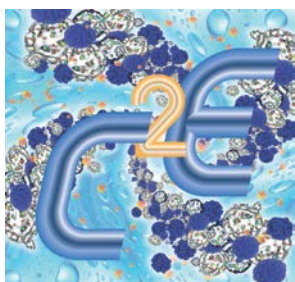
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## Colloids and Complex fluids for Energies – C<sup>2</sup>E Systems understanding: From preparation to process design

IFPEN, Rueil-Malmaison, 4-6 December 2017

### Oral sessions

#### Tuesday 5 December

##### Session 1 - Dynamic interfaces and complex fluids

[O/1] Particle stabilized emulsions via “ouzo emulsification”

V. Sötz<sup>1</sup>, J.Causse<sup>1</sup>, W. Kunz<sup>2</sup>, T. Zemb<sup>1</sup> (1 Institut de Chimie Séparative, France, 2 Univ. Regensburg, Germany)

[O/28] Hydrophobization of silica nanoparticles in water: nanostructure and response to drying stress

S. Moro, C. Parneix, B. Cabane, J-B d’Espinose, N. Sanson (ESPCI, UPMC, Saint-Gobain Recherche, France)

[O/5] Zwitterionic Supraparticles as novel pickering emulsifiers

M. Maas, K. Rezwan (Univ. of Bremen, Germany)

[O/11] Gravity driven phase separation in foamed emulsions

M. Schneider, Z. Zou, D. Langevin, A. Salonen (Univ. Paris-Sud, Lab. Physique des Solides, France)

[O/34] Multi-scale approach to understand complex interaction involved in produced water treatment by flotation, in EOR context

H. Chakibi, I. Henaut, J-F Argillier (IFPEN, France)

[O/7] Attachment of colloidal particles to a fluidic interface application to the flotation process

G. Lecrivain<sup>1,2</sup>, U. Hampel<sup>1,3</sup>, R. Yamamoto<sup>2</sup>, T. Taniguchi<sup>2</sup> (1 Institut für Fluidynamic, Germany ; 2 Kyoto Univ., Japon ; 3 TU Dresden, Germany)

##### Session 2 - Colloids synthesis, characterization behavior and modeling (part 1)

[O/12] Combination of emulsion polymerization, sonochemistry and sol-gel process for the synthesis of Pt/SiO<sub>2</sub> supported catalyst with hierarchical porosity

A.F Sierra-Salazar<sup>1,2</sup>, T. Chave<sup>3</sup>, A. Ayrat<sup>4</sup>, S-I Nikitenko<sup>3</sup>, V. Hulea<sup>1</sup>, P-J Kooyman<sup>5</sup>, F. D Tichelaar<sup>6</sup>, WS-J Li<sup>1</sup>, S. Perathoner<sup>2</sup>, P. Lacroix-Desmazes<sup>1</sup> (1 Institut Charles Gerhardt, France ; 2 Univ. di Messina, Italy ; 3 ICSM, 4 Institut Européen des Membranes, France ; 5 Univ. of Cape Town, South Africa ; 6 Kavli Institute of Nanoscience of Delft, The Netherlands)

[O/27] Aqueous suspensions of zero-valent iron nanoparticles for the in situ remediation of contaminated groundwater: experiments in porous media models and numerical simulation  
C. Tsakiroglou, K. Terzi, A. Sikinioti-Lock, K. Hajdu, C. Aggelopoulos, M. Theodoropoulou  
(Foundation for Research and Technology Hellas, Greece)

[O/25] Electrochemically-active microgel systems  
F. Plamper (RWTH Aachen Univ. Germany)

[O/2] Time resolved boehmite particles synthesis and characterization using small angle X-Ray scattering  
B. Guoze, L. Barre, E. Lécolier, V. Lecocq, A. Chaumonot (IFPEN, France)

## Wednesday 6 December

### Session 2 - Colloids synthesis, characterization behavior and modeling (part 2)

[O/36] Rheology of adsorption layers from the protein hydrophobin and its mixtures with other proteins: experiment and theoretical model  
G. Radulova (Sofia Univ. Bulgaria)

[O/15] A comprehensive simulation study of application of polymer gels for enhancing oil recovery  
A. Jahanbani Ghahfarokhi, J. Kleppe, O. Torsaeter (Norwegian Univ. of Science and Technology, Norway)

[O/21] Pore filling events in single junction micro-models with corresponding lattice-Boltzmann simulations  
I. Zacharoudiou, E. Chapman, E. Boek, J. Crawhaw (Imperial College of London, United Kingdom)

[O/18] Molecular theory of solvation for supramolecular structures and nanomaterials  
A. Kovalenko<sup>1,2</sup> (1 National Institute for Nanotechnology, 2 Univ. of Alberta, Canada)

### Session 3 - Confined systems and applications

[O/4] Foam's flow in porous media: In-situ texture characterization by small angle neutron scattering and X-ray tomography experiments  
C. Ouali, E. Rosenberg, L. Barré (IFPEN, France)

[O/37] Clogging of model pores with a Brownian suspension  
O. Liot<sup>1,5</sup>, P. Duru<sup>2</sup>, P. Bacchin<sup>3</sup>, J. Morris<sup>4</sup>, P. Joseph<sup>1</sup> (1 LAAS-CNRS, 2 IMFT, 3 LGC, France ; 4 Levich Institute, USA ; 5 Fédération Fermat, France)

[O/19] Thermoelectric energy conversion in ferrofluids  
T. J. Salez<sup>1,2</sup>, B.M Pham<sup>1</sup>, B.T Huang<sup>1</sup>, M. Bonetti<sup>1</sup>, M. Roger<sup>1</sup>, C. Filomeno<sup>3</sup>, E. Dubois<sup>3</sup>, V Peyre<sup>3</sup>, G. Demouchy<sup>3</sup>, M. Kouyate<sup>3</sup>, R. Persynski<sup>3</sup>, S. Nakamae<sup>1</sup> (1 SPEC-CEA-CNRS, Univ. Paris-Saclay, 2 Ecole des Ponts ParisTech, 3 UPMC, France)

[O/16] Osmosis for enhanced oil recovery studied with microfluidics  
E. Crestel<sup>1,2</sup>, E. Santanach Carreras<sup>2</sup>, J Bibette<sup>1</sup>, N. Bremond<sup>1</sup> (1 ESPCI, 2 Total, France)



[O/13] [Subcooling and wettability effects on gas hydrate growth in round glass microcapillaries](#)  
A. Touil<sup>1</sup>, D. Broseta<sup>1</sup>, R. Brown<sup>2</sup>, A. Desmedt<sup>3</sup> (1 LFCR Univ. Pau, 2 IPREM Univ. Pau, 3 ISM Univ. Bordeaux, France)

[O/9] [Complex fluids for the nuclear decontamination of radioactive solid surfaces](#)  
A. Gossard, F. Frances, C. Lepeyre, S. Faure, A. Grandjean (LPSD-CNRS, France)

[O/26] [From hierarchical assembly of nanoparticles to aerogels](#)  
M. Odziomek<sup>1,2</sup>, F. Chaput<sup>1</sup>, M. Sitarz<sup>2</sup>, F. Lerouge<sup>1</sup>, S. Parola<sup>1</sup> (1 Univ. Lyon, France ; 2 AGH Univ. of Science and Technology of Krakow, Poland)



# ABSTRACTS

Abstracts are listed following the program order

*The abstracts are published in their original format as they were sent to the Organizing Committee*



## PARTICLE STABILIZED EMULSIONS VIA 'OUZO EMULSIFICATION'

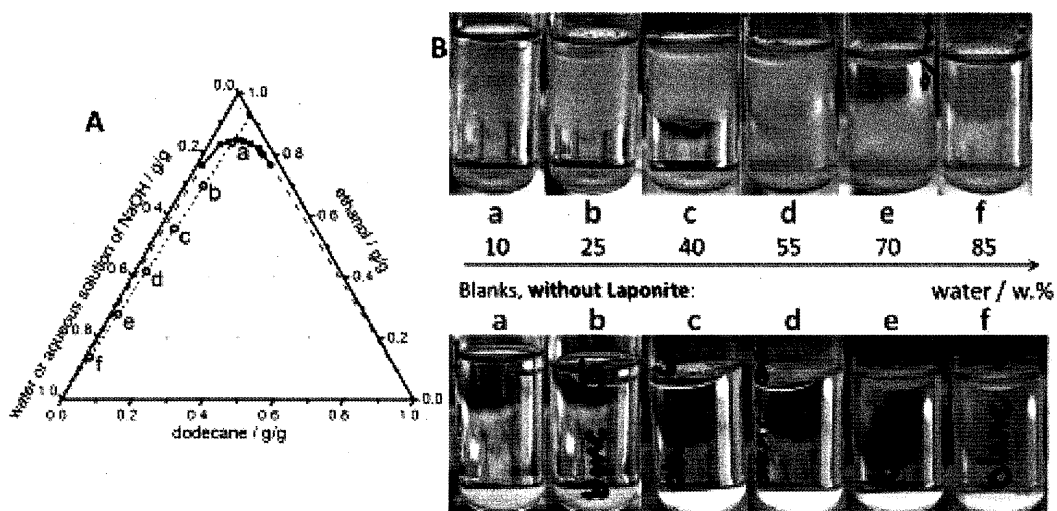
Veronika Sötz<sup>a</sup>, Jérémy Causse<sup>a</sup>, Werner Kunz<sup>b</sup>, Thomas Zemb<sup>a</sup>

<sup>a</sup>Institut de Chimie Séparative, UMR5257, 30207 Bagnols sur Cèze, France, <sup>b</sup>Solution Chemistry Group, Universität Regensburg, 93040 Regensburg, Germany

Pickering, Emulsions, Nanoparticle, Ouzo, Clay

In this study, we ask the rather fundamental question if a spontaneous emulsification process called 'Ouzo emulsification', and the principle of Pickering emulsions can be combined. Both phenomena are already studied separately, and they provide several promising characteristics, such as small droplet size, monodispersity, and outstanding emulsion stability; the ternary system dodecane-ethanol-water was investigated via dynamic light scattering (DLS) in the one-phasic region, and fluctuations of around 400nm were measured. Emulsion samples were prepared by adding an aqueous suspension of Laponite nanoparticles with a certain concentration of sodium hydroxide dropwise to a solution of dodecane in ethanol. We investigated the influence of the following parameters: Laponite content, concentration of sodium hydroxide, water ratio, the ratio dodecane to ethanol, and ionic strength on the macroscopic stability of the emulsions five days after preparation. Furthermore, the concentration of dodecane, and the laponite content in the turbid emulsion volume were measured via UV-vis and SAXS measurements.

We found that the network formed by oil droplets and Laponite nanoparticles becomes denser with increasing water content. Thus, creaming or sedimentation of the emulsions can be forced by adjusting these parameters. The weight percentage of dodecane in the emulsion remained low ( $\leq 2\text{wt.}\%$ ), irrespective of all parameter variations. The nanoparticles are able to stabilize emulsions at concentrations of sodium hydroxide above  $1 \cdot 10^{-3} \text{ mol.L}^{-1}$ . Probably, the particles start to flocculate above this concentration, and adsorption of nanoparticle aggregates on the droplets' surface is energetically more stable than adsorption of a single nanoparticle. Further explanation are based on dissolution of Laponite, and the structure of the particles. We propose that stabilization follows the typical Pickering emulsion descriptions, which report adsorption of particles at liquid-liquid interfaces. A contribution of electrostatic forces is excluded because the emulsion stability is not influenced by increasing ionic strength. Oil droplets remained in the sediment during centrifugation of the emulsion samples for 20 minutes with a gravitational force of 2665 g. We considered buoyant and gravitational forces for droplets and particles, and estimated a force of around  $10^{-15} \text{ N}$  for a link between one particle and a droplet.



Influence of the water content on the macroscopic stability of emulsions

## Hydrophobization of Silica Nanoparticles in Water: Nanostructure and Response to Drying Stress

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<sup>3</sup>Saint-Gobain Recherche, 39 Quai Lucien Lefranc, 93303 Aubervilliers, Cedex, France.

Keywords : Silica, Hydrophobization, Self-organization, Porous, Damp-proof

There is a strong environmental drive today to reduce the usage of non aqueous solvents when preparing porous materials. However, because of capillary forces, the elaboration of a damp-proof porous material from an aqueous route remains a real challenge.

