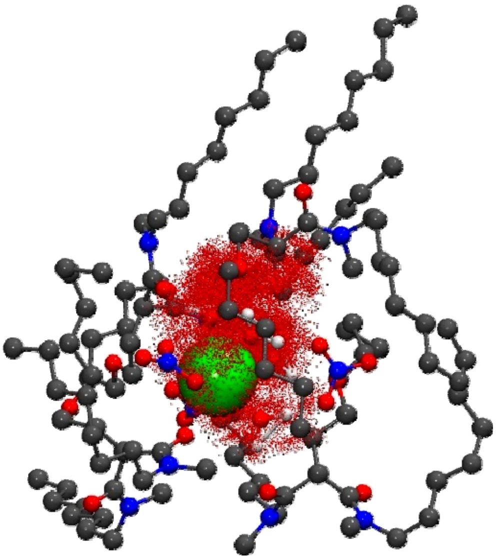
UMR 5257 CEA-CNRS-UM2-ENSCM

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

ICSM

ICSM – Centre de Marcoule
BP 17171 – 30207 BAGNOLS-SUR-CEZE CEDEX
Tél: +33 (0)4 66 79 66 28 – Fax : +33 (0)4 66 79 76 11
www.icsm.fr



Meso-scale model obtained via molecular dynamics of a reverse aggregate at the basis of selective for extraction porcesses: the multivalent ion participates in ordering the polar core, inducing high densities of presence of oxygen atoms on the surface of the polar core while protruding flexible chains are at the origin of sterical repulsion and solvent phase stability in hydrometllurgical porcesses.

(modelisation: Philippe Guilbaud DRCP-Marcoule-unpublished)

Hard X-ray (17 KeV) scattering camera in SAXS/WAXS
configuration installed at ICSM (operational Nov. 2008) –design Olivier Diat

UMR 5257 CEA-CNRS-UM2-ENSCM

SCIENTIFIC REPORT 2007 - 2010

Permanent staff at ICSM as in September 2010

Foreword

The mixed research unit “Institute for Separation Chemistry” was created jointly by CEA, CNRS, University of Montpellier and Ecole Nationale supérieure de Chimie de Montpellier has obtained authorisation to start experiments including a few grams of depleted uranium and natural thorium in January 2010. Last take-off was from our theory group, who started in October 2009. But the unit "Institut de Chimie séparative de Marcoule" existed as a team scattered in several places in France since 2007. At that time, monthly meetings gathered people for full days of open discussion every month, as "Point ICSM", where colleagues from R/D Departments of the centre of Marcoule composed half of the audience. Scientific activity began in 2007 with progressive joining of ICSM of team leaders, co-workers, technicians and students, today with 38 permanent staff and 29 non-permanent scientists and students. Most of the staff joined ICSM after or before participating to the European practical summer school in Analytical and separation chemistry, hold yearly for a full week including practical sessions since the first edition 2006 in Montpellier.

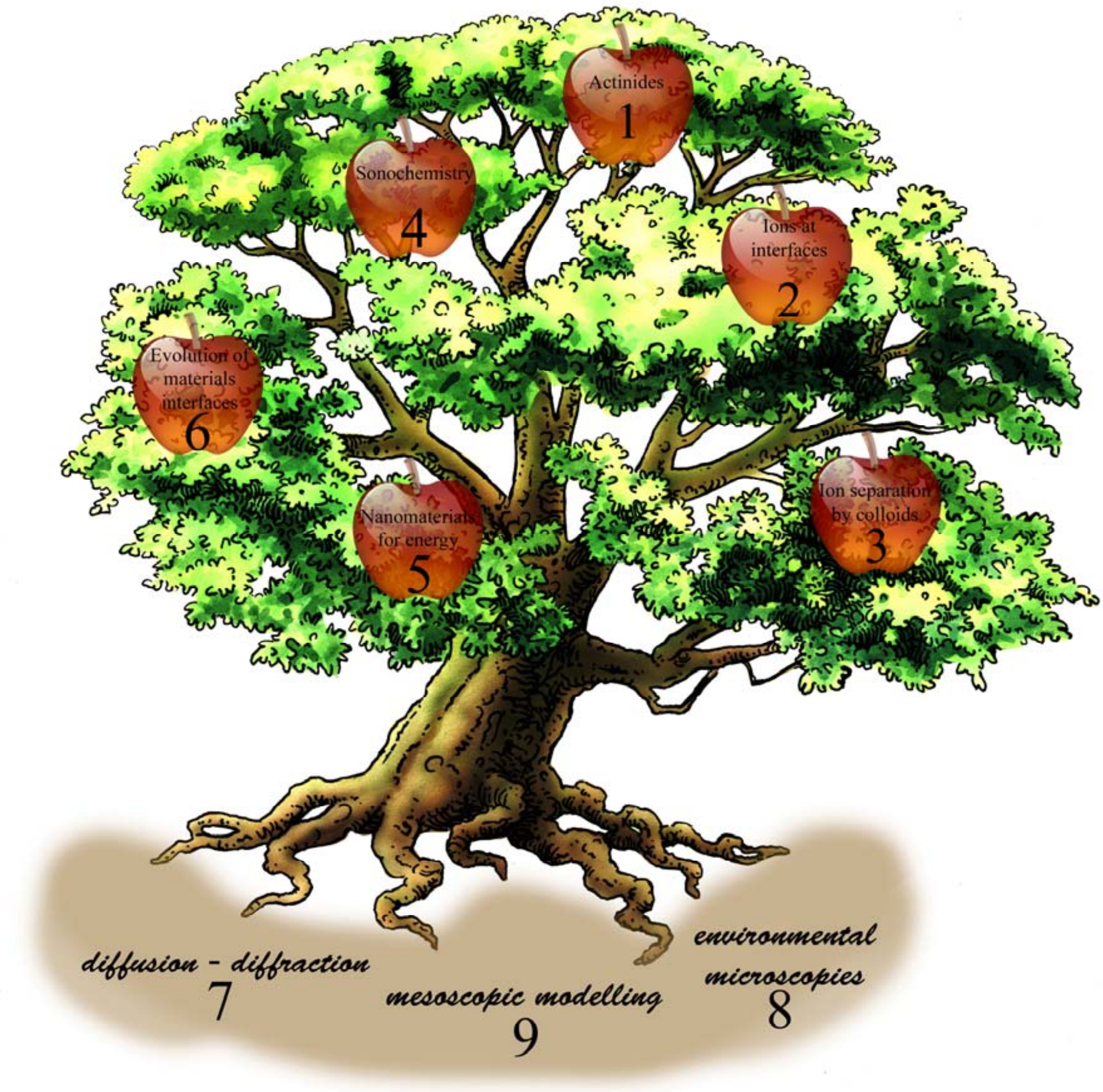
The report here gives an integrated picture of work published since 2007 (M. Leroy et al.) in the direction of the scientific open questions as defined and published by the French academy the same year. This initial definition of long terms tasks is included in this report. Nine teams have started to experiment, from synthesis to characterisation, with a strong input of modelling. The papers resulting from this work are grouped by teams. For each team, the objectives and competences are exposed together the driving force of the research and some crucial results are given in a simple format, with full references at the bottom of each page.

Resources in Uranium are scarce, if only the 235 isotope is used. Wastes related to nuclear energy production are potentially dangerous. Since fifty years, the chemistry associated to nuclear energy production always followed the principles of green chemistry. Permanent attention in devoted to closing the life-cycle of materials and fuel, minimize wastes and ascertain the acceptability by a society via knowledge of chemistry and physical chemistry involved in the chemistry used for separation. Developing knowledge in order to propose new separation processes is the central aim of the ICSM. Enlarging this central goal to surfaces of materials, sonochemistry as an example of green chemistry, chemistry and physical chemistry specific to actinides complete this picture. Thus, the ICSM is devoted to chemistry at the service of the nuclear energy of the future. The fourth generation including better usage of resources is seen as an actor for sustainable development compatible with limited resources and chemical preservation of the atmosphere.

Separation chemistry, a branch of physical chemistry, is a key part of « green chemistry ». The science required is the emerging « Nanoscience », as defined in the corresponding RST report of the French Academy by R. Corriu. Nanoscience and physical chemistry, are the roots of modern chemistry considering also non-covalent and long-range interactions, and using these weak forces in separation processes. The perspective view of former published work by scientists at ICSM, as well as access to the laboratory ATALANTE are guarantees of important progresses of fundamental research in Chemistry at ICSM, as defined by the *Haut commissaire à l’Energie Atomique* at the launching of the project in July 2004.

TZemb

Thomas Zemb
Marcoule, December, 2010


Actinides
1
Sonochemistry
4
Ions at interfaces
2
Evolution of materials interfaces
6
Nanomaterials for energy
5
Ion separation by colloids
3
diffusion - diffraction
7
mesoscopic modelling
9
environmental microscopies
8

MAJ Novembre 2010

Organigramme de l'ICSM

DIRECTION ICSM ET SUPPORT TECHNIQUE

Directeur	ZEMB Thomas
Directeur Adjoint	PELLET-ROSTAING Stéphane
Adjoint au Directeur	ALPE-CONCHY Dominique
Ingénieur Sécurité Installation	DIAS Mathilde
Exploitant	GUILLOT Gilles
Exploitant/Securité	VARON Renaud
Secrétariat	MARTIN Hélène
Ass. Gestion	VIDAL Alice
Ass. Laboratoires	RUSSELLO Vainina

TH 1 - LCPA

MEYER Daniel

BOURGEOIS Damien
GENRE Caroline
MAYNADIE Jérôme

**poste vacant Tech

DEMARS Thomas >04/10/12
GASSIN Pierre-Marie >31/08/13

CHATELAIN Grégory > 30/09/11

BORRINI Julien

TH 2 - LIIC

(DIAT Olivier)

BAUDUIN Pierre
GIRARD Luc
** Poste vacant / concours

BAUER Caroline > 31/05/11
MICHEAU Cyril >30/09/13
BRUSSELLE Damien > 30/09/13

[GASSIN Gaëlle >12/01/11

TH 3 - LTSM

PELLET-ROSTAING Stéphane

ARRACHART Guilhem
DOURDAIN Sandrine

DUBOIS Véronique

TURGIS Raphaël > 07/06/11
GRACIA Stéphanie (12/10>12/11)

TH 4 - LSFC

NIKITENKO Serguei

PFLIEGER Rachel
CHAVE Tony

** Poste vacant Ingénieur

NAVARRO Nathalie
SCHNEIDER Julia > 01/12/11
CAU Camille > 30/09/13

VIROT Matthieu > 31/03/11

TH 5 - LNAR

GRANDJEAN Agnès

GOETTMANN Frédéric
DESCHANELS Xavier
TOQUER Guillaume

REY Cyrielle > 30/09/11

DELCHET Carole > 30/09/12
SMUTEK Bernhard > 11/10/11
EL MOURABIT Sabah > 21/03/13
GUILLAUME Laure > 30/09/13

BRUGUIER Olivier > 30/10/12

TH 6 - LIME

DACHEUX Nicolas

CLAVIER Nicolas
SZENKNECT Stéphanie
**poste vacant MDC

HORLAIT Denis > 30/09/11
CLAPAREDE Laurent > 30/09/11
CRETAZ Fanny >30/09/2013

COSTIN Dan > 31/10/12
MESBAH Adel > 02/11/11

TH 8 - LME

PODOR Renaud

BRAU Henri-Pierre
MAYNADIE Sandra
RAVAUX Johann

CASTANIE Sandra >30/09/13

PAILHON Damien > 01/10/11

TH 9 - LDD

DIAT Olivier

CAMBEDOUZOU Julien

**Poste vacant
CORSO Bruno

TH 10 - LMCT

DUFRECHE Jean-François

** Poste vacant / concours
SIBOULET Bertrand
** Poste vacant

MOLINA John >30/09/11

TURQ Pierre

Légende

PERMANENTS

Chef d'équipe

Chercheur

Ingénieur/Technicien

NON PERMANENTS

Doctorants

Post-Doc

Autres

Stagiaire

Organisation of the quadriennal report 2007-2010 of ICSM

The report is organised by teams: each team is form a different community and publishes in different domains and the corresponding journals, as well as international meetings.

However, a large fraction of crucial results are obtained and published in common between teams within ICSM, via collaborations which can be considered in *concentric* circles:

- internal between teams of ICSM,

or

- internal to the Marcoule research centre, thus associating R/D departments of Direction de l'Energie nucléaire to ICSM

or

- internal to The "Pole de chimie Balard of Languedoc-Roussillon" centred in Montpellier thus associating ICSM to one of the other Institutes of chemistry in Montpellier: Our colleagues of Institut Européen des Membranes, Institut des Biomolécules Max Mousseron and Institut Charles Gerhardt

or finally with our international contractual partners: ITU Karlsruhe, MPI Potsdam and very recently IPC Moscow.

Five focussed objectives of the research actions undertaken guide the choice of priorities within the large autonomy of creative chemists working at ICSM:

Understand Separation	**Understand** chemical mechanisms underlying processes of chemical **separation**
Anticipate life-cycle	**Anticipate** the **life-cycle** of materials used in the context of nuclear and alternative energy productions
Methods and Theory	Develop **theory**, with attention to mesoscopic modelling, a well as develop **methods** of characterisation of fluid and solid samples.
Green Chemistry	Develop "**Green Chemistry**" in all its facets, including sonochemistry.
Optimize Separation	**Optimize** known methods for **separation**, in order to imagine, propose and test new separation methods, including bio-inspired supramolecular systems.

Colored rectangles appearing on each page of report identify the related thematics.

Liste des fiches-actions par objectif

Understand Separation - Comprendre la séparation

Optimize Separation - Optimiser la séparation

Anticipate life-cycle - Anticiper le cycle de vie des matériaux

Methods and Theory - Méthodologies et théories de la chimie séparative

Page

Green Chemistry - Chimie Verte

Page

Origine scientifique/géographique des chefs d'équipes

T. Zemb >1/2007

D. Meyer >1/2007

O. Diat >1/2007

R. Astier >1/2007 (< 4/2010)

N. Dacheux >10/2007

Grandjean >3/2008

R. Podor >1/2008

S. Nikitenko >10/2008

S. Pellet-Rostaing >1/2009

J-F. Dufrêche >10/2009

1 – Chemistry and Physical-chemistry of the Actinides

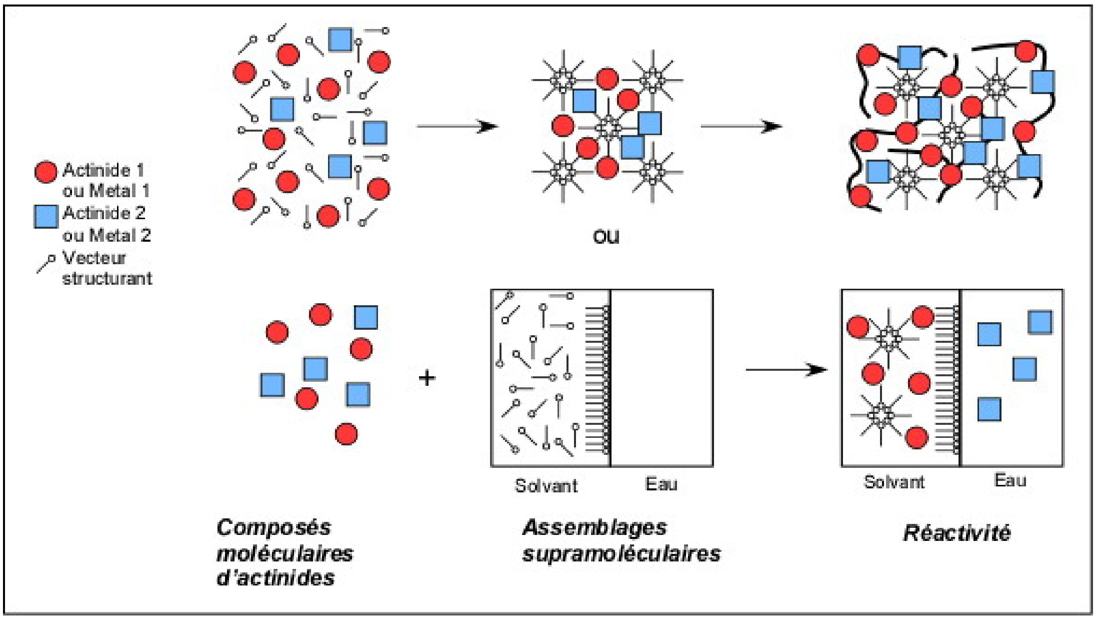
L'équipe est constituée de :
1 permanent CEA responsable d'équipe (Dr. D. Meyer),
1 chercheur CEA *(*Dr Caroline Genre)
1 chercheur CNRS (Damien Bourgeois)
1 enseignant-chercheur UM2 (Dr Jérome Maynadié)
2 thésards (Thomas Demars, Pierre-Marie Gassin)
1 post-doctorant (Dr. Grégory Châtelain).

Le cadre général de la recherche prévue au LCPA constituant la thématique 1 de l'ICSM est celui de la compréhension fondamentale de la chimie, physico-chimie et la physique des actinides qui occupent une position particulière dans le tableau périodique.
Tout en restant fondamentales, les études menées concernent dans leur majeure partie le cycle du combustible tel qu'envisagé dans les systèmes de génération IV mais avec une vision long terme. Les résultats de ces études doivent alimenter la connaissance de base nécessaire pour, dans un premier temps, essayer de comprendre certains mécanismes d'opérations, essentiellement chimique tel que l'extraction des actinides ou les modifications de matériaux d'actinides au cours de leur historique de mise en œuvre (fabrication, passage en réacteur, dissolution). Dans un deuxième temps, elles peuvent servir d'aide au déploiement d'approches innovantes pour le développement de nouveaux procédés. A ce titre les programmes de recherche du LCPA sont centrés sur la synthèse et la caractérisation de composés à base d'actinides essentiellement d'éléments transuraniens et couvre des aspects chimiques et physicochimiques en solution et en phase condensée.
Le LCPA ne dispose pas en ce moment d'installations propres permettant des études sur les éléments transuraniens. Pour cette raison, le bilan des actions se limite à des études sur d'autres éléments tel que les lanthanides, qui peuvent simuler dans certaines conditions des actinides (III), des éléments supposé jouer un rôle important au coté des actinides dans les systèmes du futur tel que le Si dans le cadre de carbure mixte SiC/AnC, combustible potentiel ou encore des études théoriques.

Les premiers résultats exposés concernent la synthèse de composés nouveaux de type polymère de coordination ainsi que des nanoparticules type oxyde ou métallique à base de métaux lourds, la structuration de carbure de silicium, potentielle matrice de combustible carbure d'actinide ainsi que des résultats de modélisation sur la réactivité de composé moléculaire d'actinides. De façon plus ponctuelle, une collaboration avec DSV sur le développement d'une méthode de détermination de protéine affine avec l'uranium a été réalisée.

a) Polymère de Coordination
Une série de composés de » type Ln_2L_3 à base d'Eu, de Nd et de Gd avec la dihydroxybenzoquinone a été synthétisée et caractérisée par diffraction des rayons-X (monocristaux et poudres), microscopie électronique et spectroscopie IR, Raman. Les composés mixtes (contenant deux lanthanides différents) forment des solutions solides. D'une façon générale nous avons observé un transfert congruent de la solution vers le solide.
L'étude de leurs propriétés magnétiques est en cours en collaboration avec l'Institut des Elements TransUraniens (ITU de Karlsruhe) et des premiers résultats montrent de forte corrélation magnétique entre métaux dans le composé.
L'étude de leur conversion en matériaux type oxyde a montré la formation de différentes phases en fonction de la nature du métal et/ou de la composition relative pour les composés mixtes.
Des premiers essais ont été réalisés sur des métaux au degré d'oxydation IV comme le Zr et le Ce(IV) afin de préparer la synthèse de ce type de polymère de coordination avec des actinides (IV). Le composé à base de Zr a été préparé et est en cours d'analyse. De même le remplacement de la dihydroxybenzoquinone par d'autre hydroxyquinone (des naphtoquinones) a montré que ces composés sont plus difficiles à obtenir.

b) Nanoparticules
En collaboration avec l'Ecole Polytechnique des nanoparticules métalliques de métaux très réducteurs – Zr et Sm ont été synthétisés par voie moléculaire. Une nouvelle voie de synthèse de nanoparticules métalliques de ces métaux, dont le potentiel REDOX standard est situé entre -1,5V (Zr) et -2,3V (Sm) a été mise au point. Il a été appliqué avec succès à l'uranium avec l'aide du CEA/IRAMIS. Des études de microscopie électronique à transmission ont montré que leur taille était comprise entre 2 et 5 nm.
En collaboration avec ITU, des dépôts de nanoaggrégats d'acétate et de nitrate d'utranyle ont été obtenu à l'aide de bloc-coplymère avec une répartition très homogène. Leur conversion en solide par plasma d'oxygène atomique semble montrer que l'organisation nanométrique du dépôt reste conservée.



Strategy for embedding or separating actinides in complex fluids or in molecular materials, as planned in the team: great attention will be taken to interactions beyond the first neighbour: thés ecompete with classical ionic and covalent interactions, especially for large and highly polarisable atoms from the actinide family.

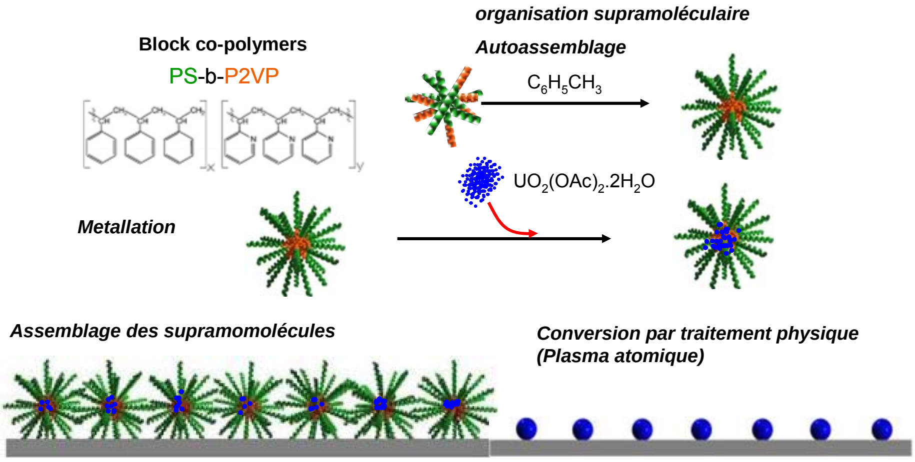
c) Carbure de Silicium
Dans le cadre de la thèse de Julien Garcia, en collaboration avec l'ENSCM, nous avons étudié la synthèse contrôlée de polysilane à partir de silane par des voies moléculaires et leur conversion en SiC. Nous avons pu montrer qu'il était possible de maitriser la structuration d'une phase polysilane à l'aide d'un empreinte solide de 500 nm et de conserver cette structuration lors de la conversion thermique en SiC. Des premiers résultats ont également montré la possibilité de structurer le SiC à l'échelle moléculaire et de le maintenir lors de la conversion. Nous avons également montré la possibilité de fonctionnaliser des polysilanes afin d'intégrer des métaux dans le polymère pour obtenir des carbures mixtes. Enfin d'un point de vue fondamental des études de mécanisme réactionnel ont permis de montrer la possibilité en une seule étape d'obtenir un polysilane fonctionnalisé. Cela est possible par une hydrosillylation et une deshydrocondensation concommitante à l'aide d'un catalyseur au titane.

d) Réactivité théorique des actinides
Dans le cadre de la thèse d'Ahmed Yahia, nous avons étudié d'un point de vue théorique la réactivité de composés moléculaires (collaboration avec Université de Toulouse et de Montpellier 2). Plus précisément, nous avons étudié le rôle de la structure électronique pour l'activation de la liaison CH dans des composés pyridine-oxime par des composés de l'U et du Th. Une approche théorique est en train d'être déterminée pour étudier la condensation entre liaison actinide-chlore et actinide-alcoxyde et la condensation redox entre actinyle (V/VI) et actinide (III/IV).

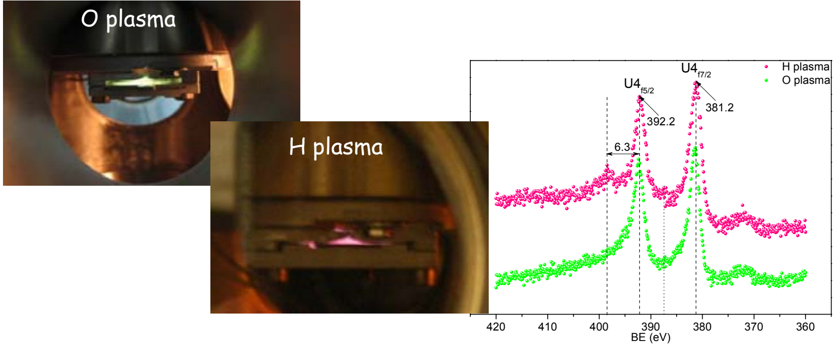
Actinides Nanoparticles

Damien Hudry, Daniel Meyer and Thomas Gouder (ITU)

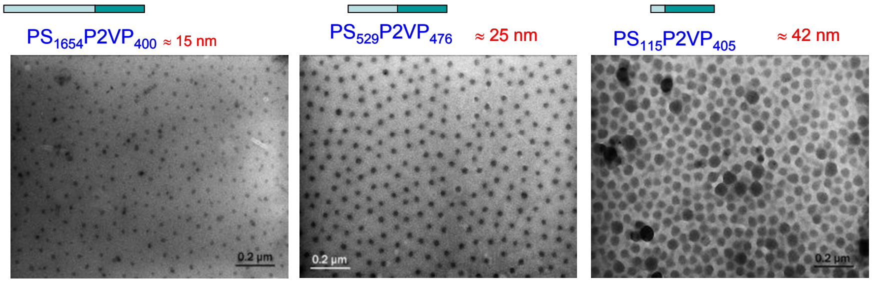
This work was initated in order to get organised layers of actinide compounds at the nanometric level. Reaching this goal, a conversion method of supramolecular thin layers into solid organised nanoparticles using atomic plasma was developed. The supramolecular system was a polystyrene polyvinylpyridine co polymer in toluene. In this media, this diblock copolymer goes into a micellar self-assembled structure. The pyridine part of the core of this structure is able to be filled with a metallic species.



Theses micelles are then deposed on a layer and exposed to an atomic plasma for conversion. Main results are the possibility to obtain several uranium oxides from ranging from UO_{2+x} to UO_3 species using oxygen or hydrogen plasma.



Spacing and size of the nanoparticles can also be controlled by the nature of the diblock copolymer.



R=4,1 R=1,1 R=0,28

References

"Controlled synthesis of uranium oxide nanoparticles by a self-assembly technique. "
Damien Hudry*[a,b], Christos Apostolidis[a], Thomas Gouder[a] and Daniel Meyer Chem Comm submitted

Comparative Theoretical Study on Actinide Complex Reactivity

Ahmed Yahia coll. Univ Toulouse and Montpellier (L. Maron, O. Eisenstein)

This work deals essentially with molecular reactivity of actinide species in order to progress in the understanding of the specific chemical behaviour of the 5f transition elements.