Here, we propose an original environmentally friendly route starting from aqueous silica dispersions.<sup>[1]</sup> We describe the different steps going from an aqueous dispersion to a porous solid. To achieve this, hydrophilic silica particles were hydrophobized in water using different organosilane precursors by accurately controlling the grafting density. The colloidal state of the modified silica dispersions was analyzed as a function of both the organosilane precursor's nature and the grafting density by a combination of small angle X-ray scattering (SAXS) and cryo-microscopy. Then, the water removal process representing the ultimate step toward a dry solid state was followed by SAXS as a function of the grafting density.

At the fundamental level, because the hydrophobic character of the silica surfaces could be continuously varied through a precise control of the grafter density, we were able to observe for how the hydrophobic interactions modulate particles interactions and aggregates structures (figure 1). Finally, the targeted usage properties, namely the residual porosity as well as the damp-proof properties, were investigated as a function of the grafting density and the nature of the organosilane precursor.

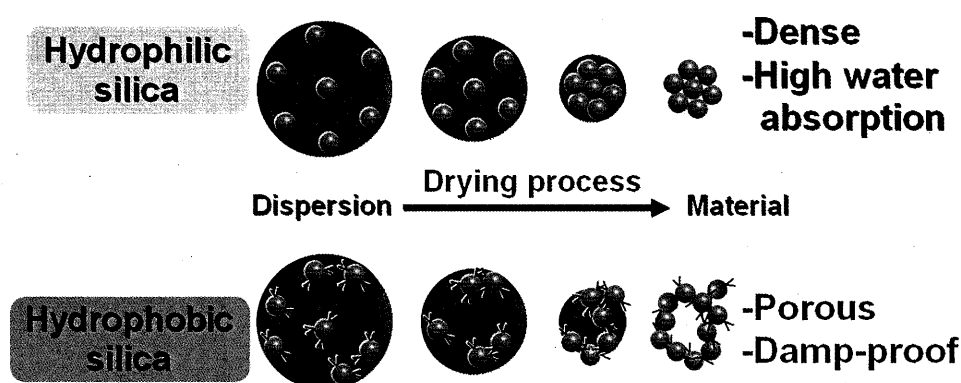


Figure 1: Nanostructure and response to drying stress of hydrophilic (top) and hydrophobic (down) silica particles

### References:

[1] Moro, S.; Parneix, C.; Cabane, B.; Sanson, N.; d'Espinose, J.-B. 2017, Hydrophobization of Silica Nanoparticles in Water: Nanostructure and Response to Drying Stress. *Langmuir*, 33, 4709.

## Zwitterionic Supraparticles as Novel Pickering Emulsifiers

Michael Maas<sup>1,2</sup>, Kuroschi Rezwan<sup>1,2</sup>

<sup>1</sup> *Advanced Ceramics, University of Bremen, Bremen, Germany*

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Keywords : Supraparticles, Patchy Particles, Heteroaggregation, Pickering Emulsion

The colloidal assembly of individually dispersed nanoparticles into well-defined clusters consisting of only a few nanoparticles promises the scalable synthesis of advanced multifunctional supraparticles with well-defined surface moieties, also known as patchy particles. However, electrostatic heteroaggregation, which is one of the simplest approaches to colloidal assembly, usually results in the uncontrolled precipitation of large particle clusters. In this work, we demonstrate the assembly of oppositely charged silica particles into well-defined core-satellite arrangements via electrostatic aggregation. To achieve controlled heteroaggregation, we studied the assembly of oppositely charged silica particles using particles with different sizes ranging from 5 nm to 150 nm at various concentrations. We found that the assembly works best with bigger particles, resulting in a fairly low polydispersity and a low amount of bridging between the individual clusters. The assembly of smaller particles produces high polydispersity, large clusters and uncontrolled aggregation and bridging. Furthermore, even with controlled aggregation into well-defined clusters in the case of bigger particles, we observe an uneven covering of the central particles with around 1-6 satellite particles absorbed to the central particle. This behavior is not predicted by simple DLVO theory which would anticipate an even spacing of the satellite particles on the core. We explain our observations by taking into account the interactions of the adsorbing particles within the ionic cloud of the central particle. We hypothesize that when the adsorbing satellite particles are small compared to the ion cloud of the core particle, they aggregate within the ion cloud and therefore do not create a well-defined monolayer on the surface of the core particle, but form small agglomerates during adsorption. The experiments were supported by modeling DLVO interactions with models of differing complexity which confirmed our hypothesis.

Finally, stable clusters consisting of APTES-coated silica particles with diameters of 150 nm and negatively charged silica particles with diameters of 80 nm at a ratio of around 1 to 4 big particles to small particles were tested for their capabilities as Pickering emulsifiers. Additionally, a part of the clusters was functionalized with OTMS (octadecyltrimethoxysilane) to render the 80 nm particles hydrophobic while keeping the APTES-coated cores unaltered. This results in either zwitterionic or amphiphilic core-satellite particles which both showed strongly increased surface activity compared to the individual particles as could be demonstrated by studying emulsion stability. Interfacial dilatational rheological tests supported the observations from the emulsion tests. Accordingly, the assembled supraparticles were shown to be superior Pickering emulsifiers that might find applications in processes that require highly efficient emulsifiers in surfactant-free systems.

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Maas, M.\*, Silvério, C. C., Laube, J., Rezwan, K. Electrostatic Assembly of Zwitterionic and Amphiphilic Supraparticles. *Journal of Colloid and Interface Science* 2017, 501, 256–266.

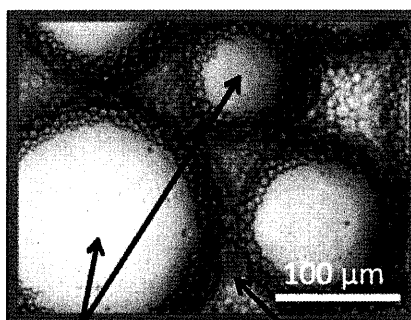
## GRAVITY DRIVEN PHASE SEPARATION IN FOAMED EMULSIONS

Maxime SCHNEIDER, Ziqiang ZOU, Dominique LANGEVIN, Anniina SALONEN

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Keywords : foam, emulsion, drainage, creaming

Mixtures of gas bubbles and oil droplets are ubiquitous in our daily lives. They are found in food products, cosmetics, oil recovery, and even in the precursors for the preparation of solid foams. A photograph of a foamed emulsion is shown in Figure 1. Oil droplets can collect at the surfaces of air bubbles and between the bubbles to stabilize them [1-3] or they can enter into the gas-water interfaces and destroy the foams [4].



**Bubbles** **Oil drops in water**

Figure 1: Air bubbles surrounded by rapeseed oil emulsion droplets.

Their industrial relevance makes it important to understand the mechanism behind their stability. We have studied the ageing of foamed emulsions by combining electrical conductivity and image analysis. This has allowed us to measure the volume fraction of the three fluids inside the foam in time and at different positions in the foam. The foam lifetime and evolution depend intricately on the emulsion volume fraction, surfactant concentration and emulsion drop size. We can distinguish three stages of emulsion ageing inside a foam: initial drainage, stabilization when the interstices between bubbles are small enough and emulsion drops block the flow and finally destruction when the drops act as an antifoam.

### References:

- [1] K. Koczó, L.A. Lobo, D.T. Wasan 1992. *JCIS*, 150.
- [2] A. Salonen, R. Lhermerout, E. Rio, D. Langevin; A. Saint-Jalmes 2012. *Soft Matter*, 699-706.
- [3] J. Goyon, F. Bertrand, O. Pitois, G. Ovarlez, 2010. *PRL*, 104.
- [4] N. D. Denkov 2004. *Langmuir*, 9463-9505.
- [5] M. Schneider, Z. Zou, D. Langevin, A. Salonen 2017. *Soft Matter*, 10.1039/C7SM00506G.

## Multi-scale approach to understand complex interactions involved in produced water treatment by flotation, in EOR context

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Keywords : Flotation, droplet-bubble adhesion, pseudoemulsion film dynamics, electrostatic repulsions.

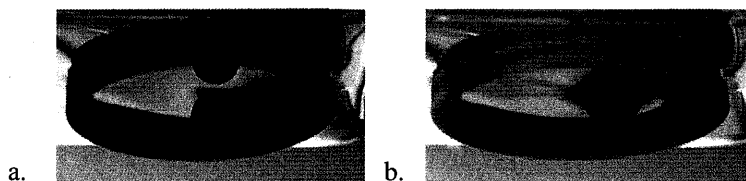
Oil extraction generates large amounts of water discharges. Gas flotation is an efficient technique to remove oil droplets from oily produced waters. This method is mainly based on air bubble and oil droplet adhesion and their combined rise. The multiphase system oil/water/air is influenced by hydrodynamics, thermodynamics and interfacial phenomena. The oil droplet adhesion on air bubble is governed by the pseudoemulsion film dynamics [1] and is strongly influenced by physico-chemical parameters of the system and fluctuations caused by the environment [2].

By studying the impact of salinity at the macroscopic level using a lab flotation column, we emphasized the importance of electrostatic repulsions for oil droplets removal: flotation efficiency increases with the ionic strength. Indeed, the oil droplet surface charge results from the ionization of indigenous natural surfactants that depends on salinity. As a result, oil droplet zeta potential decreases when ionic strength increases, which favors their adhesion with bubbles.

To understand the mechanisms involved in the air/water/oil system for the droplet-bubble attachment, we studied the dynamics of the pseudo-emulsion thin film thanks to a dedicated set up (Figure 1). With a high speed camera, we follow the approach of a rising oil droplet toward an air/water interface and we measure the necessary time to have the pseudoemulsion film rupture. To get a stable adhesion during the flotation process, the thin film has to be broken so that oil droplets can spread on the surface of bubbles. Our results show that when increasing the salinity, the rupture time of the thin film is reduced. *In fine* there is a very good agreement between the microscopic thin film stability and the macroscopic flotation efficiency.

Besides, the presence of an anionic surfactant increases oil droplets surface charge which reduces the flotation efficiency and increases the pseudoemulsion film rupture. These results confirm the importance of electrostatic interactions in oil droplets collection by air bubbles. All our results showed that there is a correlation between oil droplets zeta potential and flotation efficiency.

We also studied the impact of high molecular weight water soluble polymers on the drainage of the thin film and on the efficiency of flotation. Results show the strong influence of the rheological properties of the aqueous continuous phase when changing polymer concentration from a Newtonian behavior in the dilute regime to a shear thinning behavior in the semi-dilute regime.



**Figure 1:** Microscopic scale:  
a. Set up to observe oil droplet attachment on air/water surface  
b. Oil spreading

[1] Lobo, L.A. and Wasan, D.T., *Langmuir*, 1993, **9**, 1668-1677.

[2] Bergeron V., *J. Phys. Condens. Matter*, 1999, **11**, R215-R238.



## ATTACHMENT OF COLLOIDAL PARTICLES TO A FLUIDIC INTERFACE – APPLICATION TO THE FLOTATION PROCESS

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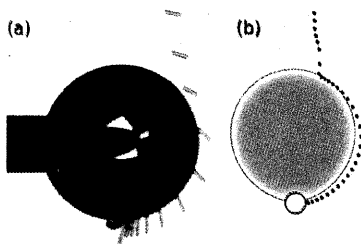
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Keywords : Colloidal particles and interfacial phenomena, experimental particle attachment to a  
fluidic interface, direct numerical simulation, flotation

The attachment of colloidal particles to the fluidic surface of immersed fluid droplets is central to a wide variety of industrial applications, among which stand out the stabilisation of emulsion (Jansen et al., 2011) and the recovery of minerals by gas bubbles (Albijanic et al., 2010), a process known as flotation. Flotation, which is here of primary interest, is a separation process which plays a major role in the mining industry. It is employed to recover a vast array of different valuable commodities such as rare earth minerals essential to the manufacture of high-tech products. The process essentially involves the attachment of hydrophobised colloidal particles to the surface of rising air bubbles. The commercially valueless hydrophilic material settles down the flotation. Experimental and numerical works dealing with the attachment of spherical and non-spherical particles to a fluidic interface are here presented (See Figure 1). Using an optical microbubble sensor the various microprocesses (Lecrivain et al, 2015) associated with the colloidal attachment of elongated fibres are first investigated. In a second stage direct numerical simulations are used to simulate the dynamics of such particles at a fluidic interface. Unlike spherical colloidal particles, it is found that plate-like particles attach more rapidly to a fluidic interface and are subsequently harder to dislodge when subject to an external force.



**Figure 1:** Attachment of an elongated colloidal particle to an air bubble immersed in water (a). Direct numerical simulation of a particle attachment (b). In the numerical approach, the two fluid-particle boundaries and the fluidic boundary are replaced with diffuse interfaces (Lecrivain et al, 2016, 2017).