A first part of this work is focused on a comparative theoretical study of the reaction between $Cp_2M(CH_3)_2$ and pyridine N-oxide with M=Zr, Th and U leading to oxo complexes. These reactions were experimentally observed by J. Kiplinger with $Cp_2An(CH_3)_2$ complexes (An = U and th). The expected mechanism is an oxygen transfer from the n-oxyde moiety to the metal but the C-H activation route can also be considered. A first series of calculation on the transition state complex shows an unfavourable electrostatic repulsion between the methyl groups (figure 1a), hindering the oxygen transfer whereas the C-H activation route is thermodynamically favourable (figure 1b).

Fig. 1: (a) Transition state for oxygen transfert *(b) Transition state for C-H activation*

From the metal point of view, the reaction looks favourable for Th and U and critical for Zr. The simulation approach shows that the electronic back donation from the ligand to the metal is ten times lower for U and Th as for Zr. This electronic effect is probably responsible of higher stabilisation of the Zr complex than the Th and U homologues leading to a less reactivity for the Zr species.

The C-H activation study on lanthanides complex was started in order to understand the f orbitals (4f *vs* 5f) role in this kind of reactivity (figure 2). First results show that the La complexes are more reactive than the Y.

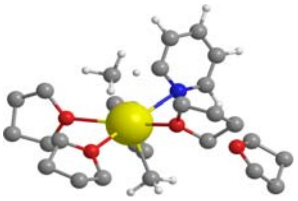


Fig. 2: Transition state of C-H activation

References

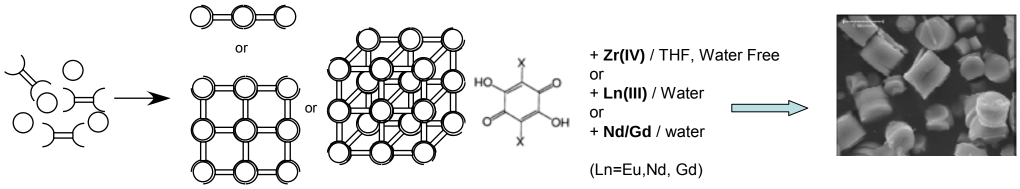
A DFT study of reaction between Pyridine N-Oxide and $Cp_2M(CH)_2$ with M=Zr,Th and U. Yahia, L. Maron, D. Meyer and O. Eisenstein, 25th Rare Earth Research Conference, June 2008 Alabama, US.
"Splitting a C-O bond in dialkylethers with bis(1,2,4-tri-tert-butylcyclopentadienyl)cerium hydride does not occur by a sigma-bond metathesis pathway: a combined experimental and DFT computational study"
Werkema EL, Yahia A, Maron L, Eisenstein O and Andersen RA New journal of Chemistry, 34(10) 2010 pp 2189-2196
"A DFT study of the reactivity of actinidocenes (U, Np and Pu) with pyridine and pyridine N-oxide derivatives"
Castro L., Yahia A. and Maron L. Dalton Trans. 39 (29), 2010, 6682-6692
"A Theoretical Study of Uranium(IV) Bis-Methyl Complexes: Towards the Predictive Formation of a Transient Uranium(IV) Carbene Complex"
Yahia A, Castro L. and Maron L. Chem-A Eur. J., 16(19), 2010, 5564-5567.
"Are 5f Electrons Really Active in Organoactinide Reactivity? Some Insights from DFT Studies"
Castro L, Yahia A and Maron L. ChemPhysChem, 11(5) 2010, 990-99

Metal Organic Frameworks

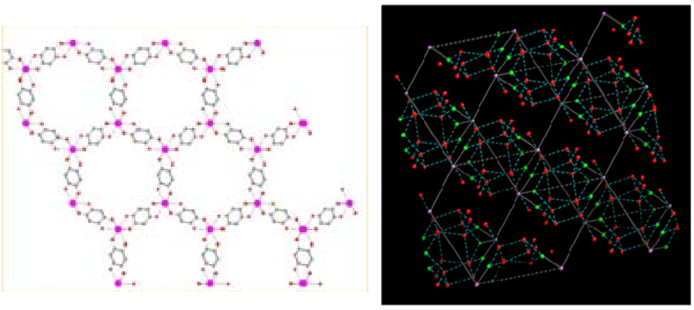
Jérôme Maynadié, Thomas Demars, Caroline Genre, Maria Boltoeva, Daniel Meyer

Main aim of theses studies is to develop new synthetic ways to original actinide compounds and to get fundamental information such as chemical (reactivity…) and physical (conductivity, magnetism…) properties. More specifically, this work intends to study structurally characterised metal organic frameworks obtained by self-assembling between metallic moieties and polyfunctionnal organic molecules. By this approach, mono and poly metallic hybrid materials can be obtained, expecting tuneable properties through the organic linker and the nature of the metal species.

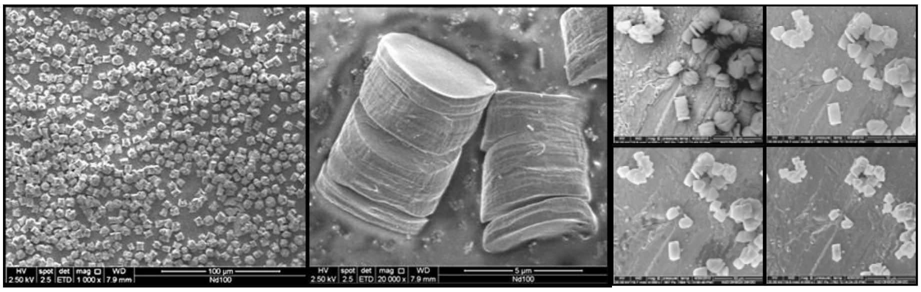
Outside the actinide community, these kinds of compounds have shown a strong development in the past decades revealing interesting properties in several fields such as the catalysis or electrode materials.



Mainly focused on dihydroxybenzoquinones (DHBQ), first results obtained with lanthanides shows an original structure consisting of 2D strong bonded layer connected by a water molecule cluster



As chemical properties, theses compounds can easily be converted into several ceramics materials. Thermal conversion of this kind of precursors under air leads to oxides and under inert atmosphere to intermetallic species.



Left the lanthanide precursor, right the conversion to oxide.

That way, single metal and polymetallic oxides were obtained with a control of the specific area by using different precursors obtained by different synthesis methods. Precursors obtained by condensation of a metal complex with the DHBQ ligand in aqueous solution are converted to oxides at 800°C with a specific area of 4-5 m^2/gr. The compound obtained by reaction between a lanthanide compounds with the DHBQ ligand under strict anhydrous conditions is converted to the same type of oxides with a specific area of 15-30 m^2/gr.

Metals of the group (IV) (Zr and Hf), simulating the actinides (IV), were also synthesised and characterised under strict anhydrous conditions in order to avoid any hydrolysis of this kind of compound. The thermal treatment under strict anoxic atmosphere of the Zr or Hf containing MOF at 1300°C lead to a carbon containing intermetallic compound.

These new architectures are somewhere in between pure molecular materials (molecular cristals) and condensed matter like metallic state opening a wide range of physical properties such as conductivity or magnetism.

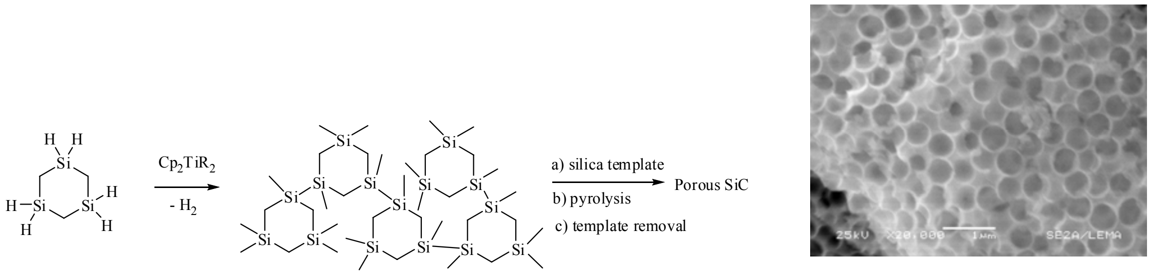
Multiscale Organised SiC/MC (M = Actinide)

Julien Garcia, Daniel Meyer - Collaboration Joël J.E. Moreau, M. Wong Chi Man (ICG LN2M Montpellier), D. Guillaneux (CEA/DEN/DRCP Marcoule).

This work is done in the frame of the development of new synthetic ways to obtain mixed carbides (SiC/ActinideC) using soft chemistry. Controlling the multiscale structure of the SiC material to insert an actinide fuel element is the main aim of these studies. Silicon carbide is usually a dense non-porous material and recently efforts are being made to obtain porous SiC. This works focuses on the synthesis of a primary polycarbosilane phase by the dehydrogenative polymerisation of a cyclic monomer, 1,3,5-trisilacyclohexane which was transformed SiC.

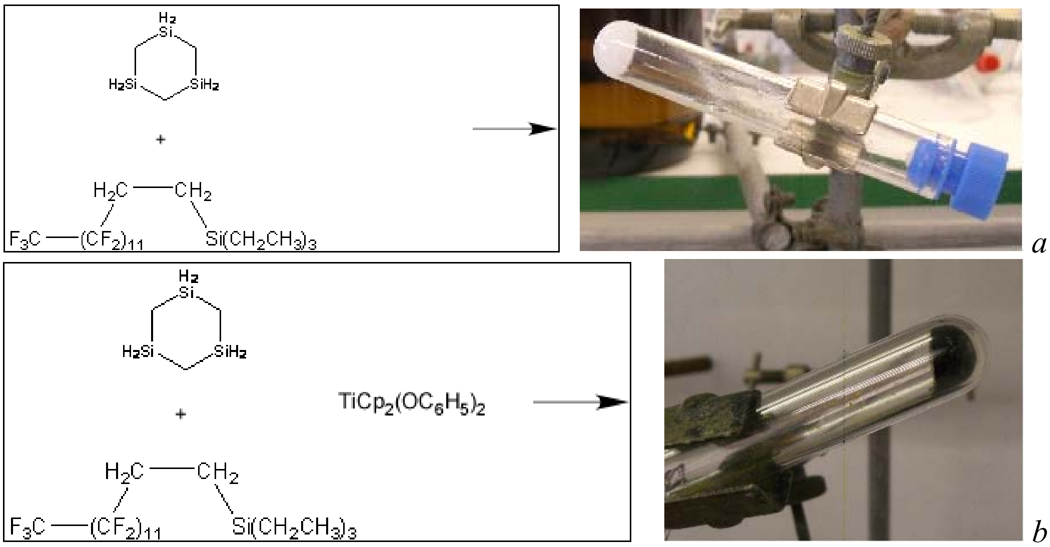
The first step of this reaction is done under fluid conditions and the multiscale control of the SiC matrix was achieved by using several solid or fluid template approaches.

The first level of control was done at 500 nm. A solid SiO2 template was used during the primary polysilane formation. The resulting SiC was successfully imprinted after thermal treatment and SiO2 dissolution.



Structured SiC obtained by molecular reactivity in the presence of a solid template

The second level of control by a direct organisation of the initial reaction solution is under progress. This organisation is expected by the use of molecular fluid modifier. We have developed a specific molecule which shows self-assembling properties under strict non-aqueous conditions. This “surfactant” molecule is composed by a fluorinated, a hydrogenated and a silylated part. The mix between the 1,3,5-trisilacyclohexane precursor and the surface-active molecule lead to a thermal reversible gelification of the initial fluid.



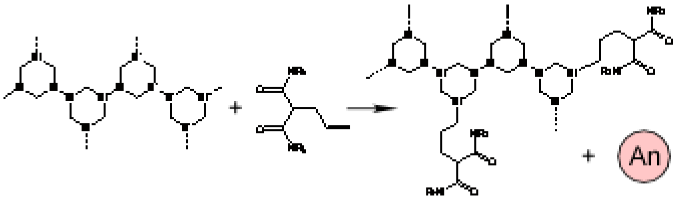
Gelification (a) Mix of precursors (b) Primary silane phase obtained from gel

Studies on the phase diagram are under progress. The dehydrocondensation reaction under this condition by adding the Ti catalyst is on hand.

Further to insert the actinide part, several routes are actually studied. The actinide can be introduced directly as carbide form, substituting the SiO2 template described in earlier.

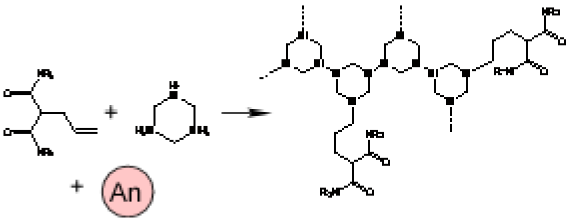
Two more molecular routes will be considered by taking advantage of the functionalisation of the primary polysilane phase using an actinide specific extractant, in our case a diamide function.

1 - The heterogeneous route, which consist of an actinide fixing by a functionalized primary phase.



Postfunctionalisation

2 - The concomitant route where the actinide will be added during the initial stage of polymerisation in the presence of functionalized precursors.



Concomitant functionalisation

In both cases the metal free functionalised primary phase was successfully obtained. For route one, it was possible to graft the diamide extractant on the polisylane using classical hydrosillylation reaction. For route two, a new reaction which combine a dehydrocondensation of the 1,3,5-trisilacyclohexane and a hydrosillylation using a diamide vinyl derivative has been developed. To complete the studies, the insertion of metals is actually under progress. After testing non radioactive compounds (Zr, Lanthanides), moving to the actinides elements will be considered.

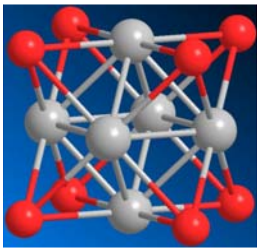
References

- “Porous silicon Carbide”, Julien, Garcia; D. Guillaneux; Joël J.E., Moreau; Michel Wong Chi Man and Daniel Meyer, 4th European Silicon Days, 9-11 September 2007 Bath, England

Reduced Dimension Actinide Species: strong 5f-5f interactions

Daniel Meyer - Collaboration Patrick Batail (CIMMA Anger) and Franck Wastin (ITU-JRC Karlsruhe)

In these studies, as described we attempt to synthesise actinide cluster showing a metal-metal interaction. The approach was inspired from the Re6 cluster synthesis [J.C. P. Gabriel et al, *Chem. Rev.*, 2001,101, 2037]. Any success in these syntheses is expected to trigger many significant subsequent developments in actinide solid state and coordination chemistry; provide exciting opportunities to explore the quantum chemistry and chemical physics of actinide clusters and the physics of unprecedented strongly correlated f-electron systems.



Expected actinide-actinide cluster

There is no known example today of a molecular compound were any actinide-actinide bond has been identified and theoretical predictions are scarce [L. Gagliardi et al, *Nature*, 2005, 433, 848]**.** This project propose to try and take the first steps in the exploration of diverse synthetic routes to molecular forms, and extended framework solids alike, of polynuclear inorganic actinide species capped by Q^{2-}, (Q = S, Se, Te); Cl^- or Br^-. An entry into this chemistry, unknown today, can be considered as new paradigms in the actinide chemistry and physic which parallels the Re and W cluster chemistries.

Several reactions will be attempted, targeting the pure uranium based two-dimensional polymer, $U_6Se_8Br_{4/2}Br_2$, or the mixed uranium rhenium $URe_5Se_8Br_{4/2}Br_2$ and the discrete molecular cluster form $Cs_3[U_6Se_7Br(Br)_6]$, both eventually with an hexanuclear, octahedral cluster core. In another direction, the synthesis of the molecular, eventually trigonal prismatic N-centered cluster form, $Na[U_6NCl_{18}]$ will also be considered.

$U_xRe_{6-x}Se_8Br_{4/2}Br_2$ x=1 and x=6

These compounds are expected to be obtained by mixing uranium metal, selenium and an excess of bromide in the desired ratio under an Ar atmosphere and then heated at around 800 °C. The conversion to the molecular entity $Cs_3[U_xRe_{6-x}Se_7Br(Br)_6]$ will eventually be considered.

$Na[U_6NCl_{18}]$

This compound is expected by following the reaction:$6\ UCl_6 + NaN_3 + 6\ Bi \rightarrow Na[U_6NCl_{18}] + 6\ BiCl_3 + N_2$ The reactants are mixed under dry inert (Ar) atmosphere and placed in a Pyrex tube sealed under vacuum and heated at 500°C. After cooling at room temperature $Na[U_6NCl_{18}]$ is expected.

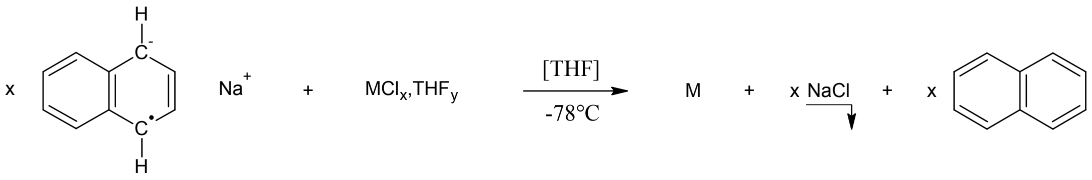
The **$U_xRe_{6-x}Se_8Br_{4/2}Br_2$ x=1 and x=6** experiments have been done in time. The analysis of the experimental results is actually under progress. In addition of known U_xSe_y intermetallics, we observe an unknown compound unstable. Due to a lack of time, we were not able to realise the **$Na[U_6NCl_{18}]$** experiment. These first “results” looks positive and the extension of the studies is foreseen.

Actinide Metallic Nanoparticles

Nicolas Vigier, Frédéric Goettmann and Daniel Meyer – collaboration P. Le Floch, N. Mézailles (Ecole Polytechnique Palaiseau), J.C. Berthet et M. Ephritikhine (IRAMIS/SCM Saclay)

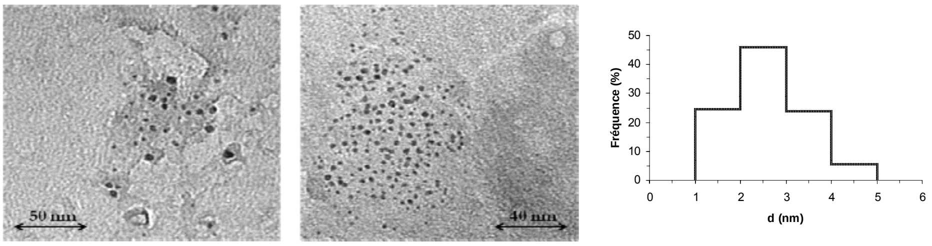
This study aims to obtain metallic Actinide compounds of nanometric size from molecular engineering at low temperature (below 100°C) and to investigate their reactivity with carbon sources such as carbon nanorods or molecular organic species, to form actinide carbides. A decrease of the synthesis temperature is expected by using this approach, which usually guarantees a better control of the nanostructure of the final ceramic. The main difficulty to form metallic particles is the very negative standard redox potentials of the actinide compounds (i.e.U^{3+}/U^0, E° = -1.798V; Pu^{3+}/Pu^0, E° = -2.031V). For this reason, all experiments need to be done under controlled atmosphere and in an adequate solvent (non aqueous). Also the resulting metallic compounds are expected to very reactive especially as strong reducing agents.

A first set of experiments was done using Zr and Sm (Zr^{4+}/Zr^0, E° = -1.45V; Sm^{3+}/Sm^0, E° = -2.379V). Metallic nanoparticles were obtained successfully by the reduction of the anhydrous chloride compound in THF by naphthalene sodium (eq. 1.)



Eq. 1. Chloride reduction by naphthalene sodium in THF (M=Zr, x=4; M=Sm, x=3).

Nanoparticles ranging from 1 to 5 nm are observed in the presence of polystyrene during the reduction of the chloride (fig. 1).



A B C

Fig 1: TEM picture obtained for Zr (A) and Sm (B) and size distribution for Sm from TEM (C).

These results clearly show the potential application of this approach to obtain metallic actinide particles. Preliminary experiments with uranium (UCl_4) have been done very recently under identical conditions and the overall observed reactivity is similar to this observed for Zr and Sm and the characterisations are in progress. Our next goals are to complete the characterisation of the obtained particles, to transpose this reactivity to transuranic compounds (Np and Pu) and to start reactivity studies between nanorods of carbon and metallic nanoparticles.

References

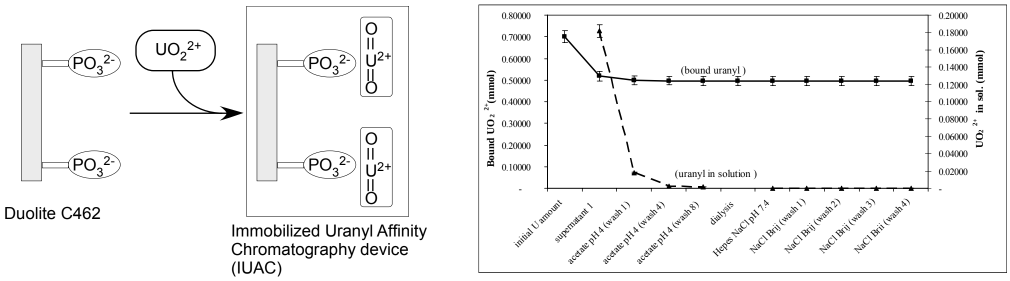
- Reactive Sintering of Nanoparticles of Actinide Metal, N. Vigier, D. Meyer, D. Goettmann, N. Mézailles and P. LeFloch, 38eme Journées des Actinides, 12-15 april 2008 Wroclaw Pologne.
- Sintering of Reactive Metallic Nanoparticles, N. Vigier, F. Goettmenn and D. Meyer, Plutonium Futures, 7 – 11 july 2008, Dijon France.

Uranium - Protein screening

Daniel Meyer, collaboration Claude Vidaud, Christian Basset, Alain Dedieu, Philippe Guerin, et Eric Quemeneur (CEA-DSV)

In order to progress in the understanding of the biochemical processes implicated in the toxicological behaviour of uranium, the protein targets showing strong uranyl affinity needs to be identified. Protein screening techniques based on Immobilized Metal Affinity Chromatography (IMAC) are now widely used to indentify metal binding proteins from biological extracts, but the chemical behaviour of uranyl compounds prevents the use of available IMAC support.

In these studies, an uranyl immobilized device based on aminophosphate complexing groups was developed and characterised. The loading of uranyl compound on a Duolite C462 support was followed by varied conditioning steps to reach the necessary physiological pH (fig1A). The selective capture of proteins requires a protein extract loading followed by successive washings, dialysis, and elution under varied buffering conditions. Furthermore, the process continuously needs high ionic strength and surfactants in the solutions to prevent ion exchanges and hydrophobic interactions respectively. The developed device showed a remarkable stability during these steps and no uranium was released (fig 1B).



A B

Fig 1: (A) IMAC device; (B) stability of the IMAC phase along the chromatographic process

The overall batch process was first developed with human apotransferrin as model protein which can bind 2 uranyl cations. The uranyl-loaded phase was then validated using two fractions of human serum. These experiments allowed the selective capture of a group of uranyl binding proteins directly from the serum extract (fig 2).

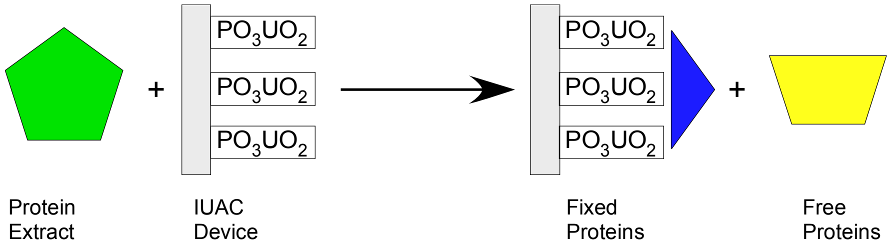


Fig 2: Uranyl affinity chromatography principle

Recently it was successfully applied to kidney cell extracts (in submission). Rather adapted to abundant proteins in the sample, an improvement of the process needs to be done to enhance both selectivity and sensitivity.

Reference

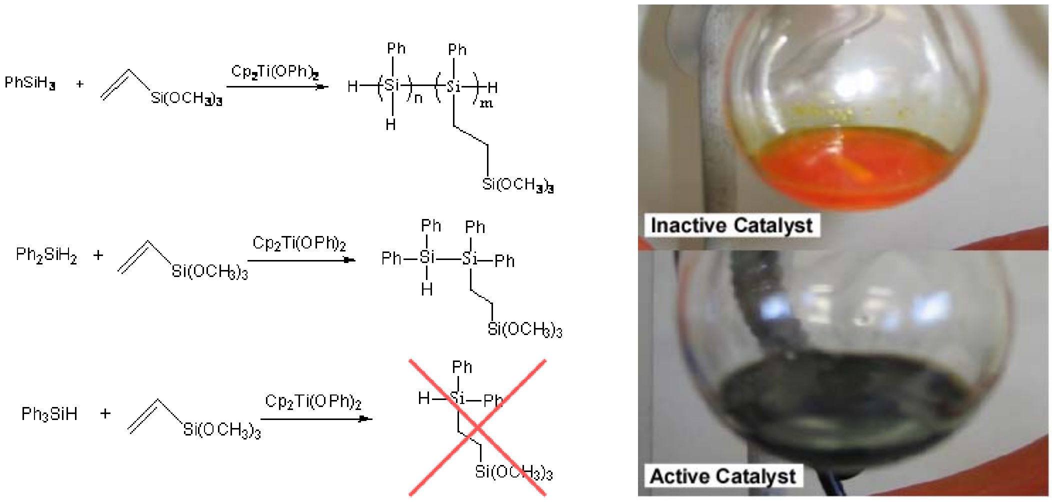
- Specific Capture of Uranyl Protein Targets by Metal Affinity Chromatography, C. Basset, A. Dedieu, P. Guérin, E. Quéméneur, D. Meyer and C. Vidaud, J. Chromato. A, vol. 1185, 2, p. 233-240 (2008).

New reaction: One-Pot Condensation and Functionalisation of Polysilane

Julien Garcia, Daniel Meyer - Collaboration Joël J.E. Moreau, M. Wong Chi Man (ICG LN2M Montpellier), D. Guillaneux (DRCP/SCPS/LCAM).

These studies are undertaken in the frame of the development of a new concept to achieve a mixed carbide SiC/MC (M = actinide) as model of carbide generation IV fuels. This work aim to synthesise the SiC matrix using the conversion of a primary functionalized silicon phase (polysilane, polycarbosilane) obtained by reaction of several molecular precursors in solution such as skeleton or function units.

In our particular case, the synthesis of the functionalized primary phase was done using a dehydrocondensation reaction of a 1,1,3,3,5,5-trisila-1,3,5-cyclohexane using a $TiCp_2(OR)_2$ catalyst coupled with a hydrosyllilation of a diamide vinyl derivative. This coupled reaction is surprising with Ti based catalyst. Regarding these results, a series of studies using different silicon hydrosilanes were done to understand this specific reactivity (figure 1).



Studies on $SiPh_xH_y$ reactions with vinyl derivative (Ph = Phenyl) and primary phase synthesis

Whereas the primary and the secondary hydrogenated silanes lead to the functionalized polymer or dimer, the tertiary hydrosylane show no hydrosyllilation despite the presence of a Si-H bond. The results indicate that the mechanism will be probably a deshydrocondensation, leading to a Si-Si bond and followed by the Si-H addition, where the Si is also bonded to another Si. The Si-Si bond is most likely the reason of this specific addition, usually not catalysed by Ti in the case of polycarbosilane and observed for the tertiary $SiPh_3H$.

In these studies, a new one-pot reactivity of polysilane has been discovered allowing the synthesis of a functionalised silicon based primary phase. Actinides can be implanted in the case of a functionalisation by an extractant by solid-liquid techniques or directly by adding the actinide in the early stages of the formation of the primary phase.

Reference

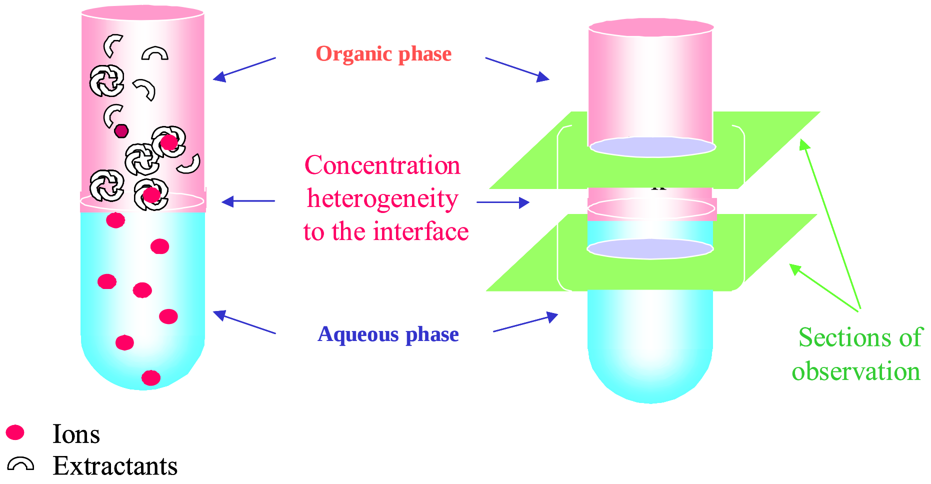
- One-Pot Synthesis of Functionalised Polysilane, J. Garcia, Fifth International Workshop of Silicon-Based Polymers, Cinéma Le Taurus, Mèze, 25th-27th June 2007.

In-situ measurement by Z-imaging NMR of the extraction rate of lanthanides and uranyl.

C. Mantel, P.-A. Bayle, S. Hediger, C. Berthon, M. Bardet.

In the reprocessing of the nuclear waste, the technique of extraction in liquid/liquid phase is widely used. The understanding of mechanisms involved during the process depend first on a better knowledge of the chemicals found at the interface to complex metallic ions and secondly on the features of these formed metallic complexes to migrate. The first aspect relies from thermodynamics and/or kinetics process and the second from broadcasting processes. On each side of the liquid/liquid interface significant differences appear both in the nature of the molecular species and in their respective concentration. All theses different processes are in competition and drive the overall efficiency of the extraction. Therefore, in order to progress in the comprehension of these mechanisms, it is important to reach the profile of concentrations of the various species intervening during a liquid/liquid extraction.

The Nuclear Magnetic Resonance (NMR) appears the adapted method to obtain such information. With NMR it is possible to record selective spectra in space and more precisely to edit spectra corresponding to sections through the solutions perpendicular to a Z axis. The evolution of organized molecular systems (micelles, micro emulsions, colloids, etc) in the vicinity of the interface where with place the ionic trapping can thus be examined.



Principle used to carry out spectra on sections near the liquid-liquid interface by NMR.

The NMR is especially known for its applications in the medical field where one exploits the nuclear relaxation times localised in various points of space in order to build an image in three dimensions of this space. The localised spectroscopy is also a technique of NMR but which makes it possible to obtain NMR spectra in any point of a given volume. The use of the NMR to study mechanisms of liquid/liquid extraction covers an aspect completely innovating. The most original aspect of this technique consists in studying NMR spectra with more close to the liquid/liquid interface.

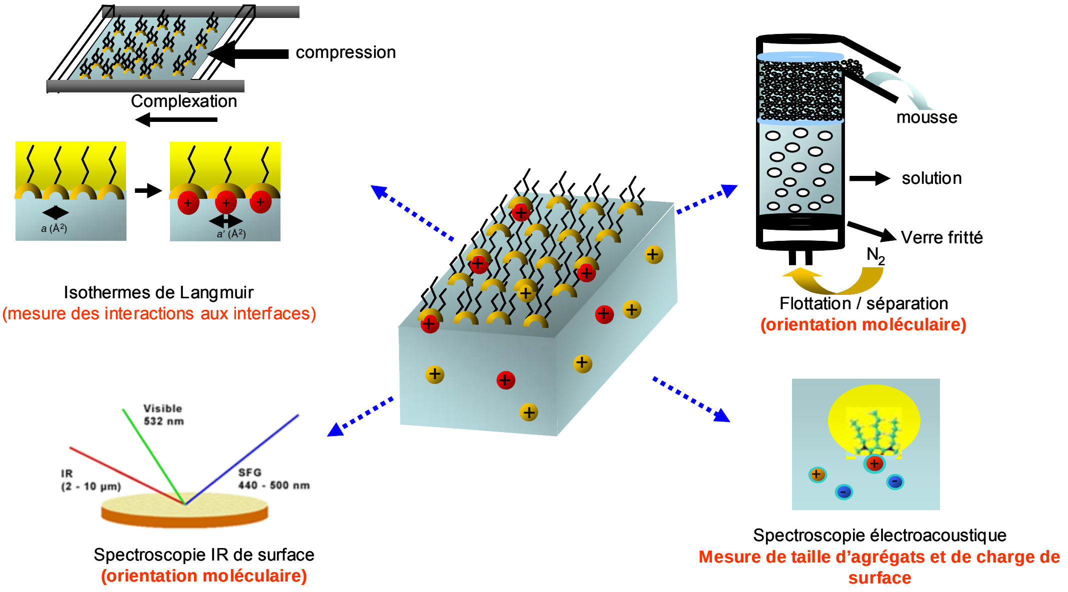
This project is being developed around two main axes: (1) development of NMR pulse sequences for editing NMR spectra of sections along the NMR tube containing the heterogeneous medium, (2) application of pulse sequences on non-radioactive model-systems and on radioactive systems.

Réf : Claire Mantel, Pierre-Alain Bayle,Sabine Hediger, Claude Berthon et Michel Bardeta "Study of liquid–liquid interfaces by an easily implemented localized NMR sequence", Magn.Reson.Chem.**2010**,48,600–606

2 – Ions at Interfaces

L'équipe est constituée de :
1 permanent CEA responsable d'équipe (Dr. O. Diat),
1 chercheur CEA (Dr. P. Bauduin),
1 enseignant-chercheur ENSCM (Dr. L. Girard),
4 doctorants (C. Bauer, D. Brusselle, C. Micheau et P.-M. Gassin)
1 post-doctorant (G. Gassin)

Parmi tous les phénomènes physiques et chimiques liés à la fabrication du combustible nucléaire et des déchets de dissolution, à la problématique de l'extraction et la séparation des ions et de leurs stockages dans différents types de matrices, au vieillissement de ces matériaux sous différents stress chimiques ou radiatifs, le groupe des "ions aux interfaces corrosives" (3 chercheurs dont un enseignant chercheurs à l'ENSCM) prend plus particulièrement en charge une recherche fondamentale concernant la distribution d'espèces telles que des ions, des molécules ou des agrégats à proximité d'interfaces d'échange ainsi que les conséquences de cette répartition sur la réactivité chimique de ces interfaces.



Ions to be separated between phases must cross fluid interfaces: knowledge of distributions in the last 3 nanometers is crucial to understand thermodynamics as well as kientics of ion séparation. The figure shows the principles of the expérimental techniques used to investigate ion distribution and mobility at interfaces.

Le génie chimique lié à cette activité de séparation et développé entre autres au CEA doit utiliser au maximum le potentiel des matières colloïdales pour assurer une sélectivité ionique et une séparation dans un processus continu après la dissolution du combustible nucléaire. Ces méthodes requièrent une connaissance approfondie de l'adsorption des ions à partir d'une solution aqueuse vers une interface liquide-solide ou liquide-liquide ou encore liquide-air. Plus que les interactions électrostatiques décrites dans une théorie DLVO, la polarisabilité, les forces de dispersion, le réseau des liaisons hydrogène, la complexation ionique, les interactions entre les ions et leurs environnements doivent être considérés; c'est pourquoi des systèmes modèles ainsi que des géométries d'analyse sont à imaginer pour permettre de mettre l'accent sur la physique et la chimie de chaque effet.

Un exemple concerne l'étude de la stabilisation de bicouches (interfaces planes) avec des agents d'extraction complexant et non complexant. Par le biais des lois de dilution de phases lamellaires, il s’agit de déterminer les propriétés amphiphiles des extractants (projet ACSEPT).

Le second système concerne non plus des interfaces planes de types bicouches mais des monocouches fluides, interfaces de microémulsions Windsor III. En effet, l’association subtile d’un tensioactif hydrophile et de la molécule TBP, référence dans d’extraction liquide/liquide dans le milieu nucléaire nous permet de contrôler la courbure de l’interface et de se déplacer dans les différent « Windsor » du diagramme de phase. Ce contrôle nous permet comme précédemment d’appréhender les effets amphiphile lié à la complexation d’ions par la molécule extractante.

Le troisième système sur lequel l’équipe s’est focalisée est un système micellaire en milieu aqueux qui nous permet de s’affranchir de la phase organique. En utilisant un tensioactif à tête pyridinium pouvant lui aussi complexer des cations bien que chargé positivement, nous avons pu étudier l’effet des anions sur l’extraction par sédimentation en utilisant les propriétés de solubilité des micelles autour de la température de Krafft (cette dernière étude est couplée avec une thèse dans l’équipe 3).

Enfin, le projet que nous voulons développer dans l’équipe concerne l’étude de la dynamique d’interfaces liquide-liquide par des techniques optiques non linéaires afin d’apporter des données significatives de la physico-chimie qui gouverne l’échange et la cinétique au sein de ces interfaces que l’on qualifiera d’actives. Cette approche sera développée dans un 4ème volet et elle implique l’ICSM et le DRCP en collaboration avec le LASIM de l’Université C. Bernard à Lyon.

Tracking an ion complexing agent within bilayers

A. Banc, P. Bauduin and O. Diat

Hydrometallurgical liquid-liquid extraction processes involve extractant molecules which are exclusively soluble in the extracting liquid phase and display a high affinity for the specie of interest. Besides, to be efficient, these molecules often demonstrate a moderate interfacial activity, enabling the contact with the second liquid phase. The kinetic of metal ion extraction is classically described by an overall mass transfer coefficient composed of diffusive contributions and a reaction rate constant. However, this reaction rate constant is complex because the reaction between extractants and cations operate at interfaces. As a consequence, in order to better control and model solvent extraction processes, the basic knowledge co ncerning the interfacial mechanisms of extractant molecules must be improved. Our approach is to study the numerous model plane interfaces formed into mixed lamellar phases of extractant and surfactant molecules. The advantage of this system is to confine extractants into interacting bilayers at the thermodynamic equilibrium which can be well characterized. In this work, we used N,N dimethyl-dibutyltetradecyl malonamide (DMDBTDMA), a molecule used to separate minor actinides from high level radioactive liquid wastes in nuclear industry, and pentaethyleneglycol dodecyl ether ($C_{12}E_5$), a well known non ionic surfactant. First, the establishment of a phase diagram enabled to identify a mixed lamellar phase system. Then, the structural properties of the system were characterized by X-ray scattering, and the orientation of molecules at interfaces was studied by microRaman spectroscopy experiment performed on oriented domains of samples. The combination of data enabled us to determine the position of extractants relative to the interfaces (see figure 1). Results indicate that the insertion of DMDBTDMA in a $C_{12}E_5$ bilayer induces a decrease in the spontaneous curvature of the interface, by establishing equilibrium of extractant molecules within the bilayer[1]: roughly, half of the extractant is buried within the organic part in the membrane, whereas the other half is adsorbed at the bilayer/water interface. Due to the numerous oriented interfaces we could determine the concentrations of free and bonded extractants molecules, localized either buried into bilayers or at interfaces, using a combination of SAXS and FTIR techniques. Hence, apparent free energies associated to each interfacial elementary mechanism could be calculated[2]. Results indicated that extraction by DMDBTDMA was an adsorption-desorption limited reaction. Moreover, the bonded extractants studied appeared more stable at interfaces than free extractants, contrary to an ideal extraction system for which only free extractants would be maintained at interfaces. With this study we demonstrated the efficiency of lamellar phase to model reactive liquid-liquid interfaces in general. In the future, other studies could be engaged varying parameters such as the nature of reactants. The possibility to study the energy of cation dehydration was also proposed.

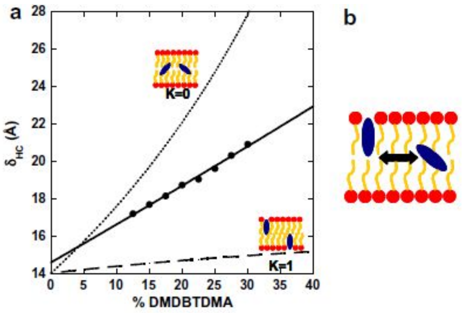


Fig.1: Evolution of the hydrocarbon bilayers thickness dHC versus the molar percentage of DMDBTDMA within the bilayers: the dotted and dashed lines display the models considering extractant molecules buried in the bilayer and at the interface of the bilayer, respectively. The experimental data (large dots), are fitted using Eq. (2) in ref 1. (b) Scheme of the 'equilibrium model' proposed to adjust our data.

---

[1] A. Banc, P. Bauduin and O. Diat, "**Tracking an ion complexing agent within bilayers**", Chem. Phys. Lett. 494 (2010) 301–305

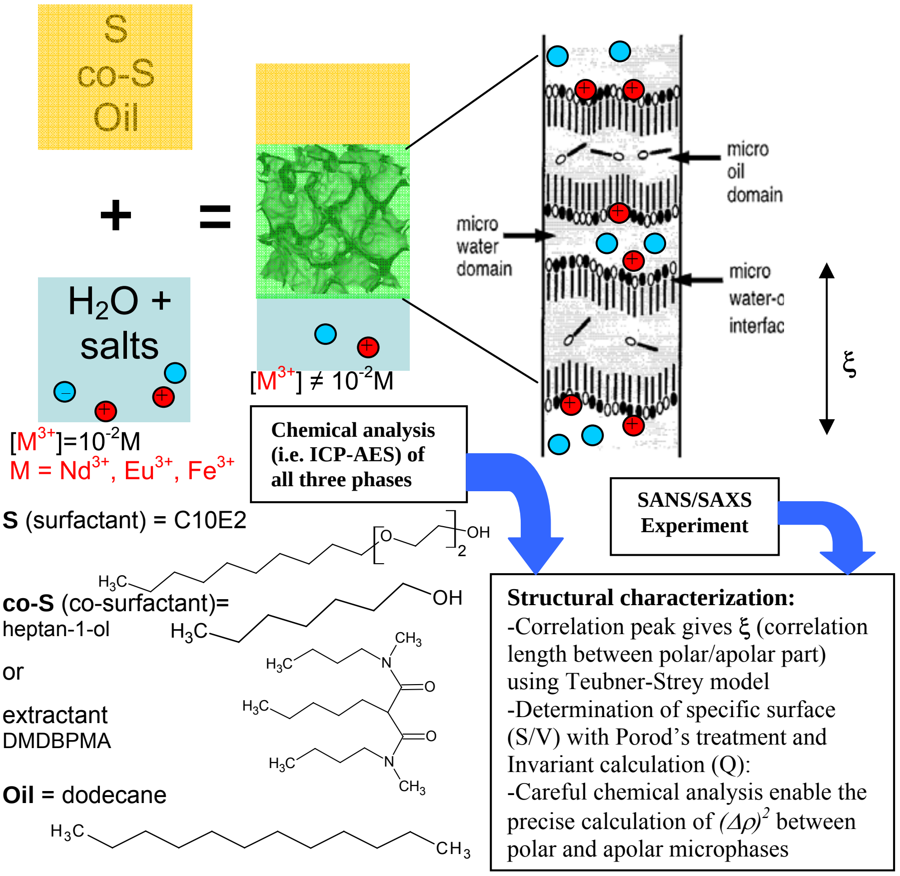
[2] A. Banc, P. Bauduin, B. Desbat, I. Ly, O. Diat, J. Phys. Chem. B accepted

Study of lanthanides ions adsorption at the water/oil interface in microemulsions as model systems of high surface specific areas

C. Bauer, P. Bauduin, O. Diat, T. Zemb

In colloids chemistry microemulsions, being isotropic mixtures of water and oil co-miscible with the use of surfactant and co-surfactant (see Fig.), have shown interesting ion specific effects. The very large specific area (S/V) offered by microemulsions, whose interface between aqueous and oil microdomains is covered by surfactant and co-surfactant, is the host for ion adsorption. In order to understand the underlying physico-chemical effects leading to specific ion adsorption at surfactant/co-surfactant surface a precise description of microemulsion structures at the supramolecular scale is required.

The goal here was to formulate Windsor III microemulsions, i.e. triphasic liquid systems, with extractant as co-surfactant to study the ion repartition between the bulk and the interface (see Fig.). This is of great importance in separation chemistry, especially in the nuclear field. Therefore the study of the structure of such microemulsions using SANS/SAXS will be investigated and compared to the structure of more classical microemulsions formulated with n-alcohols. The system chosen is inspired from the work of Kabalnov et al. (J. Phys. Chem. 1995) and is adapted by using extractant molecules. Fish cuts in the quaternary phase diagram were defined and compared mixing a sugar type surfactant (C8G1) either with classical alcohol as a cosurfactant and or with the TBP, the benchmark extractant in the liquid/liquid extraction for nuclear processes. SANS treatment gave us S/V ratios as well as the size of aqueous/oil microdomains which plays an important role in specific ion effect. Ion surface adsorption or depletion can be evaluated with good confidence from careful chemical analysis with techniques like ICP-AES to determine the metal ion concentrations in the different phases. The studied microemulsions are described as model in terms ion adsorption isotherms at liquid/liquid interfaces in complex confined media.



Structural characterization:
-Correlation peak gives ξ (correlation length between polar/apolar part) using Teubner-Strey model
-Determination of specific surface (S/V) with Porod's treatment and Invariant calculation (Q):
-Careful chemical analysis enable the precise calculation of $(\Delta\rho)^2$ between polar and apolar microphases

Fig. Illustration of the principal experiments carried out with triphasic microemulsion systems

It was proved here that TBP can play efficiently the role of a co-surfactant in the formation of balanced microemulsions. The phase diagram of TBP microemulsions in the three phase region is comparable to the ones formulated with the more classical co-surfactants: n-pentanol and n-hexanol. However TBP appears to be three times more efficient in mole than hexanol in the formation of three phase microemulsions. This effect is reflected in the interfacial film composition with a surfactant to co-surfactant mole ratio of 1:1 for TBP and 1:3 for n-hexanol. This is directly related to the difference in the packing of TBP and hexanol, TBP having three alkyl chains compared to one for n-hexanol. It is interesting to note that the film composition is "adjusted" in order to obtain a near zero curvature of the interfacial film, a condition necessary for the formation of three phase microemulsions. Moreover it was observed that replacing hexanol by TBP also induces a salt dependence on the microemulsion structure. A subtle change in the microemuslion structure according to the type of salt added is highlighted in the ΣD^{*} *vs.* ϕ_W dilution plot (Σbeing the specific surface, *D* the characteristic distance and ϕ_W the water volume fraction). This effect was rationalized in terms of Hofmeister series and the complexant property of TBP[1].

---

[1] C. Bauer, P. Bauduin, O. Diat and T. Zemb, « **Study of extractant molecules as cosurfactant at the water-oil interface in microemulsions** » in proceedings CED40 2010-11-12
C. Bauer, P. Bauduin, O. Diat and T Zemb, **"Ion Extractant as Cosurfactant at the Water-Oil Interface in Microemulsions"**, Tensile Surfactant and Detergents 05, 2010 pp 307-311
C. Bauer, P. Bauduin, O. Diat and T Zemb, "**Liquid interface functionalized by an ion extractant: the case of Winsor III microemulsions**", Langmuir accepted.

Dynamics at interfaces

G. Gassin, PM. Gassin, D. Meyer, JF Dufrêche, T. Zemb, O. Diat
L. Couston (DRCP/MAR), P.F. Brevet (CNRS/LYON)

Ion separation by transfer of phase (liquid/liquid extraction) which are the most selective are also the slowest. Fundamental reason comes from the statistics of organized fluids. The Brownian agitation of the hydrated ions selected by amphiphilic extractant molecules explore the number of ways (or of try) across the interface of both non miscible phases in contact to which are associated activation energies. Beyond the cycle of nuclear fuel, this is also valid in various fields such as enzymology or the catalysis, the membrane permeation or the reprocessing of polluted waters.

We have seen in the previous pages how it is important to better understand the amphiphilic properties of the extractant molecules involved in the liquid/liquid extraction processes. In order to also be able to analyse the kinetics of ion transfer, the dynamic of such molecules at the water oil interface has to be probed. This is why we have chosen, in complementary to techniques already developed in our laboratory, to develop in collaboration with LASIM at Lyon and the DRCP (CEA Marcoule) a non linear optical technique. Indeed, the second harmonic generation is a suitable technique for probing the activity since the non linear susceptibility vanishes for isotropic media and is non zero at interface. Indeed solvent molecules as well as surfactants may adopt a preferred orientation in the nanometer scale layer which is difficult to analyse but has to be quantified during an ion transfer.

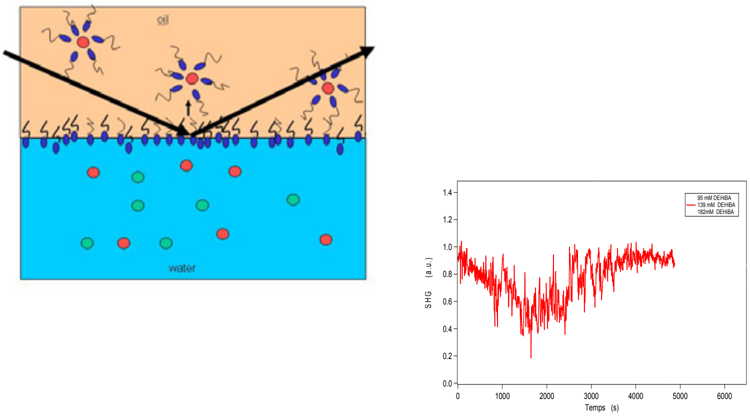


Fig.1: Schematic view of an L/L interface with selected ion transfer. Right: fluctuating SHG signal as a function of time during an extraction process of acidic molecules with monoamides (DEHiBA).

In analysing the correlation function[1], it could be possible to access to the lateral density fluctuation (amplitude and frequencies) as well as perpendicularly to the interface (molecular protrusion with the associated wavelength). Of course, the data obtained via this technique have to be correlated with those obtained using surface tension or scattering techniques.

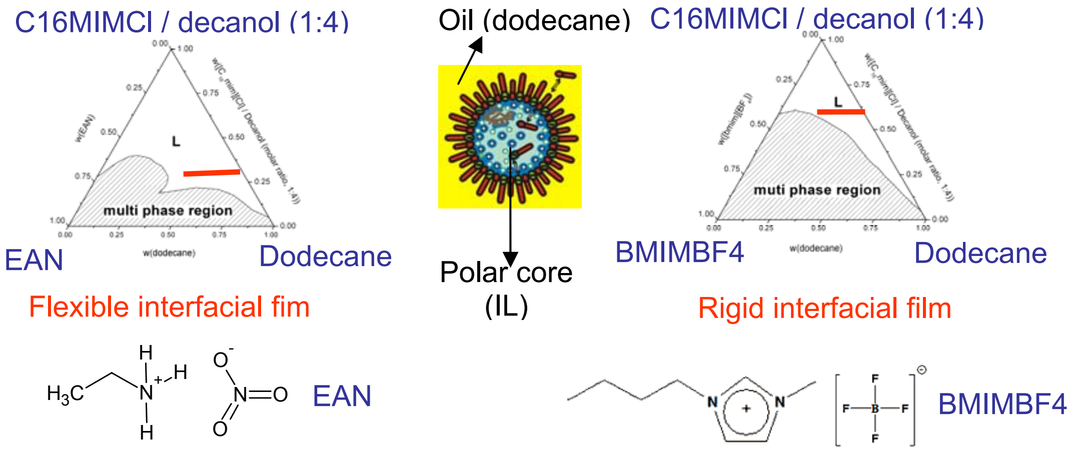
---

[1] Martin-Gassin G., Gassin P.M., Couston L., Diat O., Benichou E., Brevet P.F., PCCP submitted.

Microemulsions with an ionic liquid surfactant and room-temperature ionic liquids as polar nano-droplets

<u>P. Bauduin</u> – Collaboration O. Zech, S. Thomaier, D. Touraud and W. Kunz (University of Regensburg, Germany)

Over the last years the interest in room-temperature ionic liquids (RTIL) has increased rapidly because of their unique properties such as high solvent abilities, negligible vapor pressures, extremely high electrical conductivities and thermal stability. Hydrophobic ILs are investigated as potential extraction medium for ion separation based on ion exchange process. Ultimately the extraction and separation of minor actinides are targeted in the nuclear industry. Aggregation of amphiphilic molecules is part of ion liq/liq. extraction processes hence self aggregation phenomena of ILs have to be understood and controlled.



In this investigation we present for the first time microemulsions comprising an ionic liquid as surfactant and a room-temperature ionic liquid as polar microenvironment.
Microemulsions containing the long- chain ionic liquid 1-hexadecyl-3-methyl-imidazolium chloride ([C16mim][Cl]) as surfactant, decanol as cosurfactant, dodecane as continuous phase and room temperature ionic liquids (ethylammonium nitrate (EAN) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]][BF4]), respectively) as polar microenvironment have been formulated. The phase diagrams of both systems determined at a constant surfactant/cosurfactant molar ratio show typical topologies of flexible and rigid interfacial film microemulsions for EAN and [bmim][BF4], respectively.
The presence EAN micro-regions in oil have been confirmed with conductivity measurements. In presence of EAN a model of dynamic percolation could be applied. DLS measurements indicated a swelling of the formed nano-structures with increasing amount of EAN, a linear dependence of the EAN weight fraction on the hydrodynamic radii was observed. Both systems exhibited a single broad peak in SAXS and follow a characteristic q^{-4} dependence of the scattering intensity at large q values. The Teubner-Strey model was successfully used to fit the spectra giving f_a, the amphiphilic factor, and the two characteristic lengths of microemulsions namely the periodicity, d, and the correlation length, ζ. Furthermore the specific area of the interface could be determined from the Porod limit and the experimental invariant. Those anhydrous systems are potentially interesting as reaction medium at relatively high temperatures (T=200°C) for the synthesis of new nano-materials.