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- Lecrivain, G. et al. (2017), Direct numerical simulation of an arbitrarily shaped particle at a fluidic interface, *Physical Review E*.

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## COMBINATION OF EMULSION POLYMERIZATION, SONOCHEMISTRY AND SOL-GEL PROCESS FOR THE SYNTHESIS OF Pt/SiO<sub>2</sub> SUPPORTED CATALYST WITH HIERARCHICAL POROSITY

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Keywords : emulsion polymerization, sonochemistry, sol-gel, hierarchical porosity, Pt/SiO<sub>2</sub>

### Summary

Materials with hierarchical porosity possess interesting characteristics for applications in catalysis: high specific surface area, high porous volume, tridimensional architecture.[1] In addition to the accessibility to active sites, their spatial distribution in the support is also a key parameter in the design of supported catalysts. We propose a strategy for the synthesis of supported catalysts totally performed in water, with a macro-meso hierarchical porosity and a localization of the Pt nanoparticles at the surface of the macropores (Figure 1). In a first step, a surface-functionalized polystyrene latex with colloidal stability at acidic pH is prepared by emulsion polymerization.[2] This latex is decorated with Pt nanoparticles by sonochemistry,[3] and then involved in a sol-gel process to synthesize the silica support of the catalyst.[4] After calcination, a material of high specific surface area is obtained (615 m<sup>2</sup>.g<sup>-1</sup>), possessing 3 nm diameter size Pt nanoparticles at the surface of the macropores (130 nm) interconnected with mesopores (2-11 nm).[5] These catalysts have been tested in the selective hydrogenation reaction of chloronitrobenzene to produce chloroaniline. This approach can be adapted for the synthesis of other hybrid materials (varying the polymer, the metal, and the catalyst support).

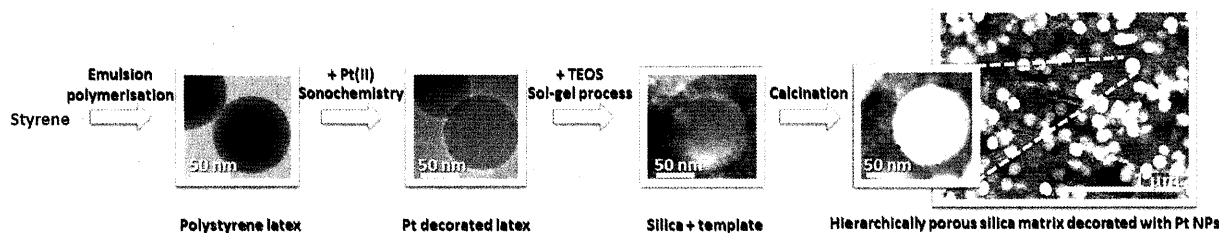


Figure 1. Synthesis of hybrid latex polystyrene/Pt for the preparation of catalytic materials Pt/SiO<sub>2</sub> with hierarchical porosity.

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## AQUEOUS SUSPENSIONS OF ZERO-VALENT IRON NANOPARTICLES FOR THE IN SITU REMEDIATION OF CONTAMINATED GROUNDWATER: EXPERIMENTS IN POROUS MEDIA MODELS AND NUMERICAL SIMULATION

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Keywords : Porous media, Zero valent iron, Nanoparticles, Numerical modeling, In situ remediation, Dechlorination, particle size distribution, shrinking core model

Aqueous suspensions of zero-valent nano-particles (nZVI) are prepared by wet chemistry techniques, their stability and longevity is evaluated by physicochemical methods of characterization [1, 2], and their reactivity toward the dechlorination of per-chloro-ethylene (PCE) is examined with tests in batch reactors [1]. Visualization multiphase flow and transport tests are performed on a glass-etched pore network to measure the rate of PCE mass loss under the injection of distilled water (dissolution) and nZVI suspension (dissolution/dechlorination). The visualization tests reveal a pattern of preferential “erosion” of the upstream interfacial regions of PCE ganglia during the injection of nZVI. The rate-controlling step of the overall process might be either (i) an enhanced PCE dissolution associated with the fast depletion of dissolved PCE molecules by nZVI, or (ii) the direct reaction of bulk PCE with the nZVI deposited upon ganglia interface [1].

A statistical shrinking-core model (SSCM) is developed to simulate the dechlorination rate of chlorinated pollutants dissolved in water by zero-valent iron nanoparticles (nZVI) by accounting for the mass-transfer processes at particle-scale along with the instantaneous reaction occurring in the solid/liquid interface and the particle-size distribution [3]. Inverse modeling of batch experiments is used to estimate the kinetic parameters of PCE dechlorination along with the mass-transfer coefficients. Based on the SSCM, an analytic phenomenological model providing the overall reaction rate as a function of dissolved PCE and nZVI concentrations is suggested [3]. The nZVI injection in porous media is simulated as an advection- dispersion process by coupling the macroscopic equations of the mechanisms of nanoparticles attachment/detachment on the pore-walls, with PCE and nZVI transport equations, and accounting for the kinetics of PCE dissolution along with the kinetics of dissolved / undissolved (ganglia) PCE reactions with nZVI. The macroscopic numerical model is used as a tool to predict the rate PCE identify the mechanism of PCE ganglia remediation by nZVI in porous media.

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## Electrochemically-Active Microgel Systems

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Keywords : Electroactive Polymers, Hydrodynamic Voltammetry

### Abstract

Microgels are crosslinked polymeric particles consisting of a porous network swollen by a solvent. They have often the ability to undergo a volume phase transition with respect to environmental changes, allowing an adjustment of segmental proximity and network dynamics [1]. Introduction of charges into the microgel network leads to a possible interaction of the polyelectrolyte microgel with oppositely charged counterions based on electrostatic attraction (host-guest interplay). In case of redox-active counterions, the charge of these guest molecules can be changed by electrochemical means [2].

Hence, we address thermoresponsive cationic microgels and their influence on the electrochemistry of hexacyanoferrates [3]. Further, we investigate the influence of the counterion guests on the swelling of the microgel hosts: the size of the cationic microgel can be reversibly modulated by electrochemical switching leading to a redox-responsive microgel system [4]. Finally, also other attempts to generate electroactive microgel colloids (e.g. with permanently linked redox-active units) are discussed.

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## TIME RESOLVED BOEHMITE PARTICLES SYNTHESIS AND CHARACTERIZATION USING SMALL ANGLE X-RAY SCATTERING

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Keywords : boehmite, co-precipitation, SAXS, in situ characterization, millifluidic co-flow

### Abstract:

$\gamma$ -alumina ( $\text{Al}_2\text{O}_3$ ), is widely used into petrochemical processes as porous catalysis support. The  $\gamma$ -alumina synthesis method involve the shaping and calcination of a precursor, boehmite ( $\text{AlOOH}$ ), that can be obtained by a co-precipitation route when two aluminium salts are mixed together [1]. Alumina porosity comes from the assembly of nanoparticles, which shapes and organisation are directly linked to the boehmite initial characteristics. As boehmite strongly impact the alumina final properties, it became necessary to have a deeper insight into the physico chemical phenomena that lead to their formations by bringing some new information on how the originals properties of boehmite can modify the alumina final ones.

In this mainly fundamental study, we focused on the understanding of the first steps of the boehmite co-precipitation reaction with the objective to observe and describe the different mechanisms involved.

In a first step, a specially designed millifluidic reactor has been built in order to observe the boehmite formation under controlled conditions using a laboratory Small Angle X-ray Scattering (SAXS) set up. This homemade cell consist of two different diameters cylindrical quartz capillaries assembly to create a co-flow when injecting some fluids as shown on figure 1 scheme.

The reagents temperatures, concentrations and flow rates are controlled while injecting the chemicals, allowing to vary the conditions, and so the behavior of the nucleation, growth and aggregations of the boehmite particles. In a second time, the flow rate and the distance from the mixing point

are used to bring some kinetics information about the boehmite co-precipitation, determining a space to time equivalence inside the cell. These phenomenon can then be monitored using the SAXS patterns evolution as shown on the figure 1: large  $q$  value should be influenced by nanoparticles sizes, while low  $q$  should be more sensitive to aggregation. Other ex situ characterisation techniques on the reaction products will also allow the comparison of the synthetized boehmites with the ones obtain on the classical industrial method.

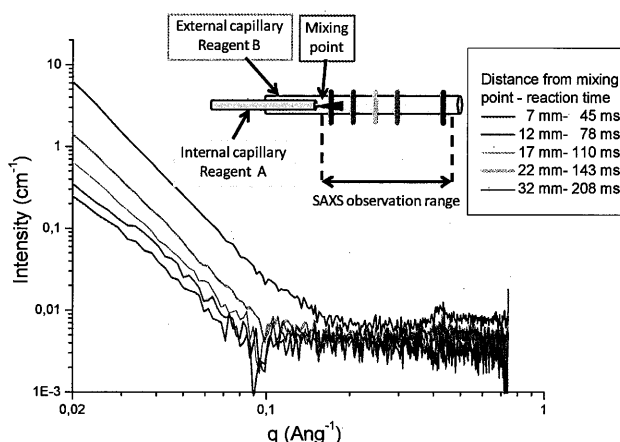


Figure 1: Dependence of the SAXS profile as the distance from mixing point increase

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## RHEOLOGY OF ADSORPTION LAYERS FROM THE PROTEIN HYDROPHOBIN AND ITS MIXTURES WITH OTHER PROTEINS: EXPERIMENT AND THEORETICAL MODEL

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Surface shear rheology, Hydrophobin, Viscoelastic Thixotropic model, Disjoining Pressure Isotherms

### Abstract

The hydrophobins represent a class of amphiphilic proteins. At air/water and oil/water interfaces they form adsorption layers with the highest surface elasticity and viscosity among all investigated proteins. Moreover, the hydrophobins are rather “sticky” molecules, which are used for surface coatings and to fix functional molecules at interfaces. We investigated the surface shear rheology of class II hydrophobin HFBII layers at liquid interface in two different dynamic regimes – fixed rate of strain and oscillations [1–3]. The rheological data obtained in both regimes comply with the same viscoelastic thixotropic model, which is used to determine the surface shear elasticity and viscosity,  $E_{sh}$  and  $\eta_{sh}$ . The resulting values for the  $E_{sh}$  show that the elasticity is insensitive to the rate of strain in a wide range of the investigated shear rates. The mixing of hydrophobin HFBII with other conventional proteins could reduce  $E_{sh}$  and  $\eta_{sh}$  proportional to the fraction of the conventional protein. However, our experiments show that the effect of mixing can be rather different depending on the nature of the additive. If the additive is a globular protein, like  $\beta$ -lactoglobulin and ovalbumin, the surface rigidity is preserved, and even enhanced. In contrast, the addition of the disordered protein  $\beta$ -casein leads to softening of the HFBII adsorption layer. Similar (an even stronger) effect is produced by the nonionic surfactant Tween 20 [4]. These results could contribute for quantitative characterization and deeper understanding of the factors that control the surface rigidity of protein adsorption layers with potential application for the creation of stable foams and emulsions with fine bubbles or droplets.

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## **A COMPREHENSIVE SIMULATION STUDY OF APPLICATION OF POLYMER GELS FOR ENHANCING OIL RECOVERY**

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Keywords: Enhanced Oil Recovery, Water Diversion, Reservoir Simulation, Polymer Gel

To improve the sweep efficiency in oil fields characterized by high water cut after production by water flooding, conformance control is required. This involves use of gels to block the high permeability or thief zones in order to divert the water into the unswept zones. In-depth placement of the gel is challenging since gelation time is normally short for the gel to penetrate deep into the reservoir. Gelation may be delayed by encapsulation of the crosslinkers into carriers through the reservoir. Gelation occurs gradually under reservoir conditions, ensuring a controlled gel placement. To evaluate the feasibility of this system, reservoir simulation study was performed and diversion potential of the gel system was investigated. Important parameters in the simulation study and challenges involved are discussed. Guidelines for selecting the best reservoir candidate and conditions of gel application are suggested. Slow gelation was assumed for the kinetics model to simulate the controlled release of the crosslinkers. A redox system may be considered for kinetics modelling before gelation process starts. Velocity-dependent gelation model was also applied to improve the simulations by preventing gel formation around the injector. Another method applied to model the in-depth gel placement is the use of pH-sensitive polymers. Numerical simulation was performed to investigate the application of pH-sensitive polymers and compare the results with waterflood and conventional polymer treatments in a reservoir. These polymers are injected into the reservoir as low viscosity acidic fluid before reacting with minerals to form a high viscosity plug in the high permeability zones. Overall, simulation results show that polymer gel systems considered can most effectively divert the injected water towards unswept zones in reservoirs with negligible crossflow between layers. Use of the polymer slug is the best way to improve the sweep efficiency in such reservoirs when there is significant permeability contrast between layers. However, polymer flooding is not very effective since the low permeability zones may be plugged by the gel.