- O. Zech, S. Thomaier, P. Bauduin, D. Touraud and W. Kunz submitted to *the Journal of Physical Chemistry* , 113 (**2009**), 465-473

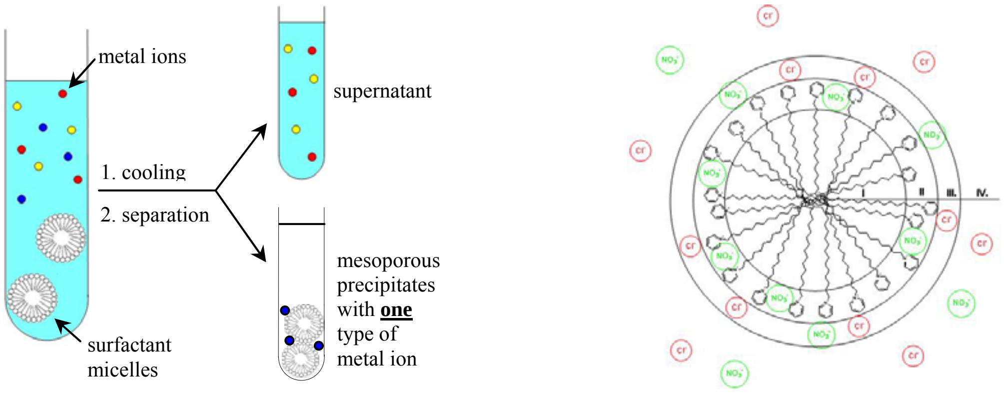
Separation of metal cations by amphiphilic cations

W. Müller, C. Déjugnat, O. Diat, Th. Zemb

In the field of selective metal ion separation, liquid-liquid extraction (especially for nuclear spent fuel treatment) is usually conducted with hydrophobic complexant placed in the organic phase. Recently it has been shown that self-organization of amphiphilic complexants could play a major role in the extraction efficiency by increasing the surface interaction between the metal ion and the self-organized aggregate. Amphiphiles can also be employed in another method which does not involve organic phase (namely the solid-liquid extraction) and it appears very attractive in the field of nuclear spent fuel treatment as several steps are omitted, reducing the amount of nuclear wastes. It consists in selectively precipitate metal ions from a bulk mixture using cationic tensides below their Krafft point. This technique has been shown to be very efficient for separation of actinides and lanthanides using long chain ammoniums or pyridiniums [Heckmann and Strnad, 1992]. A particular point of this process is the recognition of metal cations by cationic surfactants. The original proposed mechanism is the formation of a complex ion involving anionic counter-ions of the metal salt, in order to ensure electric neutrality.

We aim at understand these attractive interactions between the positively charged surfactant head groups and the metal cations before and after precipitation. Main concerns are about the influence of the surfactant head group polarizability on the separation and the role of the counter-ions. Then, we have studied the system cetylpyridinium with counterions of different hydrophilicity and complexing power. First, the micellisation properties of CPC, CPN and CP_2Ox, including the cmc and the Krafft points have been determined. Especially the latter is found to be much higher for CP_2Ox than for the two others, which show rather similar T_K at all bulk acid concentrations. Despite these differences in solubility, spherical aggregates are found for all three surfactants up to 0.01 M ionic strength. Above this concentration, CPN aggregates undergo a sphere-to-rod transition, while CPC and CP_2Ox micelles keep their spherical geometry, which is confirmed by light-, neutron- and X-ray scattering coherently. Thus, it is clear that the anions interact differently with the cetylpyridinium micelles. All data obtained for chloride and nitrate, except the Krafft temperature, go hand in hand with their classification according to the Hofmeister series and are explained by the stronger interaction of the chaotropic nitrate anion with the likewise chaotropic pyridinium head group, leading to a preferential adsorption compared with chloride. Nevertheless, there is a competition between chloride and nitrate for adsorption, when the two ions are present in solution. The hydrophilic oxalate is a special case, as it is an anion of a weak acid and its speciation (H_2Ox, HOx^-, Ox^{2-}) depends therefore on the pH and the presence of surfactant. Besides being classified as kosmotropic, it shows a strong interaction with cetylpyridinium in form of high solubility temperatures, which are closer to the ones of double-chain surfactants.

The structural parameters obtained for the CPC and CPN micelles are introduced in a free energy model, which allows determining the free energy of the polar head group per aggregate as a function of the different counterions employed. The data obtained by the model is coherent with the experimental results for nitrate, but a slight divergence between the theoretical and experimental data is found for chloride. Nevertheless, the model succeeds in discriminating between different interaction of chloride and nitrate, respectively, concerning the micellar surface. The Poisson-Boltzmann approach used is not valid for multivalent ions, which is why data from oxalate is not used. Further experiments have been conducted using cetylpyridinium chloride and nitrate (CPC) as “complexing” surfactant. The alkalin cation have been also studied but with an effect that is much less pronounced as expected[1].



Left: scheme of the solid-liquid extraction process. Right Schematic view of a cetylpyridinium micelle with its counterion distribution for chloride ions (red) and nitrate ions (green). The micelle is divided voluntarily in four different zones: (I.) the hydrocarbon core where no counterions are supposed to be located; (II.) the head group region, where nitrate is assumed to adsorb, contrarily to chloride; the thickness of this layer is modelled with 3.6 Å, the length of one pyridinium ring; (III.) in the Stern layer both nitrate and chloride are associated to the aggregate; (IV.) a zone in vicinity to the micelle, where the counterions are supposed to be “free”. By applying this classification of zones specificity for nitrate can be introduced to the model with regard to possible sphere-to-rod transitions.

---

[1] W.Müller, C. Déjugnat, O.Diat and T. Zemb, **"Effects of alkaline cations on self-assembly of cetylpyridinium surfactants"**, Tenside Surfactants and Detergents, accepted in 01/2011 issue

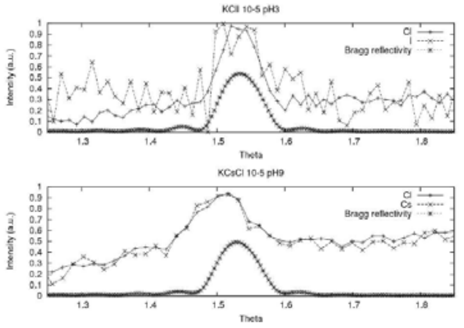
Liquid-solid interface ionic distributions measurement by x-ray

L. Girard - Collaborations J. Daillant, V Padmanabhan, O. Spalla, L. Belloni (LIONS CEA Saclay), S. Mora (LCVN UM II), D. Novikov (HASYLAB Hambourg)

Ion specificity, i.e. effects of ions in solution which cannot be explained by Coulombic interactions only, is known since the work of Hofmeister (1888). Since then, the so called Hofmeister series, ranking the ions according to their effect, have been found in a large variety of fields. Ion specificity is generally not a very large effect, but it plays a key role in a number of important phenomena or processes in which the interfacial behaviour of ions is essential. In contrast to the long list of available experimental data at the macroscopic level, there is no general theoretical understanding of ion specificity based on physical concepts. The experiments that we have performed are part of a more general project (supported by the ANR blanche physique SICSI) including theoretical developments, in particular to treat water molecules explicitly, and the measurement of ionic distributions with sub-nm resolution for a direct comparison to the theoretical profiles. The adsorption of ions using mixtures of salts at the air/water interface was already measured in the LIONS [V. Padmanabhan et al. PRL 99, 086105, 2007].

The aim our experiments was to work on solid/liquid interface and to go a step forward by changing the polarisability of the solid phase in contact with water in order to vary the magnitude of dispersion forces. Among possible x-ray experiments, grazing incidence x-ray fluorescence experiments is element specific but does not have the spatial resolution necessary for determining a profile. We used x-ray standing waves method (XSW) [M. Bedzyk et al. Science 248, 52, 1990] which is element specific and can have a good spatial resolution at DESY HASYLAB on BW1 and resonant x-ray reflectivity (RXR) [C. Park et al. PRL 94 (7), 076104, 2005] at ID1 at ESRF which allows the incorporation of element-specific information into the x-ray scattering methods. XSW consists in creating a standing wave field at the interface by interference between the incident electromagnetic field and the field reflected or diffracted by the substrate. The standing wave field is used to excite the fluorescence of the ions. The period of the standing waves is on the order of 3 nm, thus allowing one to probe the diffuse Gouy-Chapman layer.

RXR technique makes use of the anomalous dispersion in the atomic scattering factor of an atom near its absorption edge. We compared the effects of the anions, and mono- and trivalent cations. The substrates considered were polished silicon wafers (crystals) and Si/Mo multilayers substrates. In order to increase the specific absorption, to get a large fluorescent signal with a low ionic concentration, the surface charge and the magnitude of electrostatic forces were controlled by changing the pH (via the protonation-deprotonation of silanol groups). In order to check the feasibility of the experiment and treat the data, we developed different software (fluorescence, reflectivity, anomalous reflectivity). We are currently carrying out the data processing.



Reflectivity and normalized chloride, iodide and cesium fluorescence intensity profiles vs incident angle q. The sample is a Mo/Si multilayer immersed in two aqueous solutions containing respectively KClI, KCsCl, 10-5 M at pH respectively 3 and 9. The displacement of the fluorescence maxima is the sign of an ion adsorption at the interface.

References

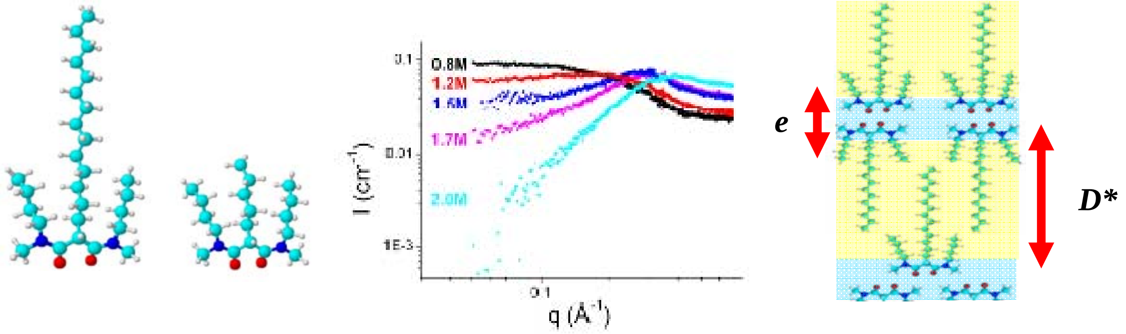
L. Belloni, Y. Chikina, V. Padmanabhan, L. Girard, J. Daillant, “Ion specificity in bulk electrolytes and at interfaces: Ionic adsorption measurements and continuous vs discrete solvent description”. 21 Conferences of the European Colloid and Interface Society, Genève.

L. Girard, O. Spalla, D. Novikov and J. Daillant, “Probing ion distribution profiles at the silica water interface using x-ray standing waves”. 10 International Conference on Surface X-ray and Neutron Scattering, Paris.

Competing structures in extractant micelles: consequences on stability

P. Bauduin[1,2], F. Testard[2], L. Berthon[3], Th. Zemb[1]
1- CEA/ICSM 2-CEA/DSM/DRECAM/SCM/LIONS 3- CEA/DEN/DRCP/SCPS/LSCE

In the nuclear field, liquid-liquid extraction is today the favourite process to extract and separate minor actinides from high level radioactive liquid wastes. The organic phase used in this process is classically composed of an extractant molecule, whose role is to extract selectively ions from the aqueous phase, and of an organic solvent, usually an alkane. It is now well established that the organic phase are not molecular solutions but rather complex fluids composed for example of extractant reverse micelles at low concentrations [*Erlinger et al. Langmuir 1999*].



Chemical structures of malonamide extractant molecules DMDBTDMA and DMDBPMA, SAXS spectra of DMDBPMA/dodecane mixtures, representation of lamellar like structure obtained with DMDBTDMA in dodecane at high concentrations.

At high extractant concentrations (above 1M) phase demixion of the organic phase appear under certain conditions for instance by increasing salt concentration in the aqueous phase and/or by increasing the polarizability of the extracted salts [*Nave et al. PCCP 2004*]. This phenomenon, known as the 3rd phase formation, may lead to local high fissile materials concentrations and then lead to criticality. Although such a phase demixion is still a substantial issue in the nuclear field the supramolecular structure at high extractant concentrations still remains largely unexplored.

Here the supramolecular structures of malonamide extractants, namely *N,N'*dimethyl-*N,N'*dibutyl-tetradecyl malonamide (DMDBTDMA) and *N,N'*dimethyl-*N,N'*dibutyl-pentyl malonamide (DMDBPMA) (see Fig.) in dodecane is studied over the whole range of concentrations by Small angle X-ray and Neutron Scattering (SAXS/SANS) [*Bauduin et al.*]. Hence the effect of the main alkyl chain length of the extractant on the supramolecular structure is stressed. Relations between the supramolecular structures at high concentrations and the 3rd phase formation are also highlighted. The results are described in a consistent way by the packing parameter concept and by expressing steric repulsion versus Van der Waals inter-aggregate interactions, both curvature dependants. The role of modifier molecules, which are highly hydrophobic amphiphilic molecules added to extractant phases in order to avoid third phase formation, on the supramolecular structure is also stressed. The ability of modifiers to break the supramolecular structure of extractants at high concentrations, from lamellar-like structures to H-bound inter-connected structures, is highlighted. This effect is found to prevent third phase formation.

- Bauduin, P.; Testard F.; Berthon, L.; Zemb Th. Relation between the hydrophile/hydrophobe ratio of malonamide extractants and the stability of the organic phase: investigation at high extractant concentrations Physical Chemistry Chemical Physics **2007** 9 (28), 3776-3785.
- Bauduin, P., Testard F., Zemb Th. Journal of physical Chemistry B, 112, 39 (**2008**) 12354

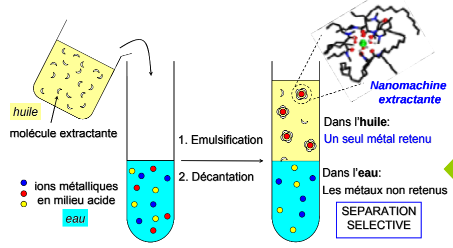
3 - Ion separation using supra-molecular self-assembled colloids

L'équipe est constituée actuellement de :
1 permanent CNRS responsable d'équipe (Dr. S. Pellet-Rostaing),
1 enseignant-chercheur UM2 (Dr. G. Arrachart)
1 ingénieur CEA/DSM (S. Dourdain)
1 technicienne CEA (V. Dubois)
2 post-doctorants (R. Turgis, S. Gracia)

Initiées depuis la création de l'institut, les différentes thématiques que développe l'équipe « Tri Ionique par des Systèmes Moléculaires Auto-assemblés »(LTSM) s'appuient sur les compétences et le savoir-faire des chercheurs qui composent l'équipe, aidés d'une technicienne (Mme Dubois, arrivé en 2009). Au départ cette équipe était constituée de 2 chercheurs (Pr. Thomas Zemb et Christophe Déjugnat, nommé CR2 en 2006 qui a quitté l'institut en décembre 2009). En plus de l'activité scientifique débutée dès 2007 (définition et mise en place des axes de recherche), la période 2007-2009 a essentiellement consisté à mettre en place le laboratoire du point de vue logistique (aménagement dans les nouveaux locaux, sorbonnes, paillasses, armoires à solvants, documents de sécurité associés, commande et installation des appareillages : zétamétrie, analyse d'ions…).

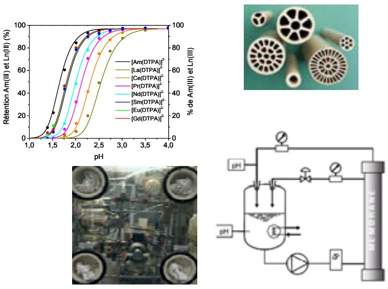
Depuis janvier 2009, l'équipe s'est renforcée du Dr Stéphane Pellet-Rostaing (nommé Directeur de Recherche en octobre 2010), expert dans la synthèse de systèmes chélatants pour la séparation d'ions et nouveau responsable de l'équipe. La nomination de Guilhem Arrachart au poste de Maître de Conférence UM2 et récemment de Sandrine Dourdain comme Ingénieur CEA/DSM affectés au LTSM a permis à l'équipe de débuter concrètement ses travaux de recherche dans le domaine de la synthèse de ligands spécifiques pour la séparation d'ions et d'isotopes stables, mis en œuvre dans des procédés d'extraction liquide/liquide, solide/liquide ou membranaires, avec une orientation dans la compréhension des mécanismes qui gouvernent la séparation.

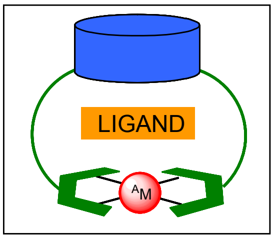
Dans les procédés associés au recyclage –nucléaire ou non-, lorsqu'un ion en solution est en équilibre à travers une interface avec une dispersion de complexants en conditions d'usage. La phase aqueuse, ainsi que la phase non-aqueuse sont des solutions loin de l'idéalité. Ce sont des systèmes moléculaires organisés : micelles, microémulsion, colloïdes, cristaux liquides, que l'on peut considérer par la thermodynamique statistique comme des « nanophases » réactives. Ces nanophases dispersées présentent des effets coopératifs très puissants et sélectifs qui sont la base des procédés de tri ionique efficaces et maîtrisés. Mais, *via* des « effets tunnel » dus aux espèces adsorbées aux interfaces, ces nanophases sont aussi à l'origine du peu d'efficacité en termes de flux massiques des méthodes de tri ionique. Cet axe de recherche visant l'optimisation des procédés de tri ionique par le design et la synthèse d'extractant spécifiques originaux ainsi que par l'étude des mécanismes associés, qui gouvernent la sélectivité à base de phénomènes coopératifs supramoléculaires pilotés entre autre par les interactions à longue distance, est au cœur des missions du groupe LTSM et nécessite une modélisation à l'échelle mésoscopique des compressibilités osmotiques et de forces entre agrégats extractants actifs. La possibilité d'exalter la complexation par auto-association des complexants sous forme de micelles, fibrilles ou cristaux liquides, doit être explorée et pourra conduire à des procédés en rupture de tri ionique et isotopique qui seront ensuite à développer en partenariat avec les équipes actuelles de Marcoule de R/D en ingénierie chimique. Au-delà du domaine purement nucléaire, ces effets sélectifs sont à étudier et à mettre en œuvre dans différents procédés liés au recyclage de matières associées à la production d'énergie et plus généralement, dans les optiques de développement durable, par exemple en décontamination ou pour le recyclage sélectif.

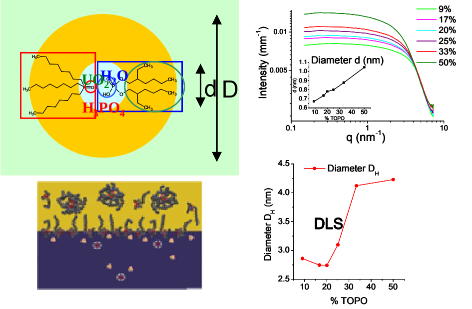


Extraction liquide/liquide

Filtration membranaire

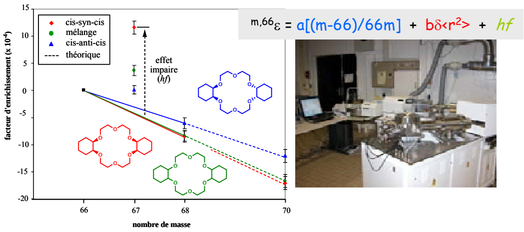






Mécanismes synergiques

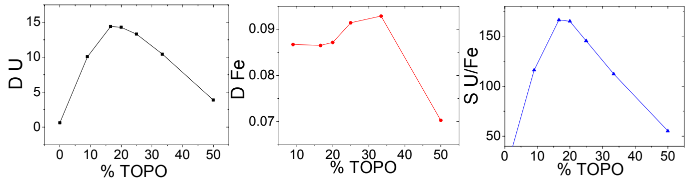
Séparation isotopique

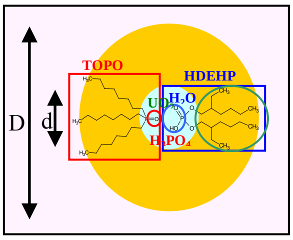

$^{m,66}\varepsilon = a[(m-66)/66m] + b\delta\langle r^2\rangle + hf$

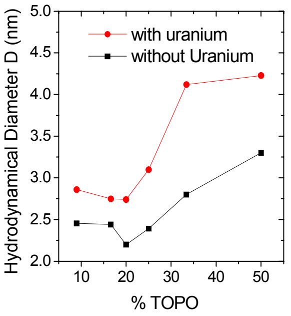
Synergistic mechanisms in liquid-liquid extraction of uranium from phosphoric ores

S. Dourdain, R. Turgis, G. Arrachart, S. Pellet Rostaing

Phosphate rocks mining, commonly used for the manufacture of phosphoric acid, could be an alternative source of uranium production. A method based on liquid-liquid extraction has been studied and industrially applied in the 80's. It was based on a synergistic mixture of bis-(2-ethylhexyl) phosphoric acid (HDEHP) and trioctyl phosphine oxide (TOPO).[1] Facing an increasing demand in uranium, it appears nowadays necessary to optimize this system by synthesizing new extracting agents, and by providing the understanding of the selective transport phenomena that govern this separation system. While applied in many extractant systems, synergistic mechanisms are not fully understood. The HDEHP extraction factor, is for example increased by a factor greater than 50, depending on the co-extractant chosen and on the molar ratio [HDEHP]/[co-extractant][22,33]. Besides, the selective extraction of uranium toward other metals is also more enhanced than it can be expected with a molecular approach. It appears therefore essential to characterize at the molecular and supra-molecular scales the physico-chemical parameters of the HDEHP/TOPO system, in order to understand the synergistic mechanisms.







In this field, we focused on the relationship between the organization of the two extracting molecules in supramolecular aggregates, and their extraction properties. The synergistic ratio was found for 20% of TOPO, which exhibit a distribution coefficient (D) value of 15 for U, and selectivity toward Fe of about 150 (see figure). X-rays and light scattering measurements gave rise to complementary results regarding the shape and the size of the aggregates formed by the HDEHP and TOPO molecules, with and without uranium. Spherical aggregates are observed with a decrease in diameter at the synergistic conditions. Several assumptions are explored to explain these phenomena, considering the relative location of the two molecules in the aggregates, the role played by extracted water and acid, or the critical micellar concentrations. Finally, measurements by infrared, Raman and NMR spectroscopy are considered to characterize the complexation mechanisms in synergistic conditions.

The same approach is applied to extractant molecules that are synthesized in the laboratory in order to optimize the extraction process. This study will provide new understanding of the synergistic mechanisms, and reach to a reasoned approach in the investigation of new extractants structures.

---

[1] F.J. Hurst, D.J. Crouse, K. B. Brown, *Ind. Eng. Chem. Process Des. Develop*, **1972**, *11*, 12.

[2] C.K. Gupta, G. Gupta, H. Singh, Uranium resource precessing, - secondary resources, Springer Berlin, **2003**.

[3] S. Girgin, N. Acarkan, A. Ali Sirkeci, J. radioanal. Nucl. Chem., **2002**, 251-2, 63.

Separation of lanthanides(III) by inorganic nanofiltration membranes using a water soluble complexing agent

J. Borrini, G. Bernier, S. Pellet-Rostaing, A. Favre-Réguillon, M. Lemaire

First separation of Ln(III) using inorganic nanofiltration membrane has been achieved. Ln(III) ions are strongly repelled by the ZrO_2/TiO_2 membrane.[1] When diethylenetriaminepentaacetic acid (DTPA) is used as water soluble complexing agent, the complexes formed with Ln(III), surprisingly passes through the membrane. The stability constant of DTPA with Eu^{3+} is higher than the one with La^{3+}. Thus $[EuDTPA]^{2-}$ complex is formed at lower pH than $[LaDTPA]^{2-}$ and so these two elements can be separated. With an equimolar mixture of Eu^{3+} and La^{3+}, a La^{3+}/Eu^{3+} separation factor of 2.5 is obtained at pH 1.9. Other polyaminocarboxylic acids have been used such as EDTA and HEDTA and similar phenomenon occurred. The best La^{3+}/Eu^{3+} separation factor has been also evaluated with a TiO_2 nanofiltration membrane and results are comparable.

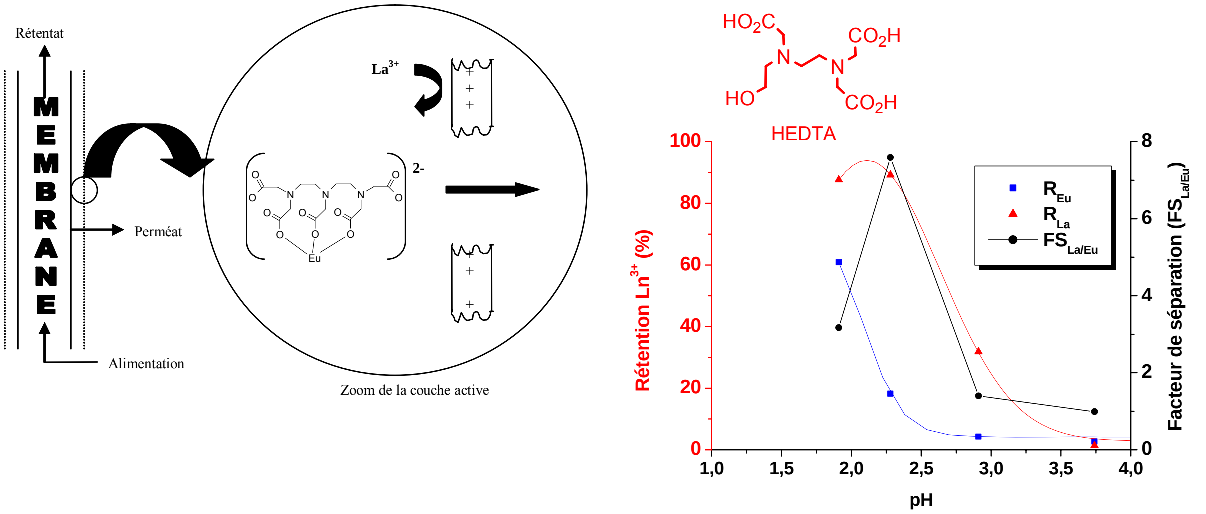


Fig. 1: Principle of ion separation with an inorganic nanofiltration membrane by complexation with the organic ligand DTPA and rejection of Eu^{3+} and La^{3+} by the membrane with HEDTA ligand versus pH. $[La^{3+}] = [Eu^{3+}] = 2.5 \times 10^{-4}$ molL^{-1} ; $[HEDTA] = \sum[Ln^{3+}] = 5 \times 10^{-4}$ molL^{-1} (black curve: separation factor versus pH)

Using organic membranes, the rejection of Ln(III) increases as the charge of the complex increases [2,3] whereas for inorganic membranes, rejection of Ln(III) decreases when increasing the charge of the complex. Thus, these results, obtained with inorganic membranes, demonstrated the potential of membrane process for the An(III)/Ln(III) separation and give rise to new possibilities for the separation of metal ion using enhanced permeability through inorganic membrane assisted by a water soluble complexing agent.

---

[1] J. Borrini, G. Bernier, S. Pellet-Rostaing, A. Favre-Réguillon, M. Lemaire, *J. Membrane Sci.* **2010**, 348, 41.

[2] A. Favre-Réguillon, A. Sorin, S. Pellet-Rostaing, G. Bernier, M. Lemaire, *C.R. Chim.* **2007**, 10, 994

[3] A. Sorin, A. Favre-Réguillon, S. Pellet-Rostaing, M. Sbaï, A. Szymczyk, P. Fivet, M. Lemaire, *J. Membr. Sci.* **2005**, 267, 41.

Modified $h_4$tpaen for the An(III)/Ln(III) separation

D. Brusselle, G. Arrachart, S. Pellet-Rostaing

N, N, N ', N'-tetrakis [(6-carboxypyridine-2-yl) methyl] ethylenediamine[1] ($h_4$tpaen) is an effective ligand for the actinides (III) / lanthanide (III) separation which could replace water-soluble ligands conventionally used in the back-extraction SANEX process with DTPA or HEDTA. Although the selectivity significantly higher than those determined with DTPA or HEDTA were observed using this ligand, its use is limited by its low solubility in concentrated media. As already shown in recent work,[2] that the functionalization at the position 4 of pyridine units had no influence on the effectiveness of chelating system, we planed to increase its solubility in water by incorporating hydrophilic substituents. A synthetic strategy was developed based on substituting chélidamique acid or acid 4-halo-pyridine-2,6-dicarboxylic and different type of nitrogenous groups such as diethanolamine, morpholine or oxygenated PEG were considered (figure 1).[3]

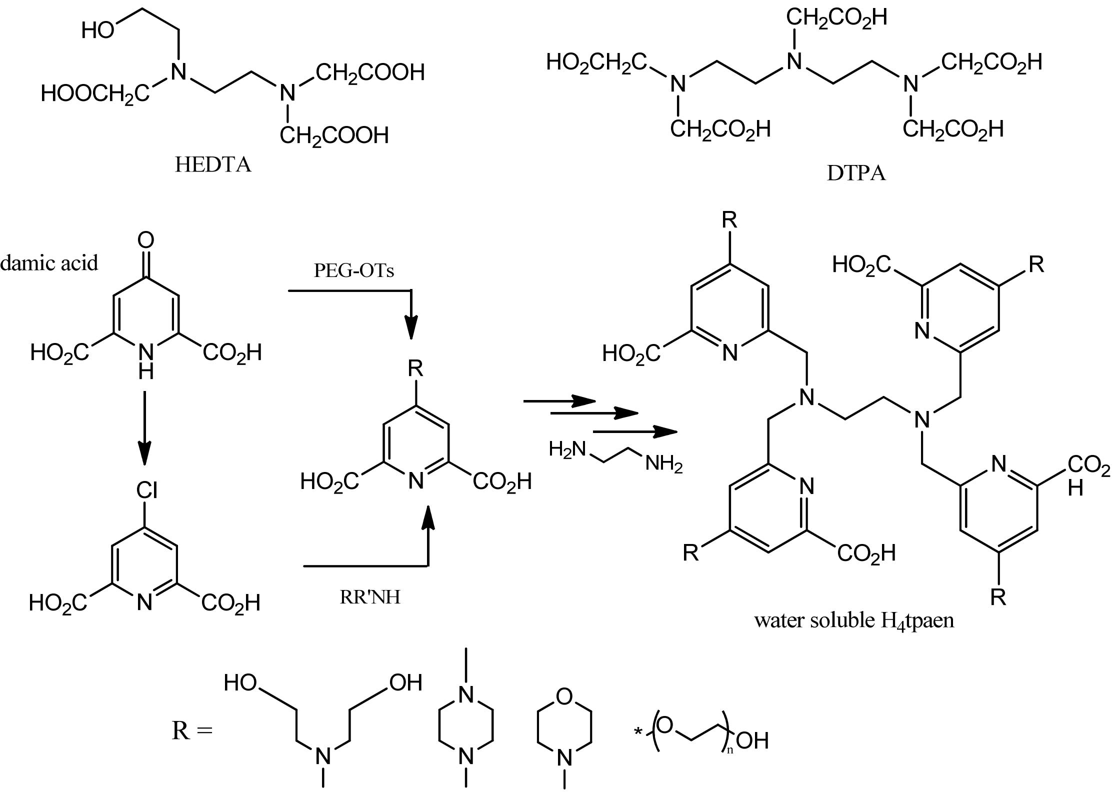


Fig. 1: HEDTA and DTPA ligands usually used in the back-extraction process for actinides/lanthanides separation and synthetic methodology for the preparation of water-soluble $h_4$tpaen chelating agent from chelidamic acid precursor

Modification of the chélidamic acid was performed allowing to obtain the morpholine and the methylpyperazine pyridinodicarboxylate derivatives which will be used as precursors for the synthesis of water soluble $h_4$tpaen analogues.

---

[1] N. Chatterton, Y. Bretonnière, J. Pécaut, M. Mazzanti, **An efficient design for the rigid assembly of four bidentate chromophores in water-stable highly luminescent lanthanide complexes** *Angew. Chem. Int. Ed.* 2005, 44, 7595-7598.

[2] J. Borrini, **Séparation actinides(III)/lanthanides(III) par filtration membranaire et extraction liquide-liquide à l'aide de ligands organiques hydrosolubles,** Thèse ICSM 2009.

[3] J. Brusselle, **Synthèse de h4tpaen modifiés pour la séparation Actinides(III)/Lanthanides(III)**, stage Master 2 CSMP, 2010.

Moreover, we have also prepared h4tpaen analogues (figure 2) by varying the nature of the diamine, in order to study the influence of the rigidity towards the actinides selectivity. 2 new compounds were obtained incorporating a cyclohexanediamine or a 2,2'-oxybis(ethylamine) which will be evaluated in collaboration with the CEA/DRCP.

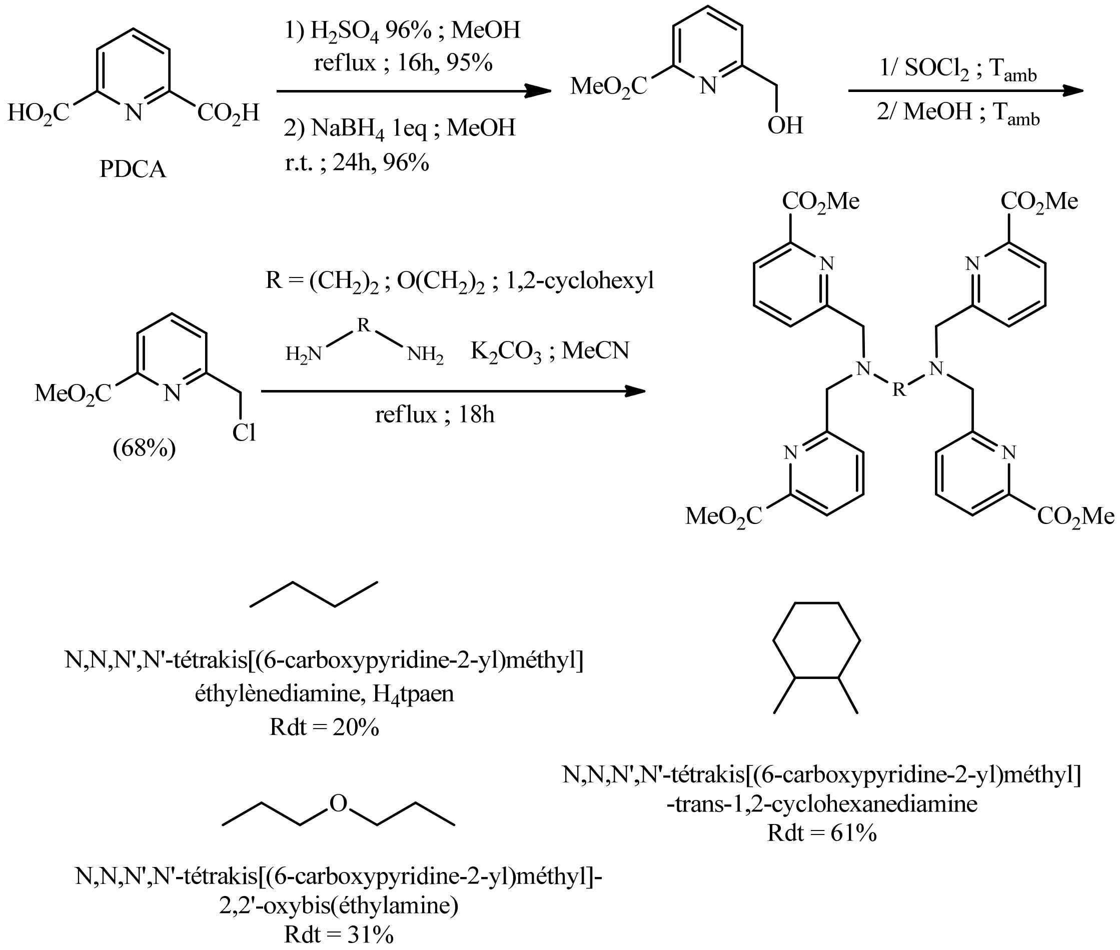


Fig. 2 : modified h4tpaen already synthesized from various diamines

Extracting silica obtained by an "all in one" approach using bifunctional surfactants.

G. Arrachart, S. Dourdain, G Toquer, A. Grandjean, S. Pellet-Rostaing

Extraction of specific targeted species (rare earth, heavy metals, transition metals, radionucleides) from industrial and nuclear effluents is an important issue in the recycling and / or decontamination process. In this field, we focused on the development of a versatile methodology to prepare silylated hybrid materials with specific chelating properties. This choice is based on one hand, on minimizing the amount of solvent used but also the effluent quantity. This separation method centred on solid-liquid extraction involves hybrid solid support. The sol-gel process is a convenient method for the preparation of hybrid organic-inorganic materials such as hybrid silica. The ability to control the structure of the materials on the nanoscale is of great interest for the design and the improvement of material properties. In this field, utilization of surfactant as external structuring agent represents a way to form periodic mesoporous hybrid materials.

The aim of this work is to develop a suitable ‘‘all-in-one’’ approach using condensable surfactant precursors either for preparation of hybrid materials or functionalization of the channel walls of mesoporous silica (figure 1). Only few studies use this kind of ‘‘all-in-one’’ approach, but without the introduction of specific organic groups.[1] Thus, we are trying to develop such condensable surfactant with a chelating functional group. These surfactant molecules exhibit two different polar head connected together through a long hydrocarbon chain:

- a polar head formed from chelating groups in order to establish the complexation of specific target species. As the nature of the chelating head directly depends on the target, specific functions will be investigated (COOH, DTPA, CMPO, phosphonate ...). Based on a recent feasibility study conducted in the laboratory[2], we propose to work initially with simple groups such as carboxylate or IDA (iminodiacetic acid) taken as model.
- a second polar head shaped on condensable $Si(OR)_3$ functionalities in order to generate the silica network after sol-gel process.

Hydrolysis of the silica precursor results in activated monomers, which can undergo self-organization and hydrolytic polycondensation. This ‘‘self process’’ ensures both the placement of the functional groups in the hybrid silica, and/or along the mesopores wall surface, as well as optimal use of the template.

The proposed work revolves around this concept with the preparation of new original chelating silylated surfactants, the study of the physicochemical properties of such self-assembled molecular systems and the preparation of resulting materials. Sorption studies will be investigated from such hybrid materials and compared to surface modification of mesoporous silica achieved by post-grafting. These studies will be conducted jointly with LNAR, and supported though a collaborative network with the DRCP in the case of actinide / lanthanide extraction.

---

[1] a) Ruiz-Hitzky, E., Letaïef, S., Prévot, V., Adv. Mater., 2002, 14, 439-443. b) Zhang, Q., Ariga, K,. Okabe, A, Aida, T., J. Am. Chem. Soc.,2004, 126, 988-989. c)Voss, R., Thomas, A., Antonietti, M., Ozin, G.A.,. J. Mater. Chem., 2005, 15, 4010-4014.

[2] Sene, S. ***Synthèse de systèmes chélatants de type acide iminodiacétique pour la préparation de précurseurs silylés.*** Stage Master I CSMP 2010.

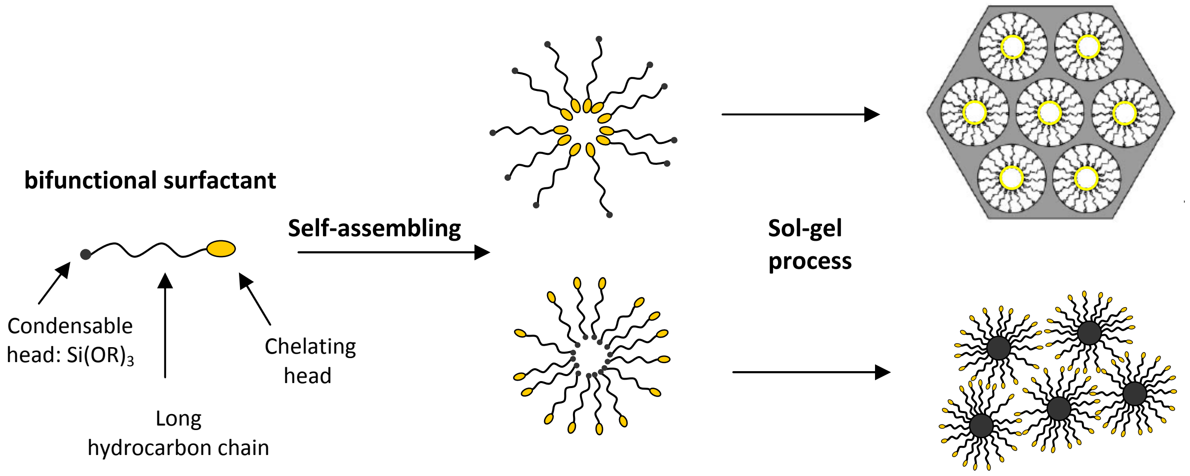


Fig. 1: synthesis and using of bifunctional surfactant containing a reactive site (Si(OR)3 and a chelating sites for the "one-pot" preparation of extracting mesoporous or nanoparticles materials.

Liquid-liquid cation extraction without solvent

Th. Zemb, F. Testard, S. Prévost and S. Nave (LIONS-Saclay),
K. Baszko, Ch. Coulombeau and Ch. Larpent (Université de Versailles St Quentin)

Chantal Larpent and co-workers have shown ten years ago that efficient solvent-free extraction can be obtained with complexing molecules of a genral class of tri-block molecules composed of one hyrophobic chain, one complexing group with "recognition" functionality as well as as temperature sensitive non ionic head. This type of molecule presents a cloud point two phase region where liquid-gas phase separtion occurs[1]. The concentrted phase made of anismetric micelles allows efficient extraction-desextraction withoit solvent. Surprisingly, process works best when comlexing group is in between the temperature sensitive head and the apolar chains[2].

Extremely efficient selectivitiées for uranium of this type of molecule have been evidenced. A drawback hindering up to now applications in hte domain of nuclear interest is the variation of the cloud point with external constraints, such as the variable amounts of radiolized compelxing surfactant. However, a large domain of stable reverse micelles, with and without iosn has been detected in the phase diagram structures[3].

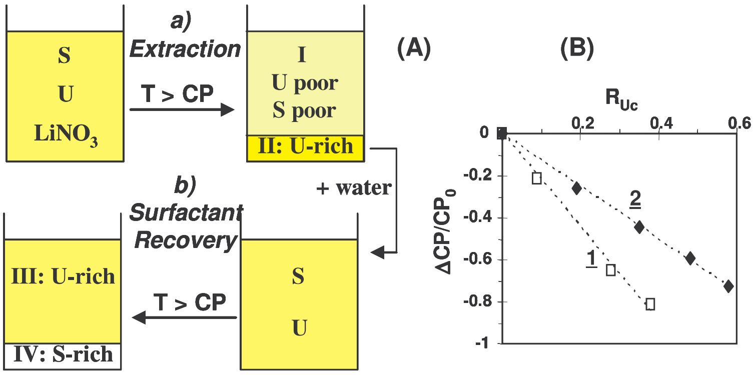


Figure 1: (A) Principle of Thermo- and salt- regulated uranyl separation (a) and surfactant recovery (b).
(B) Relative variation of the cloud point temperature versus U/surfactant molar ratio in the coacervate plots for two temperature sensitive extractant molecules.

---

[1] Larpent, Chantal; Prevost, Sylvain; Berthon, Laurence; Zemb, Thomas; Testard, Fabienne " Nonionic metal-chelating surfactants mediated solvent-free thermo-induced separation of uranyl. " New Journal of Chemistry (2007), 31(8), 1424-1428.

[2] Prevost, S.; Coulombeau, H.; Baczko, K.; Berthon, L.; Zorz, N.; Desvaux, H.; Testard, F.; Zemb, Th.; Larpent, C. " Thermo-responsive metal-chelating surfactants: properties and use in cloud point extraction of uranyl nitrate. " in Tenside, Surfactants, Detergents (2009), 46(2), 100-104.

[3] Nave S; Testard F; Coulombeau H; Baczko K; Larpent C; Zemb Th " Ternary phase diagrams of a thermoreversible chelating non-ionic surfactant. " Physical chemistry chemical physics : PCCP (2009), 11(15), 2700-7.

Instabilities in liquid/liquid extraction: a colloidal approach.

Thomas Zemb, Pierre Bauduin
Fabienne Testard (LIONS- Saclay), Laurence Berthon (DRCP-Marcoule)
W. Kunz (Regensburg), Ch. Larpent (University of Versailles) and B. Demé (ILL-Grenoble)

The interaction potential between reverse aggregates reponsible for liquid-liquid extraction can be measured via the structure factor since 1998 and papers published by Testard and Belloni. This has been recognized in all laboratories working in the world since then. It allows to predict location in phase diagram of the location of the two phase-three phase line boundary. This instabilitie is mainly of liquid-gas type induced by a short range potential, so expression of boundaries have analytical expressions. The van der Waals attraction depends on the volume of the polar core of aggregates while the Hamacker constant depends probably on the polarisibility of the core containing extracted ion pairs as well as co-extracted acid. A review off all available papers including some predictive modelling in phase behaviour has been written[1].

In this domain, most of engineering literature refers to HLB or HLD concept, while physical chemistry including statistics of fluid phases at finite temperature refer to spontaneous curvature or packing. Equivalence between this tow approaches s well as simple analytic expression in case of non-ionics is proposed [2]. Comparing the three ways of characterizing "spontaneous" lateral packing of amphiphiles are equiv.: the spontaneous curvature, the mol. packing parameter, and the refined hydrophilic-lipophilic balance known as HLD (hydrophilic-lipophilic deviation). Recognition of this equivalence, with its underlying hypothesis of incompressible fluid with lowest surface energy, reinforces the single parameter bending energy expression implicit in the classical papers by Ninham and Israelachvili, as well as all the predictive models of solubilization developed as yet.

At that occasion, it has been noticed that two types of reverse aggregates with a limited amount of polar phase of micelles exist. Indeed, three length scales have to be considered to describe microemulsions: persistence length and spontaneous radius of curvature of the surfactant film as intensive variables and ratio of volume fraction to available surface, an intensive variable linked to sizes and topologies that can be built without tearing the surfactant film. We show here that at least four types of bicontinuous microstructures have been detected so far, and can be distinguished by a simple experimental determination of the evolution of scattering peak position versus dilution[3]. Another criteria for detecting "rigid" films different from the more studied and described flexible surfactant monolayers is a peculiar behaviour of conductivity versus volume fraction of water, a non-monotonic behaviour, alias an anti-percolation. On the scale of each aggregate, a polar/non polar interface can be consistently defined and measured. Therefore, the adsorption isotherm on extracted ions can now be measured. This is the route towards parameter-free predictive modelling of liqui-liquid extraction.[4]

---

[1] Testard, Fabienne; Zemb, Th.; Bauduin, P.; Berthon, Laurence. " Third-phase formation in liquid/liquid extraction: a colloidal approach." in Ion Exchange and Solvent Extraction (2010), 19 381-428.

[2] Kunz, Werner; Testard, Fabienne; Zemb, Thomas "Correspondence between Curvature, Packing Parameter, and Hydrophilic-Lipophilic Deviation Scales around the Phase-Inversion Temperature". Langmuir (2009), 25(1), 112-115.

[3] Zemb, Thomas ; " Flexibility, persistence length and bicontinuous microstructures in microemulsions". Comptes Rendus Chimie (2009), 12(1-2), 218-224

[4] Testard, Fabienne ; Berthon, Laurence ; Zemb, Thomas. " Liquid-liquid extraction: An adsorption isotherm at divided interface? " Comptes Rendus Chimie (2007), 10(10-11), 1034-1041.

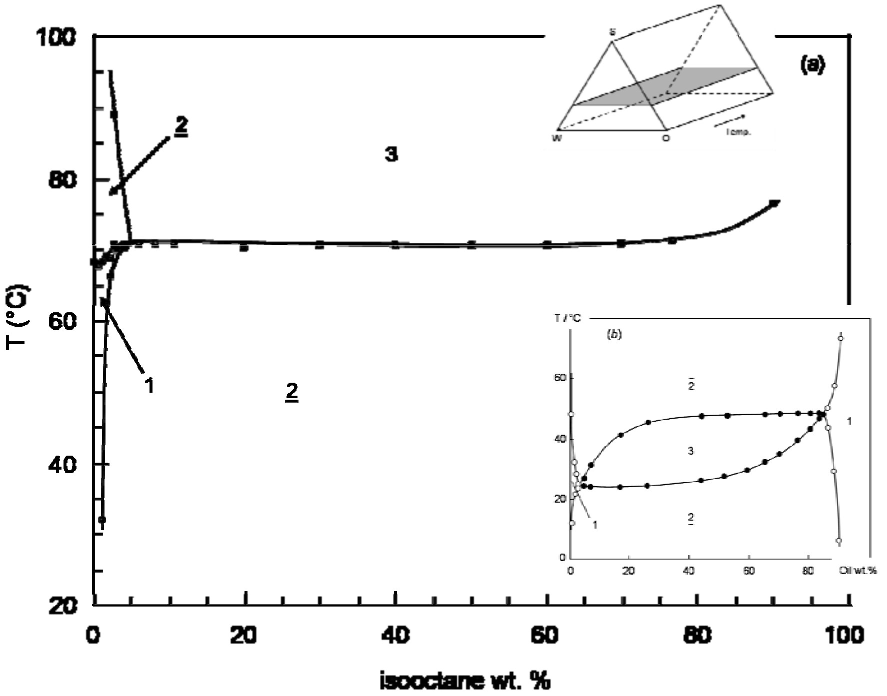


Fig.1: Constant surfactant cut in the ternary phase prism: oil-water-surfactant at different balances of water and oil content. Low water-content reverse aggregates are possible without co-surfactant, however with a limited domain available for extraction. Phase sequence and extension demonstrates that this type of microemulsions belong to the class of rigid surfactant film, with a bending constant larger than kT[1].

An example of rigid film appears if one examines ternary solutions of oil/water and di-block molecules associating a chelating group and a non-ionic surfactant. The possibility of making single phase stable microemulsions in a defined temperature and concentration range has been demonstrated on this system. The concentration is limited by the presence of a gel, containing a lyotropic liquid crystals. Microstructure, phase sequence as well as limited range all show that spontaneous curvature decrease with temperature is quenched by the presence of lysine as a grafted complexing group. The microemulsions formed are made with a rigid oil-water interface. Liquid-liquid extraction processes with this type of surfactant are possible, but will require presence of at least a fourth component.

---

[1] Nave, S.; Testard, F.; Coulombeau, H.; Baczko, K.; Larpent, C.; Zemb, Th.." Ternary phase diagrams of a thermoreversible chelating nonionic surfactant" Physical Chemistry Chemical Physics (2009), 11(15), 2700-2707.

The supramolecular mechanisms at the origin of ion extraction processes in hydrometallurgy

Thomas Zemb, Sandrine Dourdain, Véronique Dubois, Stéphane Pellet-Rostaing
Laurence Berthon, Y. Meridiano, Ph. Guilbaud (DEN/DRCP-Marcoule)

We study liquid-liquid extraction at supramolecular and colloidla scale, considering the pseudo-ternary phase diagramm ol-water-extrcatant with all ionic species as perturbations. Combined SAXS/SANS and osmometry allows to determine microstrutures formed in the solvent while

analysis for ions and water of coexisting phases in equilibrium allow to determine ion adsorption isotherms, considering the water phase as a "reservoir". Water is always co-extracted with complexing agent as well as with the extracted ion pairs[1].

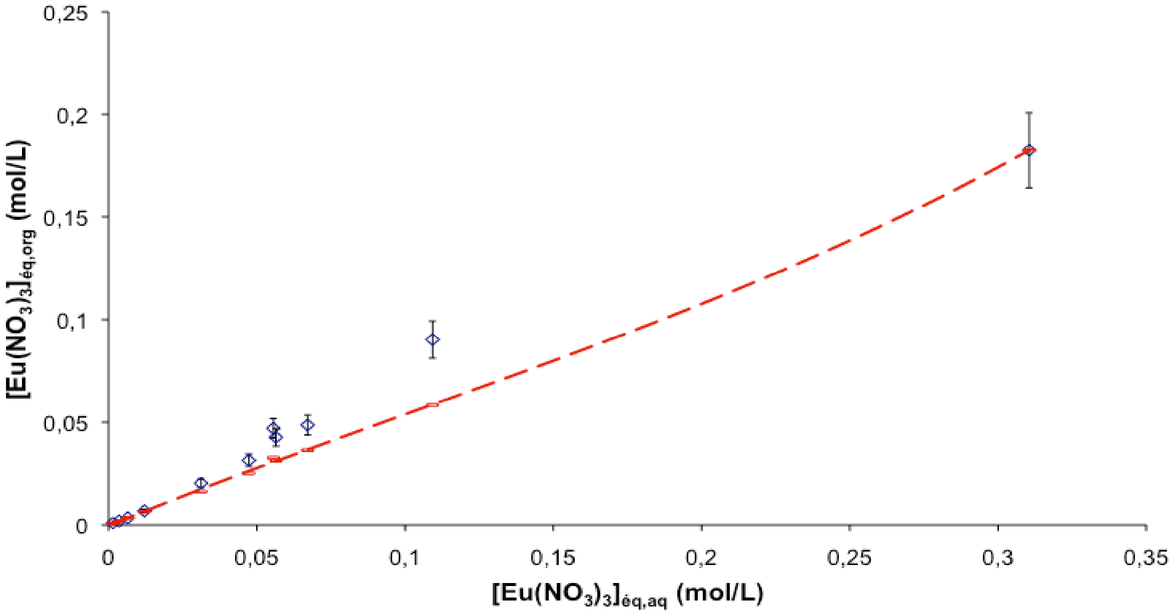


Figure 1: Simultaneous determination of ion per extractant in the organic phase and cation molarity in the aqueous phase. This type of plot allows to determine free energy of transfer from water to solvent phase and relate this to the volume and curvature of the reverse aggregate, the colloidal aggregate involved in the separation process. When dilution is such that these aggregates are not formed, free energy of extraction decreases by an order of magnitude: specific ion extraction is a property emerging from organization of amphiphilic extractant molecules.

The volume of co-extracted water participates to the instability leading to the transition from two phase to three phases, and the corresponding change in viscosity observed in pulsed columns[1]. Facing an increasing demand in uranium, it appears nowadays necessary to optimize this system by synthesizing new extracting agents, and by providing the understanding of the selective transport phenomena that govern this separation system[2].

---

[1] Berthon, Laurence; Testard, Fabienne; Martinet, Laurence; Zemb, Thomas; Madic, Charles. " Influence of the extracted solute on the aggregation of malonamide extractant in organic phases: Consequences for phase stability. " Comptes Rendus Chimie (2010), 13(10), 1326-1334.