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## PORE FILLING EVENTS IN SINGLE JUNCTION MICRO-MODELS WITH CORRESPONDING LATTICE-BOLTZMANN SIMULATIONS

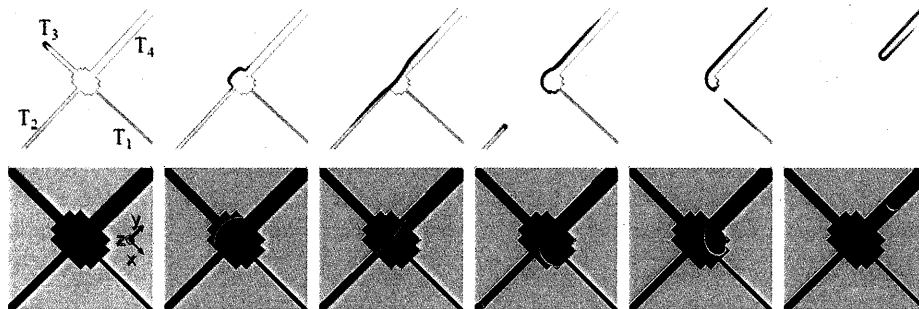
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Keywords: capillary, interfacial and free surface flows; microfluidics; micro-/nano-fluid dynamics

### Abstract

The aim of this work is to better understand fluid displacement mechanisms at the pore scale in relation to capillary-filling rules. Using specifically designed micro-models, we investigate the role of pore body shape on fluid displacement during drainage and imbibition via quasi-static and spontaneous experiments at ambient conditions. The experimental results are directly compared to lattice Boltzmann (LB) simulations. The critical pore-filling pressures for the quasi-static experiments agree well with those predicted by the Young–Laplace equation and follow the expected filling events. However, the spontaneous imbibition experimental results differ from those predicted by the Young–Laplace equation; instead of entering the narrowest available downstream throat, the wetting phase enters an adjacent throat first. Thus, pore geometry plays a vital role as it becomes the main deciding factor in the displacement pathways. Current pore network models used to predict displacement at the field scale may need to be revised as they currently use the filling rules proposed by Lenormand et al. (*J. Fluid Mech.* **135**, 1983, 337–353). Energy balance arguments are particularly insightful in understanding the aspects affecting capillary-filling rules. Moreover, simulation results on spontaneous imbibition, in excellent agreement with theoretical predictions, reveal that the capillary number itself is not sufficient to characterise the two phase flow. The Ohnesorge number, which gives the relative importance of viscous forces over inertial and capillary forces, is required to fully describe the fluid flow, along with the viscosity ratio.



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## Molecular Theory of Solvation for Supramolecular Structures and Nanomaterials

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Keywords: *Multiscale Modeling, Quantum Chemistry, Molecular Solvation Theory, Multi-Time-Step MD, Generalized Solvation Force Extrapolation, Dissipative Particle Dynamics*

In recent two decades, molecular theory of solvation for nanostructures in both aqueous and non-aqueous solution, a.k.a. three-dimensional reference interaction site model (3D-RISM) with the Kovalenko-Hirata (KH) closure relation [1-4], was systematically developed and applied to a variety of compounds, supramolecules, and biomolecules in a number of solvents, mixtures, electrolyte and non-electrolyte solutions [3-11]. From the first principles of statistical mechanics, 3D-RISM-KH theory predicts the solvation structure and thermodynamics of nanochemical and biomolecular systems, including their analytical long-range asymptotics. It yields high accuracy, efficiency, and applicability by multiscale coupling of methods at different space and time scales to provide fundamental understanding and prediction for nanomaterials and biomolecules.

The method has been coupled with quantum chemistry [3-8], molecular dynamics [9-11], and dissipative particle dynamics [12]. Examples include helical rosette nanotubes with tunable stability and hierarchy [9], water promoted supramolecular chirality inversion [10], formation and stability of self-assembling supramolecular structures of organic rosette nanotubes with ordered shells of inner and outer water [11], and accurate and efficient dissipative particle dynamics of polymer chains with coarse-grained effective pair potential obtained from DRISM-KH theory [12].

Multi-Time-Step Molecular Dynamics coupled with 3D-RISM-KH molecular solvation theory and Generalized Solvation Force Extrapolation (MTS-MD/3D-RISM-KH/GSFE) theory provides quasidynamics description of biomolecules [13]. Validation included folding of miniprotein in solution from fully extended to equilibrated state in 60 ns, which provides acceleration by two orders of magnitude time scale as compared to 4-9  $\mu$ s protein folding in experiment [13].

Recent applications of 3D-RISM-KH consist in multiscale coupling of quantum chemistry, molecular solvation theory, molecular dynamics, and dissipative particle dynamics [4, 14].

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## Foam's flow in porous media: In-situ texture characterization by Small angle neutron scattering and X-ray tomography experiments

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Keywords : Foam, porous media, tomography X, Small angle neutron scattering

### Abstract

Among Enhanced Oil Recovery techniques, foam is one of the promising tools to reduce the gas mobility and divert it to the oil rich parts of the reservoir. The properties of foam flows depend on a key parameter called "foam texture" which affects the rheology of the foam fluid and which is a means of classifying a foam according to its bubble size, shape and distribution within the foam matrix<sup>1</sup>. The description of the texture of a foam confined in a real porous medium is difficult because conventional methods do not have adequate spatial and temporal resolution or are not adapted to opaque media. The current view of a foam texture in a porous medium is deduced from 1D and 2D micromodel experiments or from texture measurements outside the porous medium.

We propose here an original method for in situ characterization of foam texture in 3D porous media based on Small Angle Neutron Scattering technique (SANS) in contrast matching conditions. SANS allows direct access to the interfacial area of the liquid-gas interfaces in the porous medium and has the unique advantage to probe nanoscopic features on centimetric volumes. In this study, SANS acquisitions are made in specific cells allowing pressure drop measurements for petrophysical characterization. The foam is generated in-situ by co-injection of gas and a surfactant solution. The porous media are made of fused silica grains. The geometric characteristics of the pore network are extracted by image analysis from X-ray microtomography images and compared to the calculated bubble size. Foam texture is measured as a function of foam quality, interstitial velocity and grain size.

In parallel, we run different coreflood experiments coupled with X-ray CT measurements in which pressure drop and saturations are measured for different foam qualities and interstitial velocities in homogeneous sandstones. These experiments provide information on the different steps of foam generation and flow within a core. From this set of experiments, we develop a methodology to calculate the in-situ mean foam texture and compare it to the SANS measurements.

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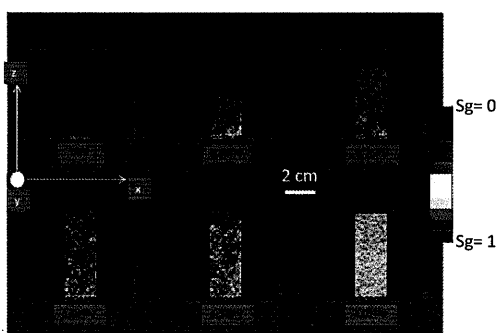


Figure: CT-scans of Foam flow in Bentheimer sandstone. Red color corresponds to the gas phase

## CLOGGING OF MODEL PORES WITH A BROWNIAN SUSPENSION

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Keywords : Brownian suspension, clogging, model pores, microfluidics

The accumulation of particles in a porous media is a complex process which involves DLVO, steric and hydrodynamic interactions. The clogging phenomenon may occur in inkjet printers or numerous other applications such as water filtration through a membrane. It has also large application opportunities in well damaging and Enhanced Oil Recovery [1]. While the fouling of a membrane at the macroscopic scale is well understood, the investigations at the pore scale are still at their beginning [1]. Very recent works have used model microchannels to study the effect of different parameters, such as ionic force or Péclet number on the clogging of pores at the micrometer scale [2-4]. The sub-micron dimensions are still unexplored in spite of strong specificities (Brownian motion, system size comparable to scales of interaction), and relevance (0.2  $\mu\text{m}$  being a typical industrial pore size). In this context, we study the clogging/unclogging of silicon-glass channels with Brownian particles. The design consists of two micro-channels connected by ten smaller "nanochannels" 10 $\mu\text{m}$  wide, 50 $\mu\text{m}$  long and 330 to 3300nm deep. We inject a suspension of latex fluorescent beads of diameter 250nm with a volume fraction  $\Phi=4.10^{-5}$ . The ionic strength is fixed using a phosphate buffered saline. A pressure drop  $\Delta P$  is imposed between the two micro-channels to allow particles to cross the nanochannels. The clog formation and/or disintegration processes are captured by fluorescent microscopy video imaging.

Figure 1 shows an example of clogs at the entrance of nanochannels. We show the dramatic influence of the ionic strength. Whereas no saturation of the clog size is observed in presence of salt, a quick saturation appears when we use only deionized water as a solvent. This is due to the repulsive/drag forces competition. But if the drag forces are large enough compared to the Brownian motion, a slow growth of the clog size replaces the saturation. It is accompanied by a change of the clog structure that we study by releasing the pressure (unclogging). Finally, by adding a crossflow in the inlet microchannel we observe that the clog size saturates due to erosion/drag forces competition.

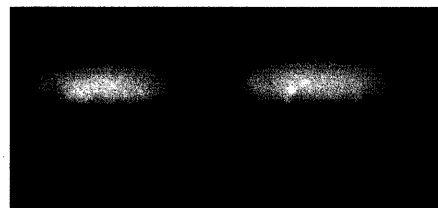


Figure 1 - Image of clogs at the entrance of nanochannels delimited by red lines.

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## THERMOELECTRIC ENERGY CONVERSION IN FERROFLUIDS

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Keywords : Thermoelectric, thermogalvanic, ferrofluids, magnetic field

### Context:

Today, much of world's consumed energy is lost to waste heat through all levels of human activity. For example, thermal loss consists 20 to 50 % of total energy consumption across different industrial sectors and as high as 60-70% in cars (gasoline or diesel engines). Therefore, if even a small fraction of 'waste-heat' could be converted into more useful forms of energy (e.g., electrical), it would result in tremendous savings to global energy consumption.

Thermoelectric (TE) materials have been considered as one possible solution to recover the low-grade waste-heat. The TE effect describes a material's intrinsic property to directly convert temperature difference ( $\Delta T$ ) applied across its body into electric voltage ( $\Delta V$ ) and vice-versa;  $\Delta V = -S_e \Delta T$ , where  $S_e$  is known as "the Seebeck coefficient." Presently, solid semiconductor-based materials are known to possess the highest thermal-to-electrical energy conversion efficiency. The thermoelectric effect also exists in liquid electrolytes and in complex liquids such as ionic-liquids (IL) and charged colloidal suspensions. Unlike in solid materials, where voltage is created solely by the diffusion of electrons (or holes) under a temperature gradient, there are several inter-dependent TE effects taking place in liquids such as thermodiffusion of charged molecules and colloidal particles and thermogalvanic effect. The resulting  $S_e$  values are generally an order of magnitude larger than the best-performing semiconductor counterparts and thus the TE conversion technology based on liquid electrolytes (known as thermocells) is currently attracting attention as an alternative path to produce electricity from low-grade waste heat [1].

### Thermocell using magnetic colloidal suspensions (ferrofluids):

Many improvements are made to enhance the thermocell performance, in particular, through electrode materials, redox-couples and electrolyte types. Recently, it has been implied that in charged colloidal suspensions such as ferrofluids (i.e., suspensions of magnetic nanoparticles (MNPs)), the Seebeck voltage induced by the thermodiffusion of colloidal particles can further enhance the overall thermoelectric effect [2]. Furthermore, the application of magnetic field is known to influence the thermodiffusion behaviour of MNPs which may have a positive impact on the TE property of the ferrofluids.[3]

Based on these considerations, we have investigated the magneto-TE effect of several types of ferrofluids made with organic solvents, water and ionic liquids, combined with suitable redox couples. The Seebeck coefficient, electrical conductivity and the power output were measured as a function of MNP concentration and/or magnetic field. It has been found that, the presence of MNPs can either increase or decrease the fluid's overall Seebeck coefficient, depending on the intricate balance involving the electrochemical reaction potential of the redox couple, ionic strength of the solution and the size and the sign of the effective surface charge of MNPs. In certain examples, the application of magnetic field was found to increase the  $S_e$  value by as much as 25 %.

The observed phenomena are analysed in terms of existing theoretical models addressing both thermogalvanic (redox couple) and thermodiffusion (NP) effects which allowed identification of key physical phenomena giving rise to a TE voltage in these colloidal suspensions. Further insight into achieving higher thermoelectric conversion efficiency by tuning the solvent and NP properties will also be presented.

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## Osmosis for Enhanced Oil Recovery studied with microfluidics

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Keywords : osmosis, micromodel, oil recovery, LSW, membrane, microfluidics, EOR

Enhanced Oil Recovery (EOR) gathers various techniques to increase the amount of crude oil extracted from an oil field. Among them, the low-salinity waterflooding (LSW) technique which, by definition, doesn't use any chemical agents not naturally present in the ground, has been used for more than 15 years [1]. Indeed, it has been shown that the use of low salinity water for injection could lead to an improved oil recovery. However, due to the lack of knowledge about the underlying phenomena, its effectiveness cannot be predicted.

LSW is creating a salinity gradient between brine, present in the oil well with the oil, and the injected water, leading to a water transfer and a reorganization of the spatial distribution of the different phases. As a consequence, the oil is expelled from the pores of the rocks of the reservoir. Among the hypotheses explaining this transfer, one is based on the osmosis which is a diffusion phenomenon through a semi-permeable membrane in order to balance chemical potentials [2]. In the EOR context, we assume that the oil is acting as the membrane between the brine and the injected water.

To identify the mechanisms at stake, a simple system was elaborated to highlight the relationship between the physicochemical properties of the fluids, in bulk and at the interfaces, and the phenomenon of transport of water molecules through the oil. The device is composed of a sealed glass capillary where an oil meniscus separates two water reservoir having different composition. This simple configuration allowed us to systematically vary the oil type, the glass surface properties and, thus, the contact angle as well as the salt concentration in the aqueous phases. In addition, a more complex formulation where surfactants, polymers or typical compounds from oil like asphaltenes, can be used for evaluating their impact on water transport. Beside this experimental setup, we developed a microfluidic device for modelling a porous medium. We end up with a two-dimensional system allowing us to observe the interaction between different pockets of salted water under osmotic pressure as a function of the geometry of a simple rock model.

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## SUBCOOLING AND WETTABILITY EFFECTS ON GAS HYDRATE GROWTH IN ROUND GLASS MICROCAPILLARIES

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<sup>3</sup>ISM (CNRS-Université de Bordeaux), France

Keywords: wettability, gas hydrate growth, microfluidic, porous media,

### Abstract

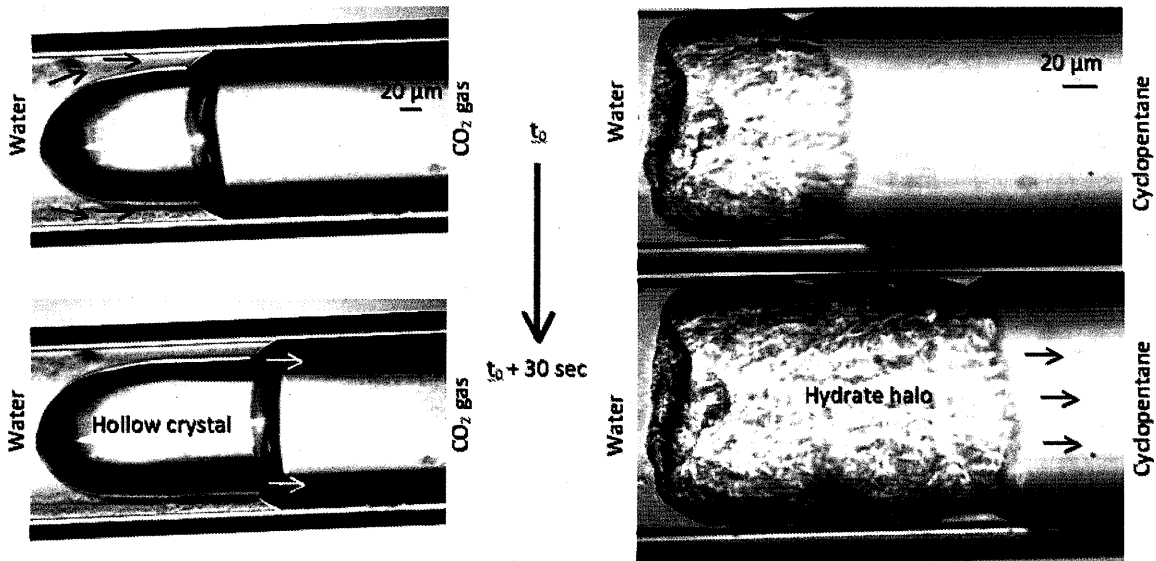
Hydrates are non-stoichiometric crystalline solids made up of cages of water molecules (hosts) trapping at low enough temperature and/or high enough pressure a different kind of ('guest') molecules such as CO<sub>2</sub>, CH<sub>4</sub>, etc. Long considered a nuisance because they are able to plug natural gas transportation lines<sup>1</sup>, they are now being viewed as promising materials for applications such as gas storage and separation<sup>2</sup>, secondary refrigeration and waste/salted water treatment. Their growth and melting mechanisms are somewhat more complex than those of ice, since they involve the guest molecules in addition to water. How these mechanisms are influenced by thermodynamic conditions, confinement and substrate wettability (which is siliceous or at least hydrophilic in most geological settings) is of utmost interest for understanding situations and designing applications involving sediment-hosted gas hydrates. The cyclopentane (CP) and CO<sub>2</sub> hydrate are formed and studied in round silica microcapillaries mimicking a cylindrical pore. Hydrate nucleation is a stochastic process. In order to force the hydrate formation, the temperature is lowered at constant pressure and cooling rate, well below 0°C. Unlike what is observed with CP hydrate, the CO<sub>2</sub> hydrate phase appears prior to ice. Raman spectra have been collected following this first formation to confirm the nature of the solid that has been formed. The gas hydrate nucleates on the water/guest meniscus, which is rapidly covered with a hydrate crust, and then propagates on both sides of the meniscus: on the guest side, as a hydrate film (halo) spreading on the silica substrate, and on the water side, as fast-growing fibers or dendrites. The temperature of nucleation of the first hydrate formed falls in a narrow temperature interval and it's less stochastic or more deterministic. When the cooling rate is decreased or the pressure is increased, the subcooling required for triggering gas hydrate formation is reduced. Subsequent hydrate growth is primarily controlled by subcooling, and by substrate wettability. With glass (water-wet) microcapillaries, hydrate advances as a halo creeping on glass on the guest side of the meniscus, fed by water flowing between this halo and the wetted glass. For low subcooling, the halo grows irregularly and slowly as an array of large monocrystals. As subcooling increases, the halo has a finer polycrystalline texture and creeps with a higher initial velocity; however, past some elapsed length in the millimeter range, the halo abruptly decelerates. With silane-treated (guest-wet) microcapillaries, the hydrate also grows along glass as a halo, but it does so on the water side rather than on the guest side of the meniscus, fed by guest flowing between the wetted glass and the halo.

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Growth of a hollow CO<sub>2</sub> hydrate monocrystal from the meniscus water/CO<sub>2</sub> gas at 22 bar and a subcooling of 0.2 °C.

Growth of a cyclopentane hydrate halo at 0°C (subcooling 7°C) from the interface between water and cyclopentane

## Complex fluids for the nuclear decontamination of radioactive solid surfaces

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Keywords: Radioactive decontamination, Colloidal gel, Aqueous Foam

Clean-up and dismantling of nuclear facilities needs decontamination operations. In this context, the CEA develops for many years chemical decontamination processes based on the use of “smart” complex fluids: colloidal gels (solid particles dispersed in a decontaminating solution) and foams (gas dispersed in a decontaminating solution). The presence of solid particles or gas bubbles gives to the complex fluids interfacial interaction properties. Thus, the use of complex fluids leads to a prolonged contact between a contaminated surface and the decontaminating solution. Then, by controlling the aging, the decontamination operation can be handled without damage the surface and producing a low amount of secondary waste. The physicochemical properties of the complex fluids (rheology, adhesion, drying, stability) are described. These properties will govern the complex fluid behaviour at the contact with a surface as well as the decontaminating efficiency. Examples of on-site applications are finally presented.

### Self-drying gels [1]

Self-drying gels consist of mineral colloidal particles (silica or alumina) dispersed in a decontaminating solution. When spread on a contaminated surface, these gels trap the contaminants by sorption. The decontaminating solution can be tailored to attack the substrate down to several microns to release incrustated contaminants. Various substrates can thus be treated. The gel finally dries and fractures into a non-powdery solid easily removable. This technology is used for the decontamination of large surfaces but can also be adapted for small and complex geometry items. The main advantage is that only solid inorganic waste is produced.

### Foams [2]

For decontamination foams, “static foams” that are used by filling the facility to treat was developed. A strategy using additives – polymers or particles- is defended to obtain high life time foams that are able to treat huge and complex shape materials such as fission products tanks or steam generator. We will show how we could modify the drainage behaviour *i.e.* the liquid flow of aqueous foams with hydrosoluble polymer or colloidal hydrophilic fumed silica aggregates.

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## FROM HIERARCHICAL ASSEMBLY OF NANOPARTICLES TO AEROGELS

M. ODZIOMEK<sup>1,2</sup>, F. CHAPUT<sup>1</sup>, M. SITARZ<sup>2</sup>, F. LEROUGE<sup>1</sup> and S. PAROLA<sup>1</sup>

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<sup>2</sup> AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Chemistry of Silicates and Macromolecules, al. A. Mickiewicza 30, 30-059 Krakow, Poland

Keywords : nanoparticles, assembly, LTO, battery, aerogels

The use of colloidal suspension of small nanoparticles to build microstructured materials by self-assembly represent convenient route towards crystalline porous systems. We introduce here methods that allow preparation of hierarchically porous powders, films or monoliths.

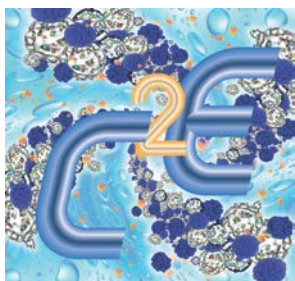
The particles aggregation permits preparation of hierarchically organized powders or films with high crystallinity. The first example of material is Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO), which can be used as anode for high-performance lithium-ion batteries. This material is particularly interesting due to its zero strain-like behaviour during lithium insertion/extraction, excellent chemical stability and good cyclability. Unfortunately it suffers from a low ionic and electronic conductivity. Well-controlled multilevel porosity would enable effective penetration of the liquid electrolyte, while distance for the Li<sup>+</sup> diffusion is minimized in the electrochemically active nanoparticles. In this work we succeeded to synthesize hierarchically nanostructured LTO. The method is relatively cheap and up scalable. It was possible to obtain uniform, well-crystallized primary 4-8 nm nanoparticles, self-assembled in porous secondary particles, with high specific surface area. Interestingly such material delivers exceptional electrochemical performance while applied in lithium-ion batteries, with recorded capacity for low current densities exceeding the theoretical one, as well as reversible capacity of 170 mAh g<sup>-1</sup> after 1000 cycles at 50 C current density with practically no signs of capacity fading [1].

Controlled destabilization of stable suspensions of nanoparticles may also lead to gelation of assembled nanoparticles and preparation of monolithic porous structures called aerogels. This approach was used to prepare oxides (YAG), fluorides (Rare Earth) crystalline aerogels and mixed-composite aerogels with high controlled porosity, mechanical resistance and optical properties [2]. This offers a wide possibility of various compositions of highly porous materials for applications in catalysis, photocatalysis, optics, sensors.

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2. M. Odziomek, F. Chaput, M. Sitarz, F. Lerouge, S. Parola, submitted for publication.