[2] Berthon, Laurence; Testard, Fabienne; Martinet, Laurence; Bauduin, Pierre; Zemb, Thomas; Madic, Charles. " Aggregation in organic extractant phases: Consequences on the third phase formation in liquid-liquid processes. " Abstracts of Papers, 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010 (2010)

We have measured for the first time to our knowledge as well the interface lateral extension than the curvature variation associated to the ion extraction and shown that first term is of the order of 5KT/ion pair while the second is one order of magnitude lower[1]. The volume and polarisability of the polar core built from the extracted ion pair, as well as co-extracted water and nitric acid is also the dominant term in the attractive interaction between reverse aggregates.

This latter term can be tuned by matching chain lengths and solvent composition, hence the "wetting" of reverse aggregates by the solvent used. [2]

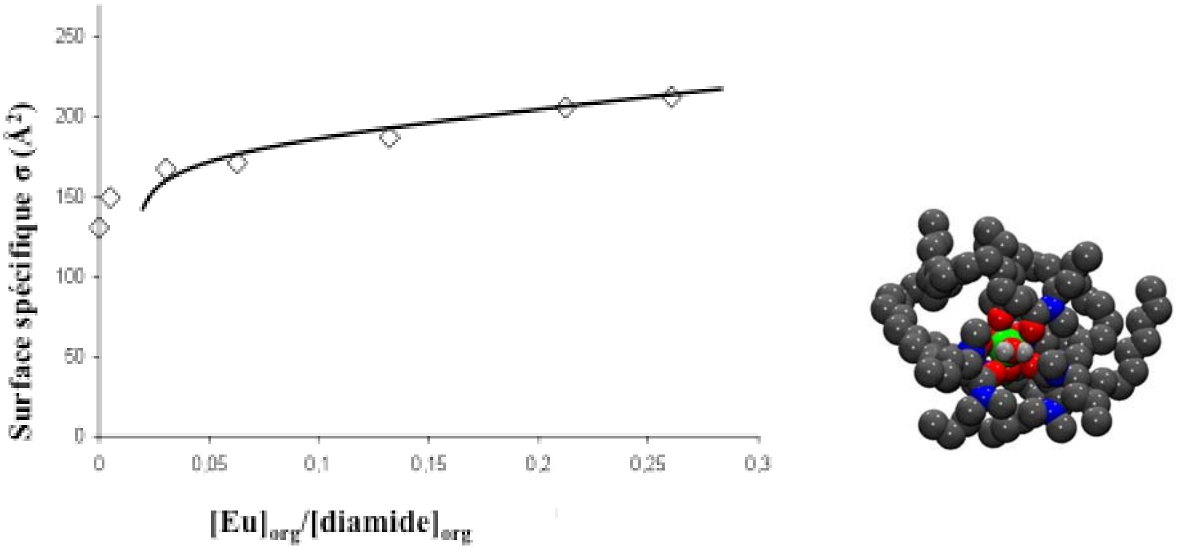


Figure 2: Area per diamide in the reverse aggregate (typical configuration of a tetramer shown) versus the amount of europium extracted per extractant molecule (with three aliphatic chain/extractant). The cost in elastic free energy associated to the increase of area molecule is of the same order of magnitude than complexation

---

[1] Meridiano, Y.; Berthon, L.; Crozes, X.; Sorel, C.; Dannus, P.; Antonio, M. R.; Chiarizia, R.; Zemb, T " Aggregation in Organic Solutions of Malonamides: Consequences for Water Extraction. " Solvent Extraction and Ion Exchange (2009), 27(5-6), 607-637.

[2] Berthon, L.; Meridiano, Y.; Lagrave, S.; Crozes, X.; Sorel, C.; Zorz, N.; Testard, F.; Zemb, T " Aggregation of organic extractant phases: consequences on extraction properties. " in Solvent Extraction: Fundamentals to Industrial Applications, Proceedings of ISEC 2008 International Solvent Extraction Conference, Tucson, AZ, United States, Sept. 15-19, 2008 (2008), 2 1017-1022.

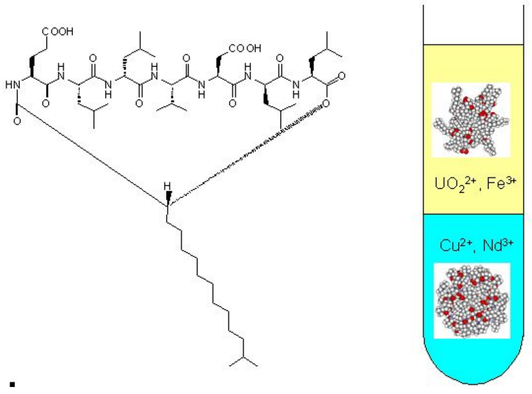
Self-assembly of amphiphilic peptides for ion separation

C. Déjugnat, O. Diat and Th. Zemb

Current processes for spent fuel treatment are based on the separation of radioactive metals ions by liquid-liquid extraction using extractants such as tributylphosphate or some diamides in the DIAMEX process. Recently these molecules have been shown to self-organize in reverse micelles that are supposed to play a key role in the separation process. Still there is no predictive model to link the efficiency of an extractant with its molecular structure and its self-organization properties; however such a model is absolutely needed for the understanding and the development of new methods required in future nuclear projects.

Based on these considerations and in a bio-inspired approach, we develop and study the self-assembly properties and separation efficiency of new amphipathic peptides. The choice of such compounds has been motivated by several complementary aspects. First, peptides can be easily synthesized with a huge structural diversity (defined by the aminoacid sequence and composition). Then, depending on their aminoacid composition they are also able to recognize and selectively bind metal ions. Being either intrinsically amphiphilic or after hydrophobization (lipopetides) they can also self-assemble forming various aggregates (micelles, vesicles, fibers …). Moreover, it has been recently shown that some hydrophobic peptidic sequences in viral fusogenic proteins easily dissolve in a lipid bilayer forming cylindrical reverse micelles by co-organization with the phospholipids.

On tie-lines between water-rich and alkane-rich solutions, we show via scattering experiments that the natural lipopeptide surfactin self-assembles in direct and reverse micelles in equilibrium. Elongated direct micelles in the aqueous phase are present together with small reverse globular aggregates. These latter are made from hydrated surfactant without any "water-pool" in the organic phase. The obtained biphasic system is used for liquid-liquid extraction of model metal cations. It is efficient with iron and uranium but not with copper or neodymium. Competitive extractions show high selectivity towards iron[1].



Surfactine molecule that allows metal selective extraction in biphasic system.

---

[1] Small submitted

Actinides (III) / Lanthanides (III) separation by nanofiltration assisted by complexation

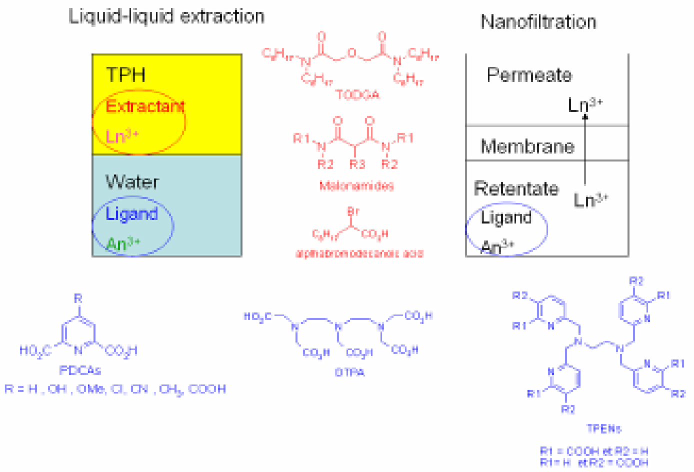
J. Borrini, S. Pellet-Rostaing - Collaboration G. Bernier, C. Hill, M. Lemaire, A. Favre-Réguillon,

In France, one of the research trend concerning the reprocessing of spent nuclear fuel consists in separating selectively the very radiotoxic elements with a long life by recycling them (Pu) or by transmuting them (Am, Cm, Np). The aim of this PhD is to find a new way to separate actinides (III) from lanthanides (III). This new method consists in chelating selectively actinides (III) with an organic ligands first and them filtering it on a nanomembrane. Because of its weight the complex can not go through the membrane but the free lanthanides (III) can. The complex goes to the retentate and the lanthanide to the permeate. Thanks to this strategy we are able to separate these two kinds of ions who are difficult to separate because of their similarity. The originality of this project is that ligands have to be hydrophilic.

The first part of this PhD is the synthesis of these ligands by introducing hydrophilic functions such as carboxylic acids, amides, urea, alcohols, etc. For the moment we have synthesized different carboxylic acids and the introduction of other functions will be done after the understanding of the results obtained with the first ligands.

The second part of the project is to test these new ligands on nanofiltration membrane in order to separate lanthanides first. These tests will be carried out in Lyon in non-radioactive media in order to get the good conditions. We will try these ligands on both organic and inorganic membrane to compare their separation capacity. We know, thanks to the PhD of Antoine SORIN[1] , that organic membrane are able to separate americium(III) from lanthanides(III) but the problem is that they can not resist to high radioactivity. That is the reason why we want to replace them by ceramic nanofiltration membranes more suitable for these conditions. Once the conditions are optimised, we will test these systems in radioactive media in Atalante on the site of Marcoule (CEA).

The third part is to compare results obtained with hydrophilic ligands in nanofiltration and in liquid-liquid extraction. It will offer a comparison between these two methods of separation. In the liquid-liquid extraction system we need an organic agent able to extract selectively lanthanides (III) in the organic phase which is the TPH, a mixture of branched and linear C_{12} alkyl chains. Hydrophilic ligands will extract selectively americium (III) in the aqueous phase. Principle and ligands are summarized in the following scheme.



Principe of the comparison between nanofiltration and Liquid-liquid extraction.

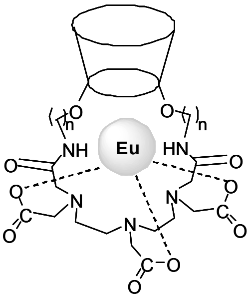
References : A. Sorin Séparation actinides(III) / lanthanides(III) par nanofiltration assistée par complexation-2006, thèse de l'université Lyon1.

Synthesis of Original Capping Calixarenes with DTPA fragment

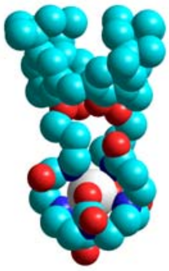
S. Pellet-Rostaing, Y. Lin, A. Leydier, E. Métay, A. Favre-Réguillon, D. Bouchu, M. Lemaire

Owing to the development of supramolecular chemistry, a number of calixarene-based ligands have been extensively studied for their coordination properties. Cation complexing ligands containing calix[4]arene building blocks have been synthesized to obtain more selective metal ion sensors. These molecules are generally O-substituted calix[4]arenes at lower rim with various chemical functionalities to ion recognition (carbamoylphosphine oxide, phosphine oxide, acid-amide, phosphonic acid among others). Surprisingly, to the best of our knowledge, combination of the architecture of calix[n]arenes with the chelating behaviour of polyaminoacetic acids such as DTPA or EDTA was not reported in the literature. Calixarenes **1-3** capped with DTPA bridges were synthesized by condensation of the corresponding 1,3-(distal)-diaminocalixarenes and DTPA dianhydride in DMF.[1] The chelating properties of the DTPA-calixarenes were evaluated towards europium and the resulting complexes were characterized by mass spectroscopy.

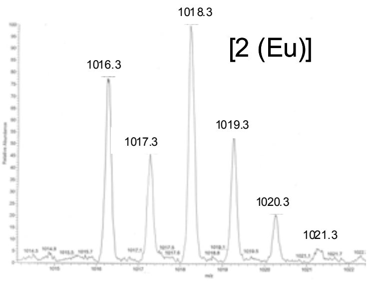
The chelating behaviour of macrocycles **1-3** was then evaluated towards europium complexation. Based on molecular modelling of **3** and its europium complex (HyperChem, MM+ and AM1), [**3** (Eu] structure would be obtained in cône conformation which showed that the DTPA macro ring of **3** would adequately embrace the metal without any interaction with the calixarene moiety (see figure below), assuming nine-coordination of the metals by means of the three carboxylates and aliphatic amines as already published for DTPA-lanthanide complexes. Europium complexes were prepared by addition of calixarenes previously solubilized in DMF to a solution of $EuCl_3$ in DMF. Characterizations of the europium complexes were done by electrospray mass spectrometry.

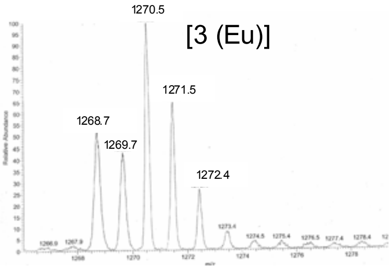


[**1**(Eu)] (n = 2) with *tert*-butyl group
[**2**(Eu)] (n = 2) without *tert*-butyl group
[**3**(Eu)] (n = 3) with *tert*-butyl group



[**3** (Eu)]





---

[1] Lin, Y.; Métay, E.; Leydier, A.; Bouchu, D.; Pellet-Rostaing, S.; Lemaire, M. " Synthesis of Original Capping Calixarenes with DTPA fragment" Journal of Inclusion Phenomena **2008**, 61, 187-193

Specific adsorption in dispersions of microporous colloids: a key to control of life-cycle of materials

Thomas Zemb,
Miles Page and Helmuth Coelfen (Max Planck Potsdam), Emiliano Fratini and Piero Baglioni (University of Firenze), Bruno Demé (ILL-Grenoble).

New methods have been developed using ultracentrifugation to determine directly the binary equilibrium phase diagrams of colloids, such as precursor for compacted materials. This method has been shown to work for anisometric particles, such as clays, a case where it is difficult to obtain behaviour under compaction[1]. This method is based on analytic ultracentrifuge and may also be extended to organic microcrystals.

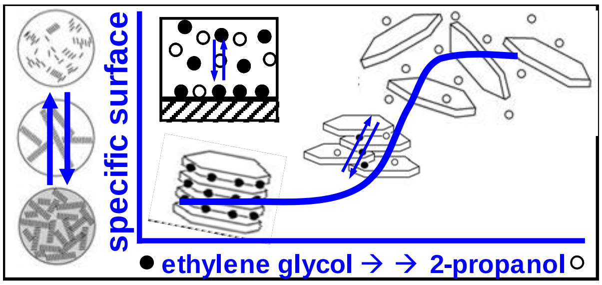


Fig.1: Calcium hydroxide particles can be stabilized by ethylene glycol or by 2-propanol. The life-time of materials obtained after compaction is dependant on the composition of the solvent used. The underlying mechanism could be explained via competitive adsorption isotherms, themselves determined by neutron scattering and contrast variation

Calcium hydroxide forms unstable reactive nanoparticles that are stabilized when dispersed in ethylene glycol or 2-propanol. The aggregation behaviour of these particles was investigated by contrast variation small angle neutron scattering (SANS), combined with small angle x-ray scattering (SAXS). Nanoparticles of the order 100 nm were found to aggregate into mass-fractal superstructures in 1-isopropanol, while forming more compact agglomerated aggregates with surface fractal behaviour in ethylene glycol. Commensurate specific surface areas evaluated in the Porod limit were more than an order of magnitude greater in isopropanol (~200 m2g–1) than in ethylene glycol (~7 m2g–1).

This profound microstructural evolution, observed in similar solvents, is shown to arise from competitive solvent adsorption. The composition of the first solvent layer on the particles is determined over the full range of mixed solvent compositions, and shown to follow a quantifiable thermodynamic equilibrium, determined via contrast variation SANS, that favours ethylene glycol over 2-propanol in the surface layer by about 1.5 kJ.mol^{-1} with respect to the bulk solvent composition.[2]

---

[1]. Page, Miles G.; Zemb, Thomas; Dubois, Monique; Coelfen, Helmut. "Osmotic pressure and phase boundary determination of multiphase systems by analytical ultracentrifugation", ChemPhysChem (2008), 9(6), 882-890.

[2] Fratini, Emiliano; Page, Miles G.; Giorgi, Rodorico; Coelfen, Helmut; Baglioni, Piero; Deme, Bruno; Zemb, Thomas "Competitive Surface Adsorption of Solvent Molecules and Compactness of Agglomeration in Calcium Hydroxide Nanoparticles". Langmuir (2007), 23(5), 2330-2338.

Ionic Liquid as an efficient formulation method for tuning microemulsion curvature.

Thomas Zemb, Pierre Bauduin
Julian Eastoe (University of Bristol) and Jingcheng Hao (University of Shandong, China)

For efficient hydrometallurgic processes, amount of co-extracted water needs to be controlled. In order to understand mechansims, adiusof the reverse aggergates, hosts for teh extracted ion pairs, must be varied. Middle-phase microemulsions in the system composed of cationic dioctadecyldimethylammonium chloride anionic sodium dodecyl sulfate (SDS), n-butanol, n-heptane, and brine were studied. An ionic liquid (IL), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF4), was dissolved in water as a special type of brine instead of inorganic salts usually used in microemulsion formulation. Investigations have been made for the effects of the concentrations of bmimBF4, n-butanol and total surfactants (WDODMAC + WSDS) on the phase behavior and the ultra-low interfacial tensions when the anionic component is present in excess in the catanionic film. Temperature effect on the phase behavior was also measured. The ultra-low interfacial tension measurements confirmed the formation of middle-phase microemulsions. Electrical conductivity, small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) experiments were also performed, indicated that the typical the typical heptane domain size is 8 nm and that the ionic liquid induces softening of the charged catanionic film Most interestingly, the IL concentration (cIL) is shown to act as an effective interfacial curvature control parameter. This represents a new approach to tuning and formulation of microemulsions and emulsions. The results expand potential uses of IL’s, but also point to design of new IL’s which may achieve super-efficient control over interfacial and self-assembly systems.[1].

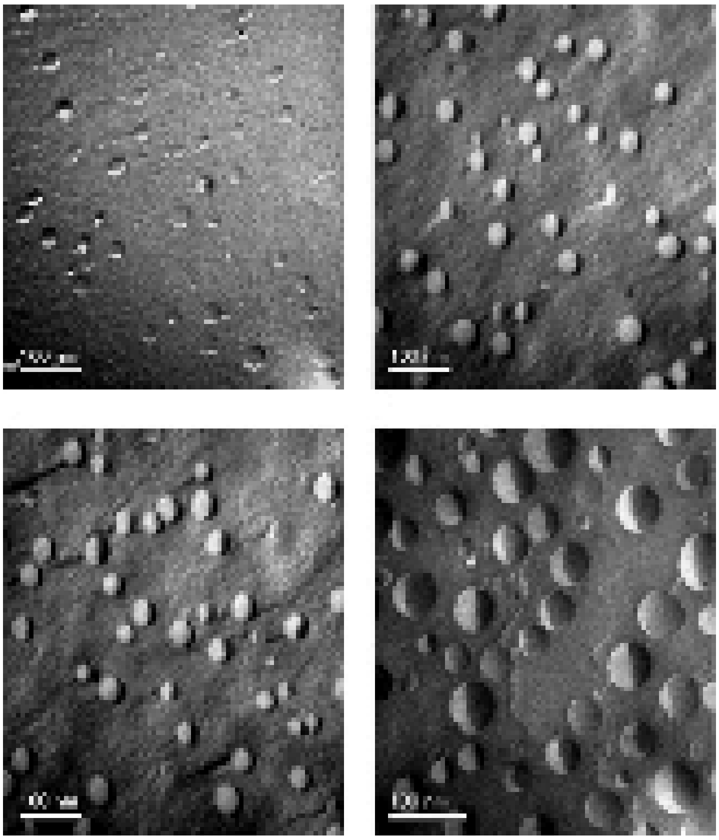


Fig.1: FF-TEM images of microemulsion samples of [bmim][BF4]/TX-100/cyclohexane with the molar ratios (R) of IL/TX-100, 0.2 (top, left), 0.5 (top, right), 1.0 (below, left), and 1.5 (below, right), respectively. The weight fraction of TX-100 is 0.45.

---

[1] Liu, Liping; Bauduin, Pierre; Zemb, Thomas; Eastoe, Julian; Hao, Jingcheng. "Ionic liquid tunes microemulsion curvature" Langmuir (2009), 25(4), 2055-2059.

4 - Sonochemistry in Complex Fluids

Sergueï Nikitenko (CNRS)
Rachel Pflieger (CEA)
Tony Chave (CNRS)
Matthieu Virot (CNRS CDD)
Julia Schneider (PhD student, co-direction MPI-KG, Potsdam, - ICSM)
Nathalie Navarro (PhD student, CEA/DEN/DRCP – ICSM)
Camille Cau (PhD student, co-direction ICGM/CMOS – ICSM, ANR NEQSON)

The general objective of this laboratory is to study the mechanisms of the processes occurred in liquids under the effect of power ultrasound. Ultrasonic irradiation of liquids generates cavitation bubbles which produce strong transient heat and highly reactive radical species during implosive collapse. In fact, each cavitation bubble can be considered as a microreactor enable to perform the chemical processes at ambient temperature and pressure either by radical reactions or by pyrolysis. Sonochemistry is often considered as part of ″green chemistry″ since this type of chemistry allows to minimize the volume of secondary wastes. The research activity of our team is focused on the following specific objectives:

(i) Understanding the origin of the sonochemical processes using the spectroscopic studies of sonoluminescence, or in other words, light emission during cavitation bubble collapse. To investigate this phenomenon we developed the multifrequency sonoreactor coupled with UV/vis spectrograph LN_2 CCD) and mass spectrometer for online detection of the sonolytical products (see Figure).

(ii) Study the mechanisms of the sonochemical reactions at solid-liquid interface. This topic is strongly related to the problem of nuclear materials dissolution.

(iii) Sonochemical synthesis of nanoparticles and nanostructured materials. This part of our activity is focused on the preparation of nanocatalysts and studies of sonocatalysis.

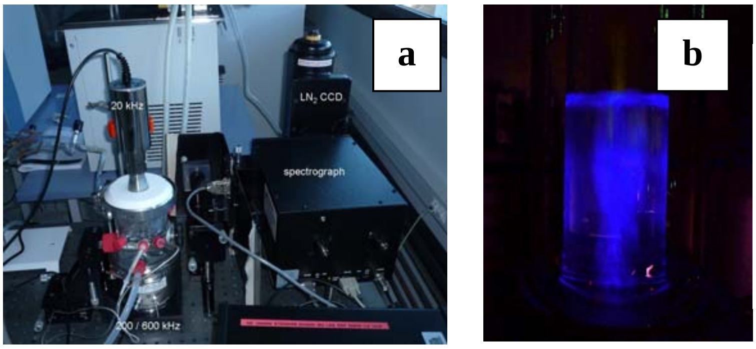


Figure: Multifrequency (20 kHz-600 kHz) sonoreactor for study the sonoluminescence and sonochemistry (a), luminescence of Luminol in 1 mM Na_2CO_3 solution initiated with 600 kHz ultrasound in air (b).

Collaborations: CEA/DEN/DRCP and ICGM-CMOS on sonocatalysis (ANR Blanc NEQSON 2010-2013), MPI-KG Potsdam on sonoluminescence (LEA SONO), and CEA/DEN/DRCP and LIME, ICSM on sonodissolution.

Nikitenko S. I., Venault L., Pflieger R., Chave T., Bisel I., Moisy P., **Potential Applications of Sonochemistry in Spent Nuclear Fuel Reprocessing: A Short Review**, *Ultrasonics Sonochemistry*, 2010, *17*, 1033-1040 (invited review).

Multibubble sonoluminescence studies: evidence for plasma formation during acoustic cavitation

Rachel Pflieger, Henri-Pierre Brau, Sergey I. Nikitenko

Sonoluminescence is the emission of UV-visible light triggered by the violent collapse of microbubbles generated in liquids submitted to ultrasonic irradiation. This violent collapse leads indeed to extreme conditions in the bubbles (T>5000 K) which are the source for the sonochemical reactions, in particular through the formation of radicals (e.g. H° and HO° in water). Hence, a better understanding of the conditions reached in the bubbles would allow an optimization of the sonochemical reactions. These conditions are probed by measuring the sonoluminescence spectrum by means of a spectrograph coupled to a CCD camera.

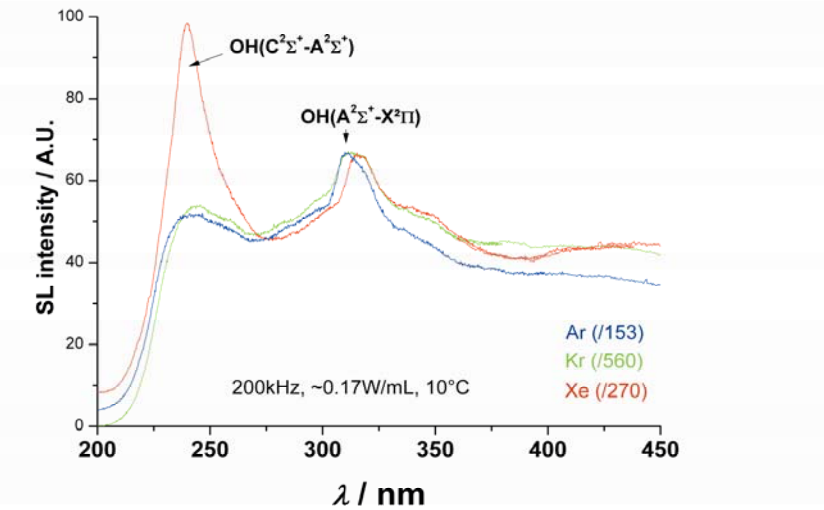


Fig.1: Sonoluminescence from OH($C^2\Sigma^+$) and OH($A^2\Sigma^+$) in water : the OH($C^2\Sigma^+$) band indicates formation of a plasma in Xe-sparged water submitted to 200 kHz ultrasound.

In this field, we focused on the effect of the ultrasound frequency and of the dissolved rare gas on the sonoluminescence spectrum of water.[1] When Xe was used, the relative populations of the vibrational electronic excited states of OH($A^2\Sigma^+$) moved away from thermal equilibrium. Besides, a new band appeared, attributed to OH($C^2\Sigma^+$), which is usually only observed in electrical discharges and in water radiolysis. These two observations point to non-thermal plasma formation during multibubble cavitation in water sparged with Xe. Until now, formation of non-thermal plasma had been reported only in concentrated H_2SO_4 in the presence of rare gases.[2-4]

---

[1] Pflieger, R.; Brau, H.-P.; Nikitenko, S. I., **Sonoluminescence from OH($C^2\Sigma^+$) and OH($A^2\Sigma^+$) radicals in water: evidence for plasma formation during multibubble cavitation**, *Chemistry: a European Journal* **2010**, *16*, 11801.

[2] Eddingsaas, N. C.; Suslick, K. S. *Journal of the American Chemical Society* **2007**, *129*, 3838.

[3] Flannigan, D. J.; Suslick, K. S. *Nature* **2005**, *434*, 52.

[4] Flannigan, D. J.; Suslick, K. S. *Physical Review Letters* **2005**, *95*, 044301

Single-bubble sonoluminescence studies: line emission and similarities with multibubble sonoluminescence

Julia Schneider, Rachel Pflieger, Sergey I. Nikitenko
Dmitry Shchukin, Helmuth Möhwald (MPIKG-Potsdam, Germany)

A single-bubble sonoluminescence (SBSL) reactor was developed as a model system for standard multibubble (MB) sonochemical reactors since the single-bubble is free of interaction with other cavitation bubbles. Mechanisms leading to MBSL and SBSL were long considered as different since MBSL spectra exhibit characteristic atomic and molecular emission lines on top of a broad continuum, whereas measured SBSL spectra were consisting of a sole continuum.[1] New perspectives to study SBSL were opened by the recent works of Young[2] and Liang[3] who determined the experimental conditions necessary to observe line emission in SBSL.

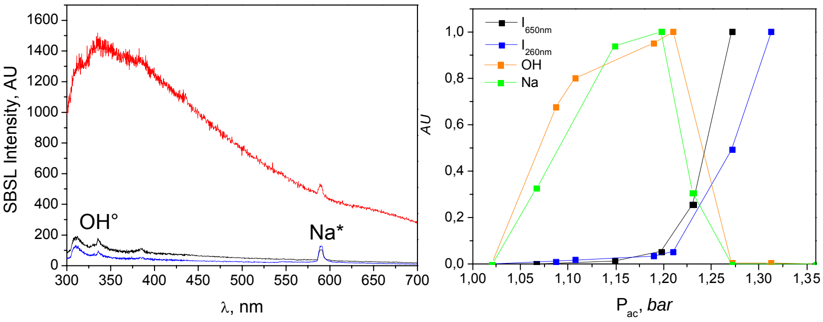


Fig.1: Left : Evolution of the SBSL spectra of 0.5M NaCl equilibrated with 70 mbar Ar with the acoustic pressure (blue: 1.13 bar, black: 1.20 bar, red: 1.25 bar). Right: Evolution with the acoustic pressure of the peak heights of $OH^\bullet$ and Na, and of the continuum (represented by SBSL intensities at 650 and 260 nm); 0.5M NaCl, 70mbar argon.*

This work[4] consists of spectroscopic studies of SBSL in water and aqueous sodium chloride solutions with defined concentrations of argon. The broad-band continuum ranging from 200-700 nm is characterised by fits using Planck's law of blackbody radiation. The obtained blackbody temperatures are in the range of 10^4 K and reveal to be independent from the presence of salt and from the acoustic pressure whereas the SL intensity is increasing more than 10-fold within the studied acoustic pressure range. The different trends followed by SL intensity and blackbody temperatures question the blackbody model.

In solutions with 70 mbar of argon line emissions of $OH^{\bullet*}$ radicals and Na* are observed. The shape of the $OH^{\bullet*}$ radical emission spectrum is very similar to that in MBSL spectra indicating the strong similarity of intra-bubble conditions of SBSL and MBSL under certain experimental conditions. Increase of the acoustic pressure causes the continuum to overlap the lines until they become indistinguishable. This is explained by non-radiative deactivation of excited $OH^\bullet$* and Na* with increasing acoustic pressure arising from quenching by hot particles issued from a plasma core.

---

[1] Matula, T. J.; Roy, R. A.; Mourad, P. D. *Phys. Rev. Lett.* **1995**, *75*, 2602.

[2] Young, J. B.; Nelson, J. A.; Kang, W. *Phys. Rev. Lett.* **2001**, *86*, 2673.

[3] Liang, Y.; Chen, W. Z.; Xu, X. H.; Xu, J. F. *Chin. Sci. Bull.* **2007**, *52*, 3313.

[4] J. Schneider, R. Pflieger, S.I. Nikitenko, D. Shchukin, H. Möhwald, **Line emission of sodium and hydroxyl radicals in single-bubble sonoluminescence spectra**, *J. Phys. Chem.A,* **2011**, 115, 136-140.

Evidence for Treanor effect during multibubble cavitation

Nikitenko S.I., Chave T.
Martinez P., Billy I. (EPOC, Université Bordeaux 1)

We studied the ultrasonically driven disproportioning of carbon monoxide (***DCO***) in water saturated with a CO/Ar gas mixture. To our knowledge, this reaction had never been studied under ultrasonic irradiation. By contrast, the plasma-chemical ***DCO*** in the gas phase has been a very active topic of research as working media for CO lasers and as a promising method for carbon isotope separation. The strongly endothermic ***DCO*** reaction ($\Delta H = 5.5$ eV·mol^{-1}, $E_a = 6$ eV·mol^{-1}) can be significantly accelerated by the vibrational excitation of CO molecules. The population of highly vibrational states $CO^*(\nu_n)$, $n \leq 40$, occurs via anharmonic vibration-to-vibration pumping mechanism (V-V), known as Treanor effect. This approach produces non-thermal plasma far from the thermodynamic equilibrium with a vibrational temperature (T_v) of CO molecules much higher than their translational (T_0) or rotational (T_R) temperatures. An experimental illustration of the Treanor V-V pumping is a kinetic isotope effect (***KIE***) during ***DCO*** in non-equilibrium plasma.[9] The coefficient of isotopic selectivity (α) for vibrationally excited isotopes can be expressed as

$$\alpha = \exp\left[\frac{\Delta\omega}{\omega} E_a \left(\frac{1}{T_0} - \frac{1}{T_v}\right)\right]$$

where $\frac{\Delta\omega}{\omega} = \frac{\omega_2 - \omega_1}{\omega_2}$ is the relative defect of resonance. In quasi-equilibrium kinetics light isotopes react faster because of their higher "zero vibration level" $\frac{1}{2}h\omega$. On the other hand, in non-equilibrium plasma heavy isotopes react faster since they have higher vibrational temperature. Moreover, the non-equilibrium ***KIE*** is much stronger than the quasi-equilibrium effect.

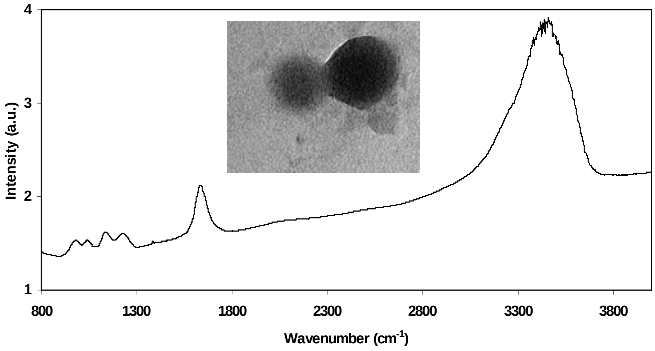


Figure: The FTIR spectrum and TEM image of the sonolytical product obtained after CO disproportionation in water at 20 kHz, 27-30°C, $\tau = 6$ h, $I = 27$ W·cm^{-2}, $P_{ac} = 0.60$ W·mL^{-1}

We found that the sonochemical ***DCO*** exhibits some similarities with that in non-equilibrium plasma. This process causes formation of hydrated polymer of carbon suboxide $(C_3O_2)_n$ (see Figure) enriched with a heavy ^{13}C isotope ($\alpha = 1.053$-1.055). This finding indicates the presence of vibrationally excited CO molecules with a non-equilibrium Treanor distribution ($T_v > T_0$) inside the cavitating bubble. The lack of thermal equilibrium during acoustic collapse is inconsistent with the currently dominated model of multibubble sonochemistry based on adiabatic heating approach.

Nikitenko S.I., Martinez P., Chave T., Billy I. **Sonochemical disproportionation of carbon monoxide in water: evidence for Treanor effect during multibubble cavitation**, *Angew. Chem. Int. Ed.*, 2009, *48*, 9529-9532.

Nanocatalyst synthesis under ultrasound irradiation: Sonochemical reduction of platinum (IV) in pure water

Tony Chave, Nathalie Navarro, Sergueï Nikitenko
André Ayral (IEM Montpellier) and Serge Nitsche (CiNAM Marseille)

The unique properties of platinum-based catalysts are strongly influenced by platinum particle size. Usually, the highest activity exhibits the catalysts containing monodispersed platinum nanoparticles (Pt NPs) with the average size around few nm. Pt NPs can be prepared with a large array of synthesis routes leading to specific morphological aspects and ultrasonic irradiation has also proven to be a very useful tool for such preparation[1]. The benefits of sonochemistry for the synthesis of nanocatalysts is a narrow size distribution of obtained NPs and the ability to create in situ reactive species[2].

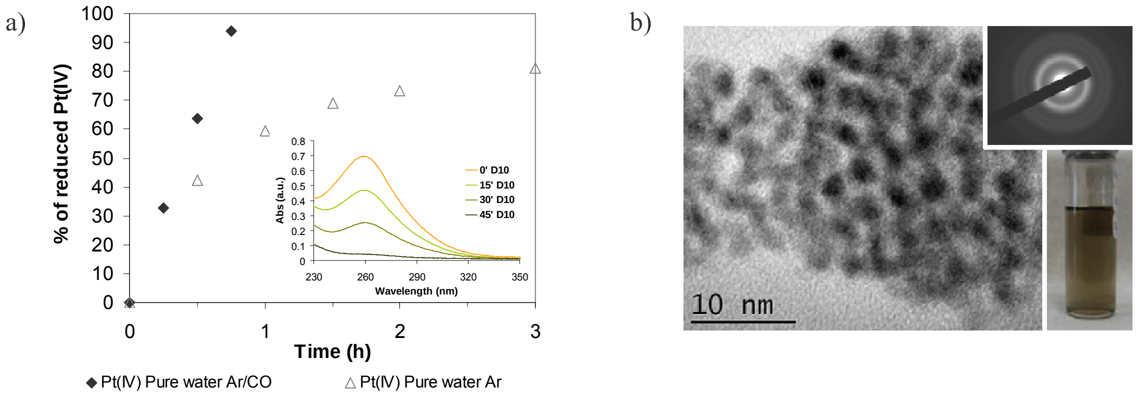


Fig.1: a) Pt(IV) reduction kinetic under ultrasonic irradiation in pure water with Ar or Ar/CO atmosphere. $[Pt(IV)]_0$ = 0.5 mM. Inset demonstrates the evolution in Pt(IV)spectra during sonication under Ar/CO mixture. b) High resolution TEM image with electron diffraction pattern of Pt nanoparticles and sample picture as insets.

Recently we reported for the first time the rapid sonochemical reduction of Pt(IV) under 20 kHz ultrasonic irradiation in pure water in the presence of Ar/CO gas mixture without addition of any surfactants or capping agents[3] (Figure 1.a). Reduction occurs by hydrogen issued from homolytic water dissociation under ultrasound. Complete platinum (IV) reduction is achieved due to OH radical scavenging with carbon monoxide inside the cavitating bubble[4]. Monodispersed nanoparticles within the range of 2-3 nanometers were obtained and exhibited a strong stability towards sedimentation (Figure 1.b). Since Ar/CO atmosphere is the only restriction of this process, this procedure can be applied in various media and is also compatible with a large array of experimental conditions. Moreover, the high efficiency of the reduction process at low frequency ultrasonic irradiation will be a further benefit when applied in heterogeneous systems with catalyst supports such as metal oxides or polymer particles.

---

[1] J.H. Bang et al. *Adv. Mater.*, **2010**, *22*, 1039-1059.

[2] T. Sakai et al. *Colloid Surface A*, **2009**, *347*, 18-26.

[3] T. Chave, N. Navarro, S. Nitsche and S. I. Nikitenko **Rapid Reagent Free Sonochemical Reduction of Pt(IV) in Water**, submitted to J. Mat. Chem.

[4] S. I. Nikitenko, P. Martinez, T. Chave and I. Billy **Sonochemical Disproportionation of Carbon Monoxide in Water: Evidence for Treanor Effect during Multibubble Cavitation**, *Angew. Chem. Int. Edit*, **2009**, *48*, 9529-9532.

Application of sonochemistry in spent nuclear fuel reprocessing: Sonocatalytic dissolution of CeO2 in nitric media

Tony Chave, Matthieu Virot, Sergueï Nikitenko

Reprocessing of actual and future MOX fuels with potential increase in Pu content is a challenging task since plutonium dioxide is particularly resistant towards dissolution in nitric media. Various processes based on redox dissolution have been studied[1] as well as the ultrasonic assisted dissolution[2] and have lead to encouraging results. In fact, when applied into a system, ultrasonic irradiation can drastically enhance the mass transfer at the solid-liquid interface, create in situ reactive species and therefore promote the dissolution rate of refractory oxide especially in the field of nuclear chemistry[3]. In order to improve our knowledge on plutonium dioxide dissolution, different studies were carried out within the sonochemistry laboratory of ICSM on CeO_2 used as an inactive model of PuO_2.

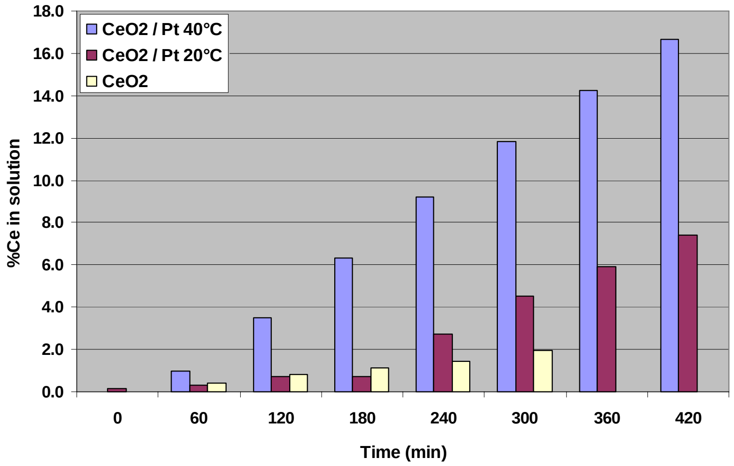


Fig.1: Percentage of dissolved cerium oxide in function of time in HNO_3 0.5M $N_2H_5^+$ 0.2M and HCOOH 1M media under 20 kHz ultrasonic irradiation for three different experimental conditions: i) CeO_2 at 20°C without catalyst ii) CeO_2 at 20°C in presence of platinum nanoparticles and iii) CeO_2 at 40°C in presence of platinum nanoparticles. Platinum (IV) solution is injected after 30 min of sonolysis.

One topic actually under investigation within our team is the reductive dissolution of CeO_2 in presence of catalyst under 20 kHz ultrasonic irradiation in HNO_3 0.5M $N_2H_5^+$ 0.2M and HCOOH 1M solution under Ar atmosphere. After reaching a steady state temperature, obtained after 30 min of sonolysis, platinum (IV) solution is injected within the system in presence of the cerium oxide powder (2.5 Pt wt. %). Complete reduction of the noble metal is achieved within roughly 1 or 2 hours respectively at 40 and 20°C and lead to nanoparticles deposited on the cerium oxide surface. Based on solution analysis, the CeO_2 dissolution curves for 3 different conditions in presence or not of catalyst are shown in figure 1. It can be pointed out the presence of catalyst within the system strongly enhanced the reductive dissolution of the cerium oxide at 20°C as soon as the main part of platinum (IV) is reduced. Noteworthy, increasing the temperature to 40°C both dramatically reduced the formation time of Pt nanoparticles and also enhanced the CeO_2 dissolution rate compared to the same experiments at 20°C. In such conditions, induction period is drastically shortened and dissolution rate seems to be steady even after 7 hours of reaction. These promising results of sonocatalytic dissolution in reductive conditions will be soon applied on plutonium dioxide in our dedicated glovebox within Atalante in collaboration with CEA/DRCP.

---

[1] X. Machuron-Mandard et al, *J. Alloys Comp.*, **1994**, *213-214*, 100-105.

[2] F. Juillet et al, *J. Radioanal. Nucl. Chem.*, **1997**, *224*, 137-143.

[3] S.I. Nikitenko, L. Venault, R. Pflieger, T. Chave, I. Bisel and P. Moisy **Potential applications of sonochemistry in spent nuclear fuel reprocessing,** *Ultrason. Sonochem.*, **2010**, *17*, 1033–1040.

Unexpected effect of ultrasonic frequency on the mechanism of formic acid sonolysis

<u>Navarro N.</u>, Chave T., Nikitenko S.I.
Pochon P., Bisel I. (DRCP Marcoule)

Over the last decade, considerable interest has been expressed in the application of advanced oxidation processes (AOP) to destroy hazardous organic compounds in industrial waste streams. Among different techniques (catalytic wet air oxidation, Fenton process, photocatalytic oxidation, ozonation) the sonochemical oxidation is considered as a promising way for the degradation of such kinds of pollutants. The kinetics and mechanism of formic acid sonochemical degradation has been studied at 20, 200 and 607 kHz ultrasonic frequencies under argon atmosphere at 20°C. Total yield of HCOOH sonochemical degradation increases in approximately 6-8 times when the frequency increases from 20 to 200 or 607 kHz. At low ultrasonic frequency HCOOH degradation is attributed to the oxidation with $OH^{\bullet}$ radicals issued from water sonolysis and to the HCOOH decarboxylation occurred at the cavitation bubble-liquid interface. At high-frequency ultrasound sonochemical reaction is also influenced by HCOOH dehydration. Whatever the ultrasonic frequency, sonolysis of HCOOH yields H_2 and CO_2 in the gas phase as well as the trace amounts of oxalic acid and formaldehyde in the liquid phase, whereas CO and CH_4 were only detected at high-frequency ultrasound. The most striking difference between low-frequency and high-frequency ultrasound is that the sonolysis of HCOOH at high ultrasonic frequencies initiates Fischer-Tropsh hydrogenation of carbon monoxide.

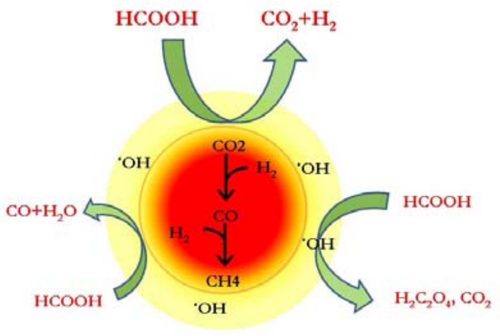


Fig. 1: Mechanism of HCOOH sonochemical degradation.

Sonochemically driven Fischer-Tropsch hydrogenation of CO causes formation of methane and formaldehyde as by-products of HCOOH degradation. Finally, we found the catalytic decomposition of sonochemically formed H_2O_2 on the surface of titanium particles originated from the cavitation erosion of the ultrasonic probe at low-frequency ultrasound. This finding is important for proper interpretation of the sonochemical experiments.

Navarro N., Chave T., Pochon P., Bisel I., Nikitenko S.I. **Effect of ultrasonic frequency on the mechanism of formic acid sonolysis**, *J. Phys. Chem. B*, 2010 (in press) dx.doi.org/10.1021/jp109444h

Acoustic cavitation at the water-glass interface

Virot M., Chave T., Nikitenko S.I., Zemb Th.
Shchukin D.G., Möhwald H. (MPIKGF, Potsdam)

Cavitation erosion results in the repeated interaction of a concentrated mechanical energy with a solid-liquid interface. This phenomenon is known to be responsible for the reduction of the lifetime of engine components such as valves, pumps, ship propellers, etc. The asymmetric collapse of the vapour filled micro-bubbles imploding at the vicinity of a solid boundary results in the generation of shock-waves and micro-jets that impinge the surface with a high velocity. These events are mainly responsible for the erosion process that is used in ultrasonic cleaning and more generally, in heterogeneous sonochemistry. Despite the numerous published data in this topic, the erosion process under acoustic cavitation is a complicated phenomenon that has not been fully understood. To the best of our knowledge, the behaviour of glass surfaces under acoustic cavitation has never been reviewed. Investigating this phenomenon should increase our knowledge concerning the approach of the dissolution of other oxide matrices, particularly ceramics, but also lanthanide and actinide oxides. Deciphering such a mechanism could thus contribute in the development of alternatives for the treatment of spent nuclear fuels and the minimization of radioactive wastes.

High power ultrasound (20 kHz, 19.9-55.8 W.cm^{-2}) has been used to investigate the physical and chemical effects of acoustic cavitation at the water-glass interface. Preliminary results suggested that the erosion of conventional sodosilicate glass was dependant on the sonotrode-sample distance and the ultrasonic intensity. Physical effects created by acoustic cavitation have been characterized using microscopy devices (optical, MEB, AFM) and image processing software (image J). Effects were found to increase (fig. 1) as a function of sonication duration according to two distinctive periods. The investigation on the behaviour of borosilicate, quartz and hydrophobized glasses showed that sonication allows erosion of glass in different ways and speeds, as a function of experimental condition settings, glass composition and hardness properties of the involved material. Chemical influence of acoustic cavitation at the interface was also pointed out with ICP-AES by determining the concentration of leached elements (Na, Si, Al, Ca, and B) during sonolysis. Observed concentrations were dependant on settings and were in good agreement with physical effects, and highlighted the chemical influence of acoustic cavitation on the interface.

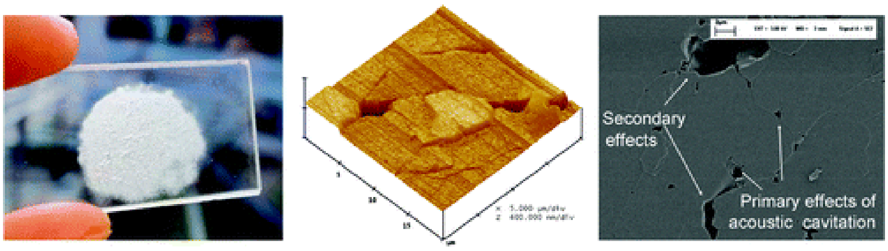


Figure: Erosion of fused silica glass sonicated during 180 min at 2 mm from the ultrasonic probe (I_{ac} = 49 W cm^{-2}).

Virot M., Chave T., Nikitenko S.I., Shchukin D.G., Zemb Th. **Acoustic cavitation at water-glass interface**, *J.Phys. Chem. C*, 2010, *114*, 13083-13091.

First synthesis of uranyl aluminate nanoparticles

Chave T., Nikitenko S.I.
Scheinost A.C. (Rossendorf Beamline, ESRF, Grenoble)
Berthon C., Arab-Chapelet B., Moisy Ph. (CEA/DEN/DRCP)

Uranium is one of the most studied elements of the periodic table. However, a survey of recent literature revealed that no uranyl, UO_2^{2+}, complexes with aluminate anions, $[Al(OH)_4^-]$, have been documented. Nevertheless, knowledge of UO_2^{2+} speciation in the presence of $Al(OH)_4^-$ anions or solid alumina, Al_2O_3, is essential for an understanding of uranium behavior in alkaline high level waste as well as its migration in the environment. For a long time, it was believed that uranyl aluminate (URAL) could not be obtained from aqueous solutions due to the strong hydrolysis of UO_2^{2+} at $pH \geq 6$, where $Al(OH)_4^-$ species become the dominating chemical form of Al(III). Recent studies of UO_2^{2+} hydrolysis in the presence of Al(III) suggested the formation of some oligomeric mixed forms, like $[(H_2O)_3UO_2(\mu\text{-}OH)_2Al(OH)(H_2O)_3]^{2+}$ or $[(H_2O)_4UO_2(\mu\text{-}O)Al(OH)(H_2O)_4]^{2+}$, in the pH range of 5−14. Furthermore, UO_2^{2+} cations are known to be readily adsorbed on alumina, gibbsite, or montmorillonite from aqueous near-neutral solutions owing to the formation of inner-sphere, bidentate complexes with aluminol groups at the solid surface. These findings suggest that URAL might be synthesized under carefully selected conditions. Herein, we report for the first time the evidence for URAL formation as nanoparticles (NPs) dispersed in alumina matrix.

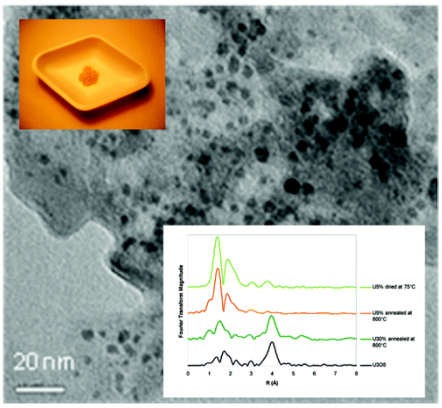


Figure: The low-resolution TEM and FT-EXAFS of uranyl aluminate nanoparticles in alumina matrix.

URAL was prepared by U(VI) hydrolytic precipitation with ammonia at pH = 11 in the presence of mesoporous alumina MSU-X under 20 kHz ultrasonic irradiation followed by annealing of the obtained solids at 800°C. TEM, XAFS, powder XRD, and ^{27}Al MAS NMR studies revealed that the speciation of uranium in this system strongly depends on uranium concentration. The sample with 5 wt % of uranium yields air-stable nanoparticles (~5 nm) of URAL. Presumably, UO_2^{2+} cations in this compound are coordinated with bidentate AlO_2^- groups. The increase of uranium concentration to 30 wt % causes mostly formation of U_3O_8 fine particles (~50 nm) and small amounts of URAL.

Chave T., Nikitenko S.I., Scheinost A.C., Berthon C., Arab-Chapelet B., Moisy Ph. **First synthesis of uranyl aluminate nanoparticles**, *Inorg. Chem.*, 2010, *49*, 6381-6383.

Development of a single-bubble sonoluminescence set-up for experiments under controlled conditions

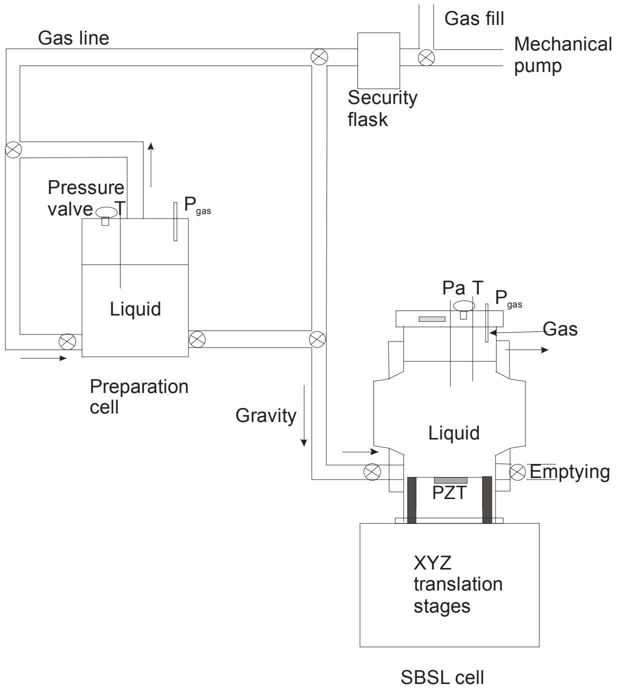
R. Pflieger, Th. Zemb, H. Möhwald (MPI-KG, Potsdam)

It is well known that the ultrasound-induced collapse of bubbles in solution can lead to the emission of light, referred to as sonoluminescence. Though extensive research has been performed in the last two decades, especially thanks to the re-discovery of single-bubble-sonoluminescence [*Gaitan, 1992*], which is light-emission by a single bubble levitated in a standing acoustic wave, the mechanisms of light emission are still subject of debate.

Two other sources of light emission from ultrasonically treated solutions are sonochemiluminescence and sonophotoluminescence. Sonochemiluminescence is the chemiluminescence induced by the reaction of radicals produced during the cavitation collapse and solutes in solution (the best known example of sonochemiluminescence is the emission from luminol solutions [*Henglein, 1989*]). As for sonophotoluminescence it occurs when sonoluminescence is absorbed by solutes in solution which in turn emit fluorescence characteristic of their excited state emission spectra [*Ashokkumar, 1999*].