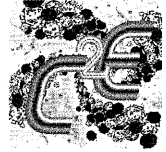
## Colloids and Complex fluids for Energies – C<sup>2</sup>E Systems understanding: From preparation to process design

IFPEN, Rueil-Malmaison, 4-6 December 2017

### Poster Session

- P/6 Interactions between kaolinite clay suspensions and anionic surfactant  
A. Suzzoni<sup>1,2</sup>, E. Kohler<sup>1</sup>, L. Barre<sup>1</sup>, L. Michot<sup>2</sup>, P. Levitz<sup>2</sup> (1 IFPEN, France, 2 PHENIX, Univ. Pierre & Marie Curie, France)
- P/8 Capillary filling and haines jump events using free energy Lattice-Boltzmann simulations  
I. Zacharoudiou, E. Boek (Imperial College, Great-Britain)
- P/10 Characterization of magnetic nanoparticle dispersions interactions by multisample analytical centrifugation  
T. Sobisch<sup>1</sup>, N. Buske<sup>2</sup>, D. Lerche<sup>1</sup>, S. Gressier<sup>1</sup> (1 LUM GmbH, 2 MagneticFluids, Germany)
- P/14 The dynamic characteristics and tracking adjustment method of ASP flooding in daqing oilfield  
P. Ye<sup>1</sup>, L. Zhong<sup>2</sup>, J. Wei<sup>3</sup> (1,2 Daqing Oil Field Company, 3 Northeast Petroleum University, China)
- P/23 Evaluation of flocculation of soft nano-or micro-particles: in situ visualization of separation behavior versus zeta-potential  
D. Lerche, T. Sobisch (LUM GmbH, Germany)
- P/30 Modeling of non-ideal multi-component multi-phase fluids by pseudopotential lattice Boltzmann model  
M. Pourtousi<sup>1,2</sup>, O. Shardt<sup>1,2</sup>, H.E.A. Van den Akker<sup>1,2</sup> (1 SSPC, Univ. of Limerick, 2 Bernal Institute, Univ. of Limerick, Ireland)
- P/31 Ageing analysis of solid and paste-like products with Rheolaser crystal  
R. Ramsch, G. Brambilla, X. Hu, P. Bru, G. Meunier (Formulation, France)
- P/32 Fast and simple average molecular weight determination with fluidicam<sup>RHEO</sup>  
Y. Lefeuvre, E. Woodcock, P. Adamska, P. Da Costa, P. Abgrall, G. Meunier (Formulation, France)
- P/33 Advantage of using multiple light scattering technique for the new safe demulsifier efficiency analysis for oil production  
C. Dalmazzone<sup>1</sup>, A. Mouret<sup>1</sup>, C. Noik<sup>1</sup>, C. Tisserand<sup>2</sup>, G. Meunier<sup>2</sup> (1 IFPEN, 2 Formulation, France)

- P/35 **Sulfonate methyl esters of fatty acids in aqueous solutions : interfacial and micellar properties**  
V. Ivanova (Univ. of Sofia, Bulgaria)
- P/38 **Sand agglomeration in oil and gas reservoirs using polymers**  
R-Y Lee<sup>1,2</sup>, P.F. Luckham<sup>2</sup>, O.K. Matar<sup>2</sup>, M. Shahrul Amir Zamberi<sup>1</sup>, N. S. Karam Chand<sup>1</sup> (1 Petronas, Malaysia, 2 Imperial College, Great Britain)
- P/41 **Polyelectrolyte/Surfactant mixtures at the bulk and interfaces**  
S. Aidarova<sup>1</sup>, A. Sharipova<sup>1</sup>, R. Miller<sup>2</sup> (1 Kazakh National Technical Univ. Kazakhstan, 2 Max-Planck Institute of Colloids and Interfaces, Germany)
- P/42 **Influence of polymer-surfactant compositions adsorption on process of clearing of oil emulsion form water and salts**  
S. Aidarova<sup>1</sup>, B. Mutaliev<sup>2</sup>, G. Madibekova<sup>3</sup>, A. Sharipova<sup>1</sup> (1 Kazakh National Technical Univ., 2 Auezov South Kazakhstan State Univ., 3 South Kazakhstan State Pedagogical Institute, Kazakhstan)
- P/44 **Laboratory assessment of nanotracers for oil reservoir characterization**  
M.Ould Metidji<sup>1,2</sup>, A. Krivokapic<sup>1</sup>, S. Kalesoglu<sup>1</sup>, M. Silva<sup>1,2</sup>, L. Cathles<sup>3</sup>, T. Bjornstad<sup>1,2</sup> (1 Institute for Energy Technology, Norway, 2 National IOR Center of Norway)
- P/45 **Inverse pickering emulsion stabilized by exfoliated hexagonal-Boron nitride (h-BN)**  
D. Gonzales Ortiz<sup>1</sup>, C. Pochat-Bohatier<sup>1</sup>, J. Cambedouzou<sup>2</sup>, S. Balme<sup>1</sup>, M. Bechelany<sup>1</sup>, P. Miele<sup>1,3</sup> (1 Institut européen des membranes, Univ. Montpellier, France, 2 Institut de Chimie séparative, Univ. Montpellier, France, 3 Institut universitaire de France)



# ABSTRACTS

Abstracts are listed following the program order

*The abstracts are published in their original format as they were sent to the Organizing Committee*



## **INTERACTIONS BETWEEN KAOLINITE CLAY SUSPENSIONS AND ANIONIC SURFACTANT**

**ARIANE SUZZONI (1, 2)\*, ERIC KOHLER (1), LOÏC BARRE (1), LAURENT MICHOT (2), PIERRE LEVITZ (2)**

(1) IFP Energies Nouvelles (IFPEN), Rueil Malmaison, 92500, FRANCE, (2) Laboratoire Physicochimie des Electrolytes et Nanosystèmes interfaciaux (PHENIX), UMR 8234, Université Pierre et Marie Curie, 75005 Paris, FRANCE

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Keywords : Clay mineral, surfactant, adsorption, stabilization

### **First-level headings (11-point Arial bold, left-justified)**

Interactions between clay minerals and organic molecules are important in numerous industrial processes and particularly, in the oil industry. For instance, one of the methods used for improving hydrocarbon recovery is to inject chemicals, such as polymers and surfactants in the well. Often, these techniques are based on the use of anionic surfactants as these molecules are only weakly adsorbed on reservoir rocks. This maintains a constant composition of the injected solutions and minimizes losses associated to adsorption. Still, especially in the presence of clay minerals, some reactions (adsorption, aggregation, deflocculation...) can occur between the surfactants and the rocks, which can, in turn, significantly impact oil recovery. It is then essential to reach a better understanding of the interaction between anionic surfactants and various clay minerals, which is the main objective of our present work.

This poster will focus on the results obtained with kaolinite.

Reference kaolinite was purified and suspensions of this mineral were contacted with a typical anionic surfactant bis (2-ethylexyl) sulfosuccinate sodium (AOT). In agreement, with previous studies (Lagaly, 1989; Welzen et al., 1981) significant stabilization of kaolinite suspensions can be observed in the presence of AOT. The effect of various chemical conditions (pH, ionic strength) and the role of adsorption on the observed phenomena will be analyzed in this presentation together with spectroscopic studies that can yield information about the conformation of adsorbed species and structural studies by scattering techniques (SAXS mainly) that provides data about the organization of particles in suspension.

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## CAPILLARY FILLING AND HAINES JUMP EVENTS USING FREE ENERGY LATTICE-BOLTZMANN SIMULATIONS

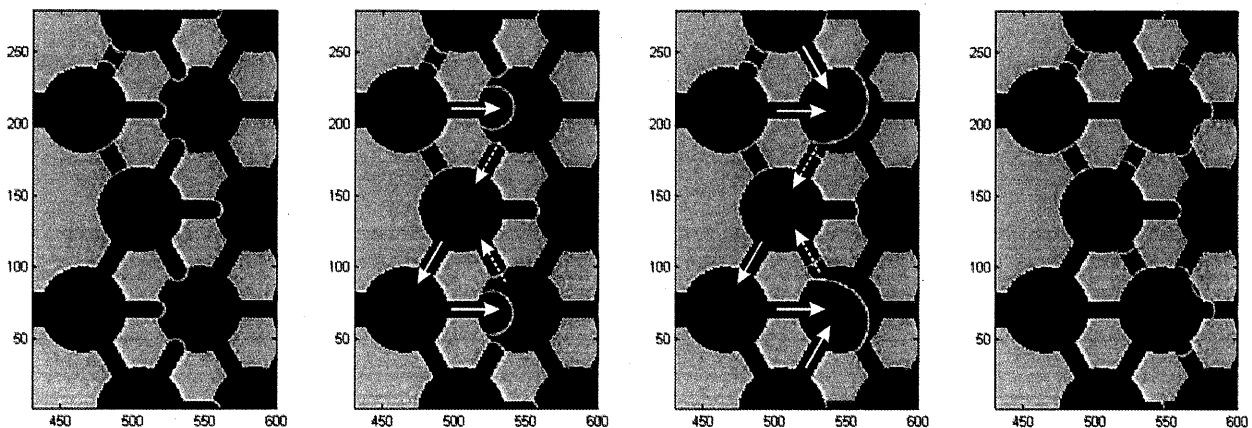
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Dept. of Chemical Engineering, Imperial College, London SW7 2AZ, UK

Keywords: capillary filling, Haines jump events, interfacial jumps, pore scale modelling, drainage

### Abstract

We investigate numerically the dynamics of capillary filling and Haines jump events using free energy Lattice Boltzmann (LB) simulations. Both processes are potentially important multi-phase pore-scale flow processes for geological CO<sub>2</sub> sequestration and oil recovery. We first focus on capillary filling and demonstrate that the numerical method can capture the correct dynamics in the limit of long times for both high and low viscosity ratios, i.e. the method gives the correct scaling for the length of the penetrating fluid column as a function of time. Examining further the early times of capillary filling, three consecutive length vs. time regimes have been observed, in agreement with available experimental work in the literature. In addition, we carry out simulations of Haines jump events in idealised and realistic rock pore geometries. We observe that the Haines jump events are cooperative, non-local and associated with both drainage and imbibition dynamics. Our observations show that the pore filling dynamics is controlled by the Ohnesorge number, associated with the balance between viscous forces and inertial / surface tension forces. Using this concept, we are able to identify the type of pore filling dynamics that will occur.



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ZACHAROUDI, I., BOEK, E.S., (2016) *Advances in Water Resources* **92**, 43-56.

## CHARACTERIZATION OF MAGNETIC NANOPARTICLE DISPERSIONS INTERACTIONS BY MULTISAMPLE ANALYTICAL CENTRIFUGATION

**T. Sobisch<sup>1</sup>, N. Buske<sup>2</sup>, D. Lerche<sup>1</sup>, S. Gressier<sup>1</sup>**

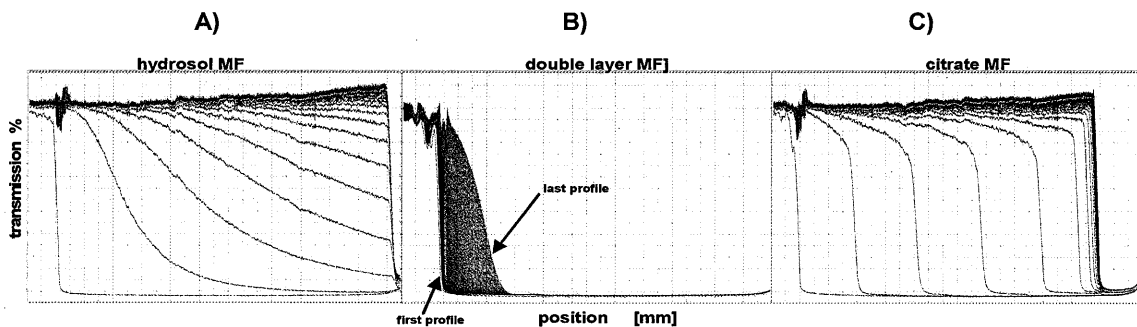
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**Keywords:** Magnetic nanoparticles interactions, Colloidal stability, Flocculation, In situ visualization of separation behavior, Zeta-potential, Analytical centrifugation

Functional dispersions based on magnetic nanoparticles are promising candidates for broad range of biotechnological and medical applications. This requires methods for in-depth characterization and fast screening of particles interactions, redispersibility of the agglomerated particles, primary and hydrodynamic size, the composition of the carrier fluid and the absence of oversized particles. Sedimentation analysis using a multi-sample analytical centrifugation with photometric detection is a rather simple but powerful method to characterize dispersed state and particle size distribution of magnetic nanodispersions.

Magnetite particles were prepared by precipitation and stabilized by different approaches:  
A) Magnetite hydrosols (pH 3–6). Particles are electrostatically stabilized, positive zeta potential  
B) Water based nanodispersions with sterically stabilized particles with a primary double layer of dodecanoic acid fixed on particle surfaces and a secondary layer of a non-ionic surfactant.  
C) Water based nanodispersions with mainly electrostatically stabilized particles with citrate as shell component. These particles have a negative zeta potential at pH 7.



Transmission profiles obtained during centrifugation at 2 300 RCA for samples stabilized differently

The double layer particle dispersion B) is the most stable, exhibiting only a small change in transmission during centrifugation. Both A) and C) exhibited relatively fast separation (large spacing between profiles). Furthermore, shape of profiles reveals marked differences in dispersion quality. A) shows a gradual increase of transmission along sample cuvette length's, i.e. individual particles and aggregates sediment with different velocities according to differences in hydrodynamic size. C) exhibits typical space filling particle network sedimentation behavior, a zone sedimentation where particles of the network separate with an identical velocity.

The analytical centrifugation method in situ visualization of separation delivers a direct information about colloidal stability of the dispersed particles, degree of particle aggregation.

### References

Magnetic nanodispersions session – Partec, 24 April 2013

## The Dynamic Characteristics And Tracking Adjustment Method of ASP Flooding in Daqing Oilfield

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<sup>3</sup> Northeast Petroleum University, China

Keywords: ASP composite flooding, response property, classification of single well group, adjusting technology

### Abstract

Although ASP flooding has obtained a good responding result, it differs dramatically in horizontal and vertical reservoir growth of single well because of various sedimentary environments of oil reservoirs and complicated connection relationships. The variations of watercut can be divided into type V, type V+, type shallow bowl bottom and type W without synchronous response property of single well. Therefore, injection parameters are required to design individually; measures are adjusted in time on the basis of different growth conditions of oil reservoirs during chemical flooding. By improving producing performance of reservoirs, keeping injection and production ability and controlling watercut rising velocity, the maximum economic index of chemical flooding can be realized. ASP flooding field test in Dandong Block of Beiyi area indicates that periodical recovery has reached more than 20% at the end of chemical flooding of class-3 wells by classification of single well groups based on their growth conditions and taking individual adjusting measures, which ensures good recovery result of ASP flooding.

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## EVALUATION OF FLOCCULATION OF SOFT NANO- OR MICRO-PARTICLES: IN SITU VISUALIZATION OF SEPARATION BEHAVIOR VERSUS ZETA-POTENTIAL

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Keywords : Particle interaction, colloidal stability, flocculation, in situ visualization of separation behavior, soft particles, analytical centrifugation, zeta-potential

During formulation of new dispersion products, properties have to be adjusted to obtain desired stability, textural and rheological properties. Often stable colloidal dispersions are required, however, in other cases weak flocculation is purposely induced to adjust structural properties or strong flocculation to separate dispersed particles. Characterization of the degree or absence of flocculation (net attractive particle interaction) has become a universal daily task for formulators and process optimization. Zeta potential measurement approach to predict stability or particle-particle interaction is common, despite generally limited to electrostatically stabilized systems. For so-called soft nano- or micro-particles, i.e. hard particles covered with an ion-penetrable layer of polyelectrolytes, electrophoretic mobility does not allow calculating a value of zeta-potential as describe by Smoluchowski approach.

Sedimentation analysis using a multi-sample analytical centrifugation with photometric detection of spatially resolved concentration changes (LUMiSizer) is powerful to characterize the dispersed state/degree of particle interaction. In situ visualization of separation behavior ranks, records, and quantifies very clearly from the fingerprints, a swarm sedimentation (stable dispersion) and zone sedimentation (flocculation, agglomeration). Complex systems with subfractions of particles exhibiting different separation behavior can be identify. Separation behavior of hard particles as Aeroxide ALU C, as well as soft nanoparticles as protein coated silica, or polyelectrolyte decorated magnetic particles, were investigated in dependence on pH or the amount/density of surface decoration.

Experimental data demonstrates that colloidal stability, degree of particle flocculation or agglomeration of the dispersed soft nano- or micro-particles is comprehensively obtained/predicted by the visualization of separation behavior fingerprints. Quantification is obtained by consolidation kinetics (alteration of sediment thickness) at increasing centrifugal acceleration / excess pressure. In contrast, particle-particle interaction is not correctly classified by values of zeta potential only calculated based on the common Smoluchowski approach, which is applicable only for hard particles. Furthermore, this new approach to characterize particles interactions can easily be apply for higher volume concentrations, any pH or ionic composition as well as for organic continuous phases.

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Evaluation of particle interactions by in situ visualization of separation behaviour  
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## Modelling of non-ideal multi-component multi-phase fluids by pseudopotential lattice Boltzmann model

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### Keywords :

Multicomponent multiphase flow, pseudopotential lattice Boltzmann model, non-ideal fluids, interaction strength

Multicomponent multiphase fluid flows are important in several industrial and engineering applications, such as the production of emulsions in the food, cosmetics and medical industries, as well as in natural processes. A variety of numerical methods, such as the volume of fluid and level set methods, can be used to compute multiphase flows based on the Navier–Stokes equations. However, while these methods can describe the evolution of the interfaces separating fluid phases, they do not model the intermolecular interactions that lead to phase separation. The pseudopotential lattice Boltzmann model can be used to describe such interactions between components, which lead to phase separation, and in this method the interfaces between phases are captured automatically. In this work, we use the pseudopotential lattice Boltzmann method to study systems with three non-ideal components, one of which models a surfactant, for small density ratios  $\lambda$  between the two liquid phases ( $\lambda \sim 1$ ).

Each component follows the Carnahan-Starling equation of state (C-S EOS), and forces between components are computed with the  $\beta$  scheme [1]. Together with forcing implemented with the exact difference method, the use of the C-S EOS and  $\beta$  scheme results in smaller spurious velocities and enhanced stability.

We report a systematic study of the effects of the interaction strength between the components and the reduced temperature ( $Tr$ ) on the number and composition of the phases present at equilibrium. These results allow us to perform simulations of emulsions at prescribed density ratios between the two liquid phases.

We also study how a third non-ideal component (surfactant), which is present in small amounts relative to the other two components and repelled by both of them, is distributed between the interfacial region and the bulk phases. We determine how this third component alters the tension of the interfaces between the fluid phases. The present model is a promising technique for simulating emulsification in shear flows.

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## Ageing analysis of solid and paste-like products with RHEOLASER Crystal

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### Keywords

Thermal analysis, Diffusing wave spectroscopy, thermal stability.

### Abstract

Cosmetic formulations must be chosen carefully to obtain maximum stability. Cosmetic products are often exposed to varying temperatures (indoor, outdoor, summer, winter), which can impact their long terms stability. Temperature shocks can lead to phase separation of the different fatty compounds used in lipsticks, creams and ointments. When phase separation appears, this can lead to exudations or recrystallization on the surface. Both phenomena are usually considered as quality problems and should be avoided.

This work presents a new innovative instrument, which combines Diffusing Wave Spectroscopy (DWS) with an accurate temperature control. This allows to analyze the microstructure evolution of a complex product during heating or cooling. Multi Speckle Diffusing Wave Spectroscopy (MS-DWS) [1, 2, 3], in which the backscattered light of a coherent LASER is analyzed with a temporal resolution, allows a correlation of the particle motion in the sample and the intensity fluctuation of the backscattered light. The use of an accurate infrared thermometer to measure the temperature in the measuring volume and a Peltier element for the control of temperature, provides information about the microstructure during thermal processing. Indeed, during phase transition, such as melting or crystallization, the microstructure evolves faster, which can be observed as characteristic peaks.

Different test protocols will be presented to show how lipsticks, ointments and other cosmetic products can be analyzed to evaluate their thermal stability. Especially, the possibility to perform easily temperature cycles in the instrument, allow to observe variation of the microstructure of the product. Two lipsticks (1 stable, 1 unstable) were compared using a series of 5 cycles consisting of 1 hour at 4°C and 1 hours at 40°C. It was shown that the unstable sample showed a shift of transition peak after the 5 cycles, whereas the stable lipstick showed the same melting peaks.

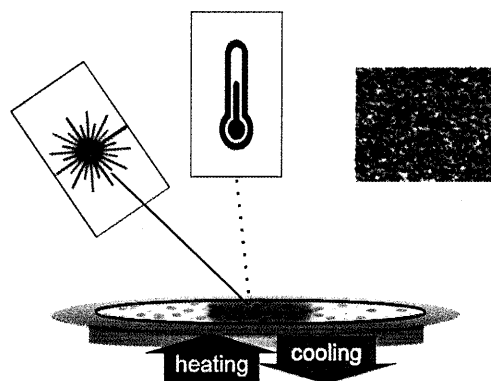


Figure 1: Experimental set-up of RHEOLASER Crystal.

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## FAST AND SIMPLE AVERAGE MOLECULAR WEIGHT DETERMINATION WITH FLUIDICAM<sup>RHEO</sup>

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The visual microfluidic rheometer, FLUIDICAM<sup>RHEO</sup>, offers a way to quickly determine average molecular weight by using viscosity measurements. The co-flow microfluidic system uses a small sample volume and can be used for a wide range of viscosities over a very wide range of shear rates (up to 10<sup>5</sup> s<sup>-1</sup>). FLUIDICAM<sup>RHEO</sup> is particularly sensitive for low viscosity solutions which makes it an ideal method for accurate molecular weight determination. The user-friendly design of the instrument and software means that the method is suitable for fast quality control and routine testing without an expert operator.

### Visual Microfluidic Rheometer Technique

FLUIDICAM<sup>RHEO</sup> uses a co-flow microfluidic principle to measure viscosity. The sample and a reference solution are simultaneously introduced into the microfluidic channel (typically 2.2mm X 150µm) with controlled flow rates. This results in a laminar flow where the interface position between sample and reference relates the viscosity ratio and flow rates. Images acquired during the measurement allow the software to calculate the position of the interface and directly plot an interactive flow curve

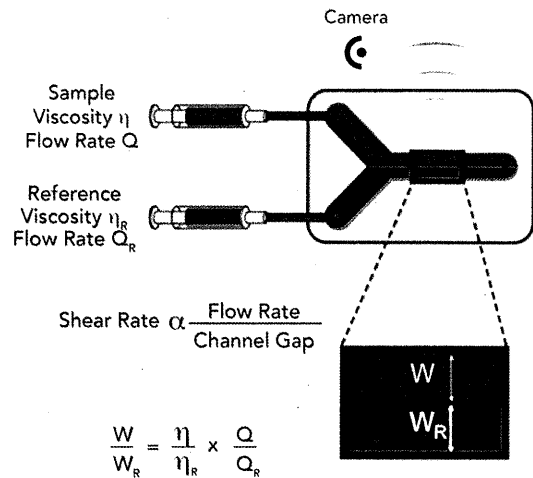


Figure 1: FLUIDICAM<sup>RHEO</sup> measurement principle

### Average Molecular Weight Determination

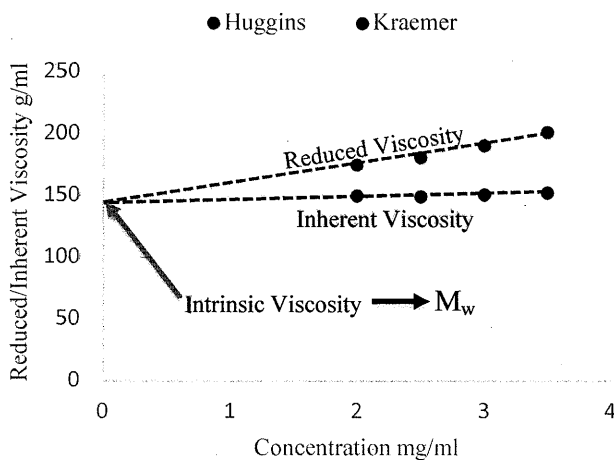


Figure 2: Huggins-Kraemer Plot for hydroxyethyl cellulose solutions

FLUIDICAM<sup>RHEO</sup> can be used to measure the viscosity of polymer solutions to determine the intrinsic viscosity which is related to molecular weight by the Mark-Houwink equation. The example shown in figure 2 is a hydroxyethyl cellulose polymer. The polymer is fully dissolved in a chosen solvent at a concentration inferior to its C\*. Multiple concentrations can be made up to produce a Huggins-Kraemer plot to determine the intrinsic viscosity graphically, see figure 2. Alternatively, the Solomon-Ciuta equation using a single concentration for an even faster determination.

## Advantage of using Multiple light scattering technique for the new safe demulsifier efficiency analysis for oil production

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The formation of stable water-in-crude-oil emulsions during oil production poses significant challenges during oil/water separation in surface production facilities. These emulsions can be very stable because of the presence of rigid films formed by polar compounds, such as asphaltenes and resins, and other fine solids.

Effective separation of crude oil and water is an essential operation in order to ensure the quality of crude oil but also of separated water phase at the lowest cost. Chemical demulsification appears as an essential step in crude oil dehydration. Demulsifiers are generally polymeric surfactants (copolymers ethylene oxide, propylene oxide, polymeric chain of EO/PO of alcohols, ethoxylated phenols, nonylphenols, alcohols, amines, resins, sulphonic acid salts...). Commercial demulsifiers are formulated in solvents like short-chain alcohols, aromatics or heavy aromatic naphtha and can contain a mixture of several active matters. Most of these products are not safe from an environmental point of view. The increase of environmental constraints makes therefore necessary the development of safer formulations in order to replace toxic chemicals like aromatics or nonylphenols.

Several methods are used to evaluate the efficiency of demulsifiers by measuring the separated phases properties with bottle tests, microscopy, rheology, differential scanning calorimetry... This study will show advantage of using Multiple light scattering technique which consists in sending photons (NIR light source, 880nm) into the sample. These photons, after being scattered many times by the particles (or droplets) in the dispersion emerge from the sample and are detected by the 2 detectors placed in backscattering and transmission. These light intensities are measured versus the sample height every 40 microns. By repeating these measurement versus aging of the sample, the operator can detect particle size change (coalescence, flocculation) and phase separation (sedimentation, creaming). The optical device based on this MLS technique (Turbiscan) enables to measure and elucidate instability phenomena in liquid colloidal dispersions from 0 to 95% in volume fraction, with particles from 10 nm to 1 mm, up to 200 times quicker than the naked eye.

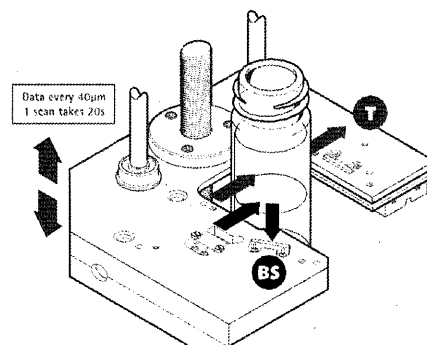


Figure: Principle of measurement of Turbiscan®

We will first present MLS theory and principle of measurement of Turbiscan® device. Then we will show application examples extracted from different studies in IFPEN laboratory on the evaluation of demulsifiers efficiency. The results will show that compared to classical bottle tests, MLS enables to determine quickly and objectively all the demulsification process from flocculation/coalescence to phase separation. The technique permits to quantify the separation kinetics, the amount of extracted water and the clarity of the separated water.

## Sulfonated methyl esters of fatty acids in aqueous solutions: Interfacial and micellar properties

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Sulfonated methyl esters; interfacial properties; micellar properties; surface tension isotherms

### **Abstract**

The interest to sulfonated methyl esters of fatty acids (SME) has been growing during the last decade, because these surfactants are considered as an environmentally friendly and renewable alternative of the linear alkyl-benzene sulfonates (LAS). Here, we present a quantitative study on the properties of aqueous SME solutions, and especially on their surface tension isotherms, critical micelle concentration (CMC) and its dependence on the concentration of added NaCl. It is demonstrated that the CMC of an ionic surfactant determined by electrical conductivity is insensitive to the presence of a small nonionic admixture, so that the CMC values determined by conductivity represent the CMC of the pure surfactant. We have demonstrated the application of a new and powerful method for determining the physicochemical parameters of the pure ionic surfactant by theoretical data analysis ("computer purification") if the used surfactant sample contains nonionic admixtures, which are present as a rule. This method involves fits of the experimental data for surface tension and conductivity by a physicochemical model based on a system of mass-balance, chemical-equilibrium and electric-double-layer equations, which allows us to determine the adsorption and micellization parameters of C12-, C14-, C16- and C18-SME, as well the fraction of nonionic admixtures. Having determined these parameters, we can further predict the interfacial and micellization properties of the surfactant solutions, such as surface tension, adsorption, degree of counterion binding, and surface electric potential at every surfactant, salt and co-surfactant concentrations [1,2].

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## **Sand Agglomeration in Oil & Gas Reservoirs using Polymers**

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Sand production is an age-old problem faced by the oil and gas industry which can have severe cost implications if not controlled properly. Approximately 70% of the world's remaining hydrocarbons are located in sand-prone reservoirs and current approaches to handle sand production are still facing many challenges. The aim of this work is to explore the use of polyacrylamide-based polymers in agglomerating formation sand and clays to improve the effectiveness of standalone sand screens. Polymer bridging interactions, charge neutralization and bare patch attraction are the three main agglomeration mechanisms being considered due to their capability of forming aggregates with superior shear resistivity and size. Preliminary results using Scanning Electron Microscopy (SEM) and Laser Particle Size Analysis (LPSA) have indicated a median growth in particle size of around 5 times when treated with cationic polyacrylamides only. Multi-polymer agglomeration systems were able to produce sand agglomerates of similar sizes but with much higher resistance to shear and more able to retain its structure upon drying. The novelty of this multi-polymer agglomeration system when coupled with sand screens is in the ability to potentially provide a very cost-effective means to solve sand production issues at the source, eliminating the need for costly remedial solutions at the topside and resin-based sand consolidation methods which impair reservoir permeability.

## **POLYELECTROLYTE/SURFACTANT MIXTURES AT THE BULK AND INTERFACES**

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**Keywords :** Polyelectrolytes, surfactants, water/oil interface, bulk properties\

The behaviour of polyelectrolyte/surfactant mixtures is important to study because of their industrial, technological and domestic applications. To understand their behaviour different techniques are used at the interfaces, such as surface and interfacial tension, dilational and shear rheology, ellipsometry, and in the bulk (DLS and zeta potential measurements). The properties of polyelectrolyte/surfactant mixtures and effect of different solution conditions like effect of surfactant chain length, effect of ionic strength, pH and temperature are studied so far mainly at the water/air interface. However, progress in this field at water/oil interface is rather slow mainly due to lack of suitable experimental techniques.

The work is devoted to the study of interfacial tension and dilational rheology of polyallyl amine hydrochloride/sodium dodecylsulphate and polystyrene sulfonate/dodecyltrimethyl ammonium bromide mixtures at the water/tetradecane interface in the presence of salt and in the bulk.

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

# INFLUENCE OF POLYMER-SURFACTANT COMPOSITIONS ADSORPTION ON PROCESS OF CLEARING OF OIL EMULSION FROM WATER AND SALTS

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**Keywords :Polymers, surfactants, emulsions**

Formation of oil emulsions leads to oil losses at its extraction, transportation and preparation for processing. Destruction of emulsions (deemulsifying) is one of the major processes of trade preparation of oil that is reached by use of various deemulgators.

One of the parameters which studying allows to give the prognosis to application of surfactants as deemulgators is the adsorption of two not mixing liquids on interfaces.

Study the colloid-chemical properties of Polyacrylonitrile derivatives compositions with surfactants have allowed to predict their application as deemulgators during oil clearing from water and salts. Results of research showed, that deemulsifier action of polymeric compositions substantially depends on the macromolecules conformation condition defined by a degree of polymer functional groups ionization. Besides deemulgation depends also on superficial activity of polyelectrolyte compositions with surface-active substances on the interface.

The values of superficial activity of polyacrylonitrile derivatives compositions with sodium salts of oleic acid showed, that formation of a composition leads to increase in superficial activity and reduction of standard free energy of polymers adsorption.

Increase of pH with growth of polymer concentration in a mix testifies about interaction between surfactant and polymer by hydrogen bonds formation that leads to change of the macromolecules adsorption parameters in mixes. As a result occurs the shielding of surfactant and polymer polar groups, that will lead to increasing of the macromolecules hydrophobicity and strengthening of intra-and intermacromolecular hydrophobic interactions in compositions. Reduction of the standard free energy of macromolecules adsorption during the complex formation testifies about macromolecules hydrophobization during compositions formation, leading to increase in their superficial activity and ability to adsorption on interfaces.

Based on results of study of colloid-chemical properties of compositions the assumption has been made that the most effective in application will be compositions of Hydrolized Polyacrylonitrile with surfactants at concentration ratio of  $\beta=4-6$  and  $\beta=0,25-0,5$ .

Researches were spent on the modelling and industrial oil emulsions, the maintenance of chloride salts in the modelling emulsions has made 176 mg/l, waters- 6,1 %, and the maintenance of chloride salts in the industrial emulsions has made up to 66000 mg/l, water- 41 %. Residual content of chloride salts CCl- in the percentage to initial made up 1,4-1,5%; volume of removed water phase made up 96,6%.

It was established that the most optimal concentration ratio of polymer with surfactant at which they reveal good effect of deemulgation is the mentioned above concentration ratio, that was substantiated by their colloid-chemical properties.

## Laboratory assessment of nanotracers for oil reservoir characterization

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Keywords : Enhanced Oil Recovery, Tracer, Nanoparticles, Fluorescence

Nowadays, tracer tests are a key tool to obtain data from the oil reservoir to design and/or evaluate enhanced oil recovery (EOR) operations. The success of such tests largely depends on the proper selection of the used tracer(s). The interest and research activities about the potential use of nanoparticles (NPs) as tracers for oil reservoirs have significantly increased in recent years. A thorough understanding of the behaviour of NPs in the porous media is crucial to achieve this. The growing interest on the use of NPs as tracers is essentially due to their high stability in the harsh conditions encountered in oil-fields, together with their high production versatility which facilitates tailoring the most adapted nanostructure for a specific environment. Most of the nanoparticles cited as tracer in the literature exhibit strong fluorescent properties, such as fluorescent-doped silica<sup>1</sup> and carbon dots<sup>2,3</sup> NPs. It is important to notice that the only nanoparticles reported so far in field tracer tests are carbon-based NPs (CDots)<sup>4</sup>.

This study focus on the transport and retention of NPs in typical oil reservoir porous media, particularly on how to assess them at the laboratory scale. The goal is to discuss the obtained results from the flooding experiments carried out with SiOx and CDots NPs in chalk and sandstone packed columns. Influence of salinity, pH and temperature was also evaluated. The laboratory dynamic flooding experiments together with static stability tests constitute key-steps for the qualification of nanotracers. Both the tested functionalized-silica and CDots have a fluorescent activity which allows easily detecting and quantifying them. This study also aims to propose how the tailoring of fluorescent NPs can overcome the drawback presented by the natural fluorescence background in production waters induce by the oil.

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## INVERSE PICKERING EMULSION STABILIZED BY EXFOLIATED HEXAGONAL-BORON NITRIDE (h-BN)

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Keywords : Pickering emulsions, inverse emulsions, 2D materials, hexagonal boron nitride

Pickering emulsions or solid-stabilized emulsions were defined at the beginning of the 20<sup>th</sup> century in pioneering works of Ramsden<sup>[1]</sup> and Pickering.<sup>[2]</sup> They are described as colloidal suspensions stabilized by solid nanoparticles instead of organic surfactants, which localize at the interface between two phases. In the last years, many researchers have paid attention to the ability of two-dimensional (2D) materials to promote the formation of special classes of Pickering emulsions.<sup>[3]</sup> We focus our attention in exfoliated boron nitride due to its high surface area and its planar structures.<sup>[4]</sup> BN monolayer has demonstrated outstanding properties such as biocompatibility, high temperature stability, enhanced oxidation resistance, a large band gap, high hardness, high corrosion resistance, and large thermal conductivity.

In this study, we reported for the first time a simple method to prepare inverse Pickering emulsions using non-modified exfoliated hexagonal boron nitride (h-BN) as stabilizer agent. Ethyl benzoate was ascribed as the oil phase, because this aromatic organic solvent is almost completely insoluble in water and has been already successfully used for preparing Pickering emulsion with graphene oxide.<sup>[5]</sup> The stability and type of h-BN Pickering emulsions formulated with different BN concentrations and by varying oil/water (o/w) ratios are studied and discussed. Besides, the BN nanosheets are characterized by AFM and SAXS and the characteristics of emulsions are discussed using a multiscale approach. First the emulsion structure is analyzed microscopically through optical and epifluorescence microscopy, and macroscopically by the study of the rheological behaviors. The average droplet size decreases with h-BN concentration whereas the emulsions achieve good stability at high BN concentrations and high o/w ratios. In all formulations, the emulsions are water-in-oil (W/O) type due mainly to the hydrophobicity of h-BN. The Pickering emulsion formulated with 2 % of BN is the most interesting due to its high long-term stability and its high viscosity. This research paves the way for the fabrication of boron nitride-based functional materials with novel nanostructures and microstructures using Pickering emulsions as soft template.

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