In the framework of the European Associated Laboratory LEA SONO (CNRS-MPG), a new single-bubble sonoluminescence (SBSL) set-up is being developed in MPI-KG, Potsdam. It aims at investigating the influence of various solutes and surfactants on the SBSL spectrum under controlled conditions of temperature, gas nature and pressure, and acoustic pressure. The latter control is very important since SL is known to be very sensitive to these parameters. The developed set-up will also be used in order to study the sonochemiluminescence and/or sonophotoluminescence of various molecules, again under controlled conditions.

The scheme below presents the developed set-up: the solution is degassed and regassed to a known pressure in the preparation cell; it is then transferred to the SBSL reactor. There a standing acoustic wave is generated thanks to a piezoelectric transducer glued to the bottom of the cell and a bubble is introduced through the septum. Temperature is kept constant thanks to a cooling system and measured. The bubble SBSL spectrum is measured through quartz windows using a spectrograph coupled to a cooled CCD camera.



Sonochemical approach to the synthesis of $Fe_3O_4@SiO_2$ core-shell nanoparticles with tunable properties

Anne-Laure Morel, Sergueï I. Nikitenko, Karine Gionnet, Alain Wattiaux, Josephine Lai-Kee-Him, Christine Labrugere, Bernard Chevalier, Gerard Deleris, Cyril Petibois, Alain Brisson, Monique Simonoff

In this study, we report a rapid sonochemical synthesis of monodisperse non-aggregated $Fe_3O_4@SiO_2$ magnetic nanoparticles (NPs). We found that co-precipitation of Fe(II) and Fe(III) in aqueous solutions under the effect of power ultrasound yields smaller Fe_3O_4 NPs with a narrow size distribution (4-8 nm) compared to the silent reaction. Moreover, coating of Fe_3O_4 NPs with silica using an alkaline hydrolysis of tetraethyl orthosilicate in ethanol-water mixture is accelerated many-fold in the presence of 20 kHz ultrasonic field. The thickness of the silica shell can be easily controlled in the range of several nanometers during sonication. Figure 1 demonstrates the TEM image of $Fe_3O_4@SiO_2$ NPs obtained after 3h of sonication. Mössbauer spectra shown in Figure 2 revealed that non-superparamagnetic behavior of obtained core-shell NPs is mostly related to the dipole-dipole interactions of magnetic cores and not to the particle size effect. Core-shell $Fe_3O_4@SiO_2$ NPs prepared with sonochemistry exhibit higher magnetization value than that for NPs obtained under silent conditions due to better control of the deposited silica quantities as well as to the high speed of sonochemical coating, which prevents the magnetite from oxidizing.

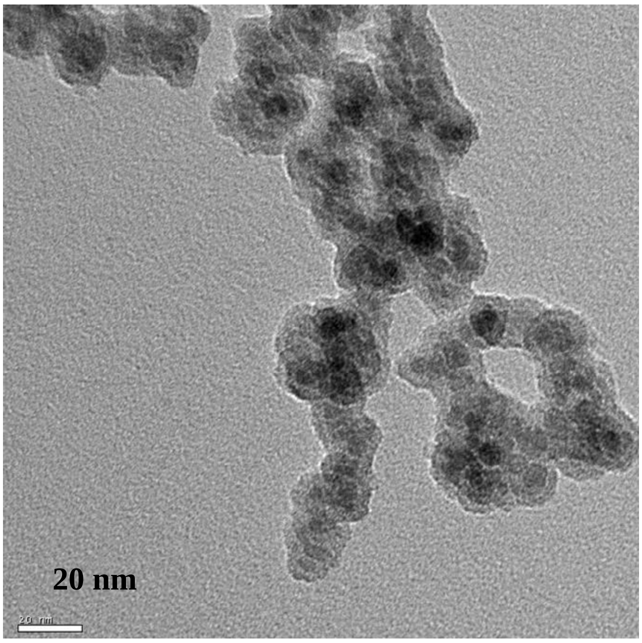


Figure 1

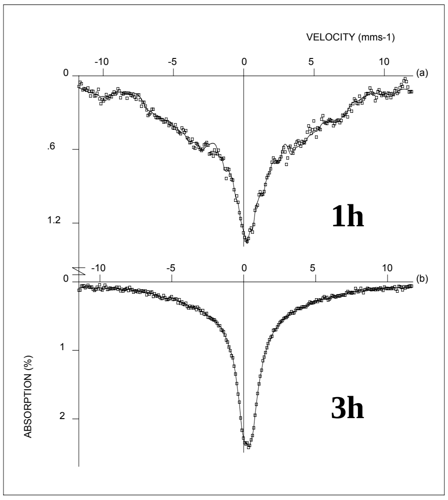


Figure 2

Reference

Morel A.-L., Nikitenko S.I., Gionnet, K., Wattiaux, A., Lai-Kee-Him J., Labrugere C., Chevalier B., Deleris G., Petibois, C., Brisson A., Simonoff M. *Sonochemical approach to the synthesis of $Fe_3O_4@SiO_2$ core-shell nanoparticles with tunable properties* **ACS Nano**, 2008, *2*, 847-856.

Immobilization of selenite on Fe_3O_4 and Fe/Fe_3C ultrasmall particles obtained with sonochemistry

Raquel López de Arroyabe Loyo, Sergei I.Nikitenko, Andreas C. Scheinost, Monique Simonoff

The sorption of selenite ions onto Fe_3O_4 and Fe/Fe_3C nanoparticles (NPs) was studied in the aqueous solutions under anoxic conditions using gamma spectrometry and XAS techniques. This is a first study related to the remedial applications of Fe/Fe_3C NPs. Fe_3O_4 NPs have been prepared by co-precipitation of Fe(II) and Fe(III) in basic solutions under power ultrasound. Stable Fe/Fe_3C NPs have been prepared by $Fe(CO)_5$ sonicating in diphenylmethane solutions and subsequently annealing the as-prepared product. Kinetic study demonstrated that Se(IV) sorption is extremely rapid : the equilibrium is reached in approximately 10 and 30 min for Fe_3O_4 and Fe/Fe_3C NPs respectively at pH= 4.9÷5.1 in the solutions of 0.1M NaCl (Figure 1). The distribution coefficients are also very high for both kinds of NPs (K_d> 3000). Increasing pH to 10.3 or adsorption of organic ligands, like L-Lysine or dodecanoate, at the surface of NPs cause the decrease in K_d values. However, even in these cases K_d values exceed 150. Magnetic NPs loaded with selenium can be easily and completely removed from solution with 0.4T permanent magnet. XAS study revealed the absence of Se(IV) reduction during the sorption onto Fe_3O_4 NPs in the pH range of 4.8-8.0. By contrast, the removal of Se(IV) with Fe/Fe_3C NPs in anaerobic conditions occurs via Se(IV) reduction to Se(-II) and subsequent formation of iron selenide at the particles surface (Figure 2). Thus, the Fe/Fe_3C NPs are superior to Fe_3O_4 NPs due to their ability to immobilize rapidly and irreversibly Se(IV) via reductive mechanism. Presumably these particles could be also effective for the removal of other contaminants such as hexavalent chromium, actinides, technetium, and toxic organic compounds.

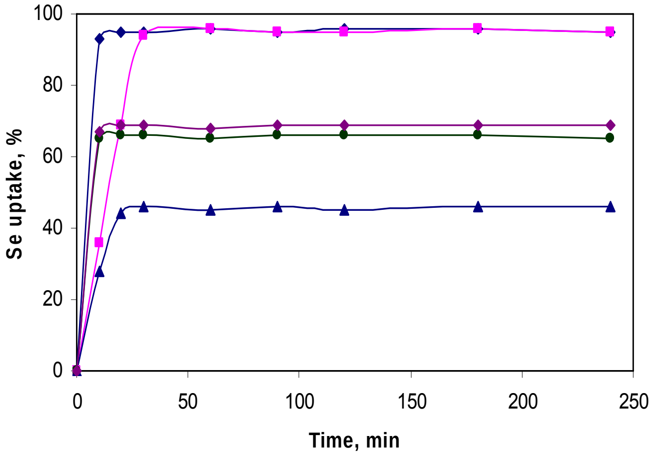


Figure 1

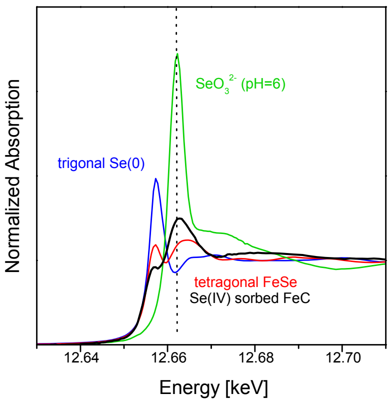


Figure 2

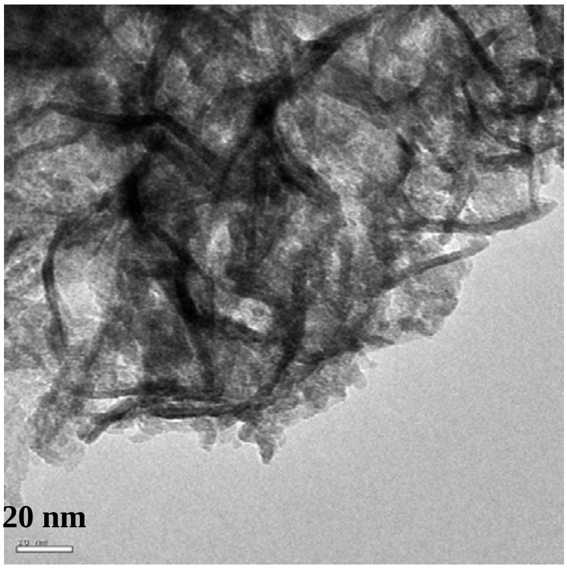
Reference

De Arroyabe Loyo R.L., Nikitenko S.I., Scheinost, A.C., Simonoff M. *Immobilization of selenite on Fe_3O_4 and Fe/Fe_3C ultrasmall particles* **Environ. Sci. Technol.** 2008, *42*, 2451-2456.

Sonochemical reactions with mesoporous alumina

Tony Chave, Sergei I. Nikitenko, Dominique Granier, Thomas Zemb

Herein, we report the sonochemical reactions with MSU-X mesoporous alumina (m-Al_2O_3) in aqueous solutions. Sonication (f=20 kHz, I= 30 $W\cdot cm^{-2}$, W_{aq}= 0.67 $W\cdot mL^{-1}$, T=36-38°C, Ar) causes significant acceleration of m-Al_2O_3 dissolution in the pH range of 4-11. Moreover, power ultrasound has a dramatic effect on the textural properties and phase composition of mesoporous alumina. Short sonication time leads to the formation of nanorods and nanofibers. The fibril morphology is preserved during the calcination at 800°C (Figure 1). Prolonged ultrasonic treatment causes high aspect nanoparticles transformation to aggregated nanosheets in weakly acid solutions or plated nanocrystals in alkaline solutions. Rapid hydrolysis of mesoporous alumina at pH = 4 results in the boehmite formation. Hydrolysis of mesoporous alumina under ultrasound in alkaline medium yields a mixture of bayerite and boehmite. Prolonged sonication at pH = 11 transforms bayerite to boehmite (Figure 2). In contrast to m-Al_2O_3, the nanoparticles of γ-Al_2O_3 (20-80 nm) exhibit a good stability in water under acoustic irradiation over the entire pH range. The effect of ultrasound on the textural properties of mesoporous alumina as well as on the transformation of nanosized bayerite to boehmite can be attributed to the transient heating of the liquid shell surrounding the cavitation bubble which caused the chemical processes similar to those occurred during hydrothermal treatment.



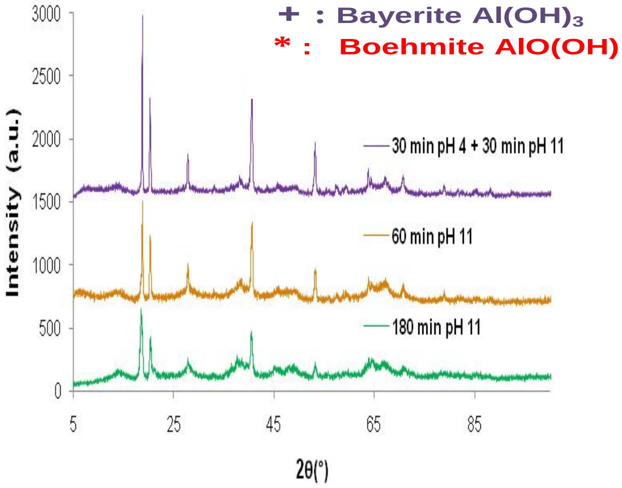


Figure 1

Figure 2

Reference

Tony Chave, Sergei I. Nikitenko, Dominique Granier, Thomas Zemb *Sonochemical reactions with mesoporous alumina*, **Ultrasonics/Sonochemistry** 2008, 16, 481-487.

Ionic selectivity and physisorption on bubbles induced by pulsed ultra-sounds

G. Toquer[1,2]*, T. Zemb*[1]*, D. Shchukin*[2] *and H. Möhwald*[2]

1- CEA/ICSM 2- Max Planck Institute of Colloids and Interfaces

Ion flotation process involves the use of small bubbles in order to separate ionic species from water. Since gas bubble interfaces in liquid allow one to assume null curvature at the molecular scale, selective ion adsorption might be more easily investigated than with liquid-liquid extraction system. Whereas in a classical flotation set-up bubbles are introduced via a glass frit, we use here a controlled sono-device (see figure 1) which generate coalesced bubbles of cavitation, stabilised by surfactants. The solution is submitted to pulsed ultra-sound waves producing an overflowing homogeneous foam which is extracted. The nonionic surfactant triton X-100 and the anionic surfactant sodium dodecyl sulfate are used respectively to investigate here non specific and specific ion adsorption. The selectivity of physisorbed alkali metals (see figure 2) at these interfaces is analysed through Induced Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Mass Spectrometry (ICP-MS) experiments. The aim is to have a fundamental understanding about the mechanism of cation selectivity via the determination of thermodynamic parameters as selectivity coefficients.

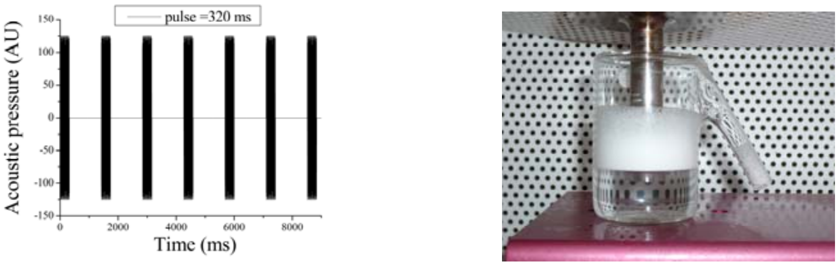


Figure 1: Home made set-up providing stable and profuse foam

Profuse foam is obtained by controlling effects (bubble creation and life time of foam) of ultra-sound waves at 20 kHz via energy density and pulse time.

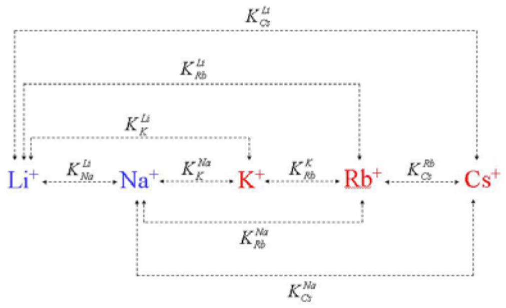


Figure 2: Investigation of selectivity coefficient of alkali metal ion pairs

Affinity towards the gas-water interface is expected to be different according to the kosmotrope (in blue) and chaotrope (in red) nature of ions.

- **References :**

Toquer, Guillaume; Zemb, Thomas; Shchukin, Dmitry; Moehwald, Helmut. " Ionic physisorption on bubbles induced by pulsed ultra-sound." Physical Chemistry Chemical Physics (2010), 12(43), 14553-14559.

Goals of the European Associated Laboratory LEA “SONO”, A common team etween ICSM and the Max Planck Institute in Potsdam

Supported by (CNRS-INC – MPG-KG) planned for 2008-2013.

mainly at ICSM :
Thomas Zemb
Sergueï Nikitenko
Rachel Pflieger
Tony Chave (> 09/2009)
Matthieu Virot
Torsten Sievers (>12/2010)
Julia Schneider

mainly at MPI :
Helmuth Möhwald
Dmitry Shchukin
Daria Radziuk
Valentina Belova
Yongsheng Han
Daria Andreeva
Oliver Zech
Julia Schneider

The sonochemical cell allowing spectroscopy of photoluminescence linked to cavitation and simultaneous control of solutes and gas

The chemical effects of ultrasound in liquids originate from acoustic cavitation: nucleation and implosive collapse of the microbubbles filled with gases and vapours. Collapse of these bubbles results in transient local temperature of about 5000 K and extreme cooling rates of 10^{10} K/sec after the bubble implosion. These extreme conditions enable unusual chemistry with a reactor basically at ambient conditions. No predictive model exists about the most famous manifestation of acoustic cavitation: sonoluminescence, which consisted in the light emission during the bubble collapse.

General objective of the cognitive research team (2008-2010) between MPIKG ICSM will be to understand and to control the primary sonochemical processes and to demonstrate their applicability. Special targets, referred as specific tasks attributed to the scientists attached to the LEA “SONO” will be:

1- Using a single bubble emittor associated to optical spectroscopy, study the sonoluminescence phenomenon, and the effect of concentrated ionic solutions (acid, bases or salt) on the light emission by cavitating bubble in the frame of modern theories modelling ions, surfactants and hydrotropes at surfaces.

2- Using a multi-bubble experimental device, study via scattering, surface chemistry and electron microscopy the link between the chemical and topological properties of powder surface and the heterogeneous nucleation and implosion of bubbles.

3- Using as initial reactives metallic ions as well as sub-micronic particles having the ability to concentrate at the liquid-vapour interface, there is a possibility of obtaining complex shapes of metal, such as hollow capsules and randomly folded sheets. The metal is molten and metallic glass may be obtained;

Application domains in general nanoscience and interface chemistry are the synthesis of nanoparticles, with special interest precursors of self-repairing nanomaterials or tracers for ultra-sound imaging. Peculiar application domains related to fundamental mastering of sonochemistry in nuclear technology are:

1- "Activation" of sub-micronic grains for better sintering or reducing the temperature-pressure conditions needed for sintering the material, such as vitro-ceramics for processes immobilizing targeted mixtures of elements in MAVL or special distribution of fission products.

2- More efficient and controlled solubilisation processes of ultra-cohesive composite materials, such as nuclear fuel elements and advanced reversible long-term storage materials. The knowledge of sonochemical transformation from initial metallic particles towards sintered nanometric metallic dispersions in solvents is needed in order to conceive "ideal" composite nanomaterials, involving a porous SiC or C3N4 network with metallic nanoparticles inclusions.

3- New waste separation processes, combining bubble formation induced by ultrasound with the flotation of particles or small colloids with the physical chemistry of flotation of material weakly bound on bubbles.

Evolution of scientific programs of the Marcoule-Potsdam LEA during 2010 go beyond sonochemsitry alone, concern several teams at ICSM and MPI-KG , typically about separation by flotation with and without US, as well as chemistry on fast moving interfaces and between poorly miscible droplets containing reactives.

5 – Self Repairing Nanomaterials

L’équipe est constituée de :
1 permanent CEA responsable d’équipe (Dr. A. Grandjean),
2 chercheurs CEA (Dr. X. Deschanel et Dr. F. Goettmann)
1 enseignant-chercheur ENSCM (Dr. G. Toquer)
1 IE de l’UM2 en CDD (C. Rey)
3 doctorants (B. Smutek, C. Delchet, S. El Mourabit)
3 doctorants en co-tutelle (L. Guillaume (LIME), A. Merceille (DTCD), C. Lavaud (DTCD))
1 apprenti ingénieur (O. Bruguier)

Résumé

Cette équipe est en charge de la recherche sur les nanomatériaux utilisés dans le domaine de l’énergie et du recyclage : l’énergie nucléaire avec la chimie séparative (solide-liquide ou par transformation de phase), et les matériaux d’usage (combustibles, matériaux de confinement) nano-structurés ; et les énergies alternatives avec le recyclage des métaux critiques, l’utilisation de la biomasse (en particulier pour une chimie séparative) ou les revêtements de nanoparticules à propriétés optiques renforcés. Les thématiques de recherche couvrent les méthodes innovantes de synthèse de matériaux nanostructurés et de leur fonctionnalisation, leur caractérisation et l’étude de leur comportement.

Il s’agit de développer une classe de matériaux à structure hiérarchique, présentant une fonctionnalité bien définie (sous forme par exemple de structures nanométriques), organisée dans un hybride micronique, suivie d’une mise en forme dans un objet macroscopique. Par ce type de structure hiérarchique, on peut obtenir pour les propriétés physiques (fissuration, tenue à l’irradiation) aussi bien que pour les propriétés chimiques (lixiviation), des « performances » hautement non linéaires par rapport à celles des matériaux de base. Une modélisation prédictive, qui utilise la connaissance structurale à différentes échelles, est nécessaire pour améliorer les performances de ces matériaux formulés.

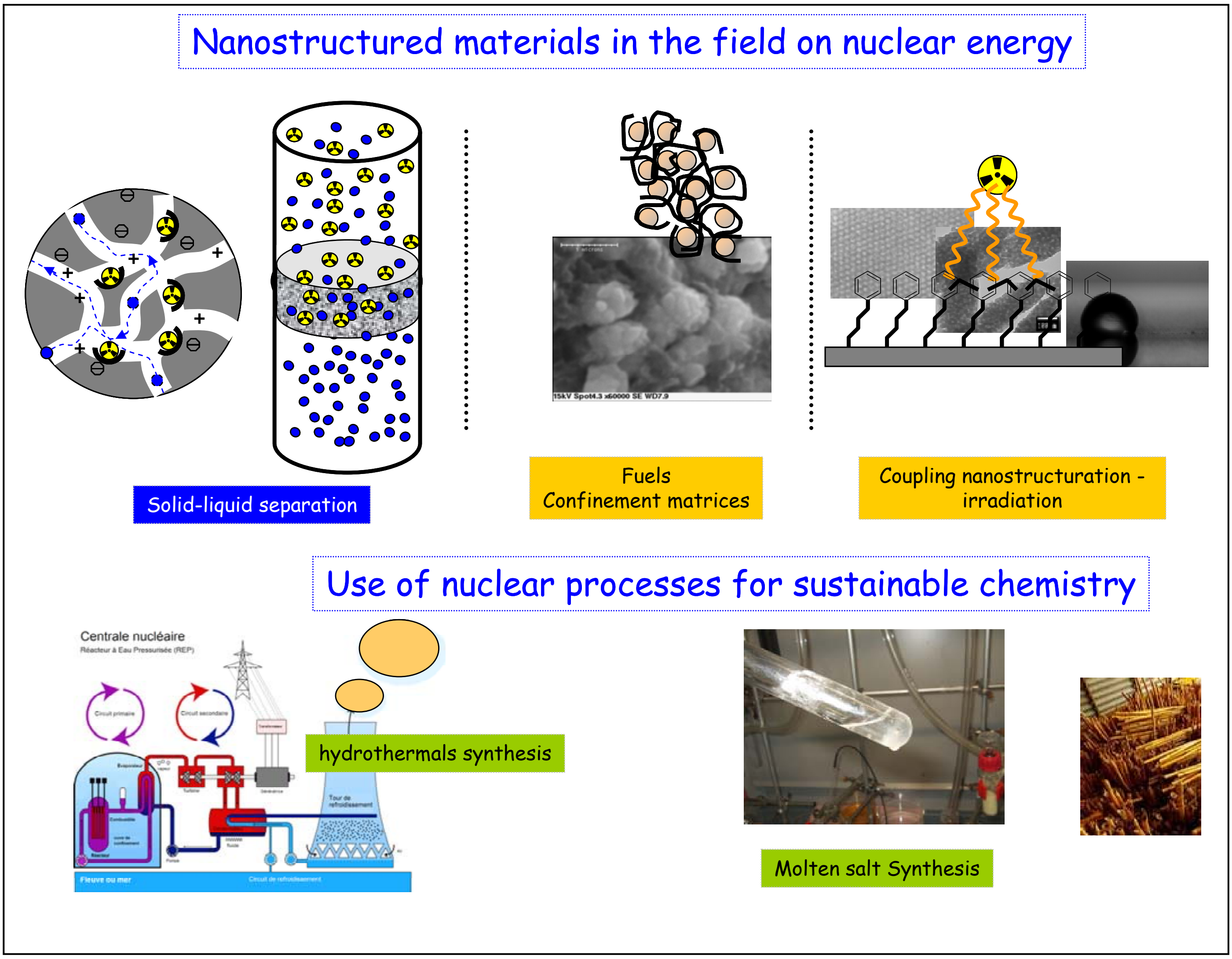
On accordera une attention toute particulière à la maîtrise de l’élaboration qui pourra intégrer les avancées modernes de la chimie douce, (sol-gel, hydrothermales, ionothermales et colloïdales), pour obtenir des réactivités lentes et contrôlées. Cette équipe utilise également des conditions de synthèses non usuelles, comme l’eau sous-critique, les liquides ioniques inorganiques ou la présence de rayonnement. Une bonne maîtrise de la « nanochimie » autour des grains élémentaires devrait permettre de concevoir des matériaux adaptés à la chimie séparative et également des matériaux auto-résistants aux stress (radiatifs ou chimiques). Ainsi l’objectif de cette équipe est de concevoir des matériaux pour lesquels leurs structures hiérarchiques et leurs fonctionnalisations induisent des réactions secondaires conduisant soit à un processus de séparation soit à une amélioration de leurs propriétés au cours du temps, notamment sous l’effet des rayonnements.

Abstract

This team deals with the research on nanomaterials used in the field of energy. This concerns the nuclear energy, with separative chemistry (solid-liquid or with phase transformation) and nanostructured materials (fuel and confinement materials).This concerns also alternative energies with recycling, used of biomass, or nanoparticles solar coatings. Research topics cover synthesis methods of nanostructured materials, their functionalisation, their characterization and study of their behaviour under stress.

The objectives are to develop materials with specific functions at a nanometer scale, inside a micrometer structure and to obtain a monolithic material use. This particular structure gives to the materials better physical (like behaviour under irradiation) or chemical properties. Indeed, nanostructured materials have non linear properties compared to "base" material which can be used to obtain high performance. Modeling properties will be used in the process of developing these materials.

Synthesis of these materials uses the "chimie douce" concept, like sol-gel, hydrothermal, ionothermal and colloidal routes. Their functionnalisation includes nanoparticles insertion, the functionnalisation by covalent bonding, or electro-phoretic routes. Controlling the nanochemistry during the synthesis allows the conception of materials well fitted to separative chemistry or with stress resistant. The objectives of this team are to develop new materials with hierarchical structure with several functionnalisation leading to a separation process or to an improvement of their properties with the time or under stress.



Nanostructured materials in the field on nuclear energy

Solid-liquid separation

Fuels
Confinement matrices

Coupling nanostructuration -
irradiation

Use of nuclear processes for sustainable chemistry

hydrothermals synthesis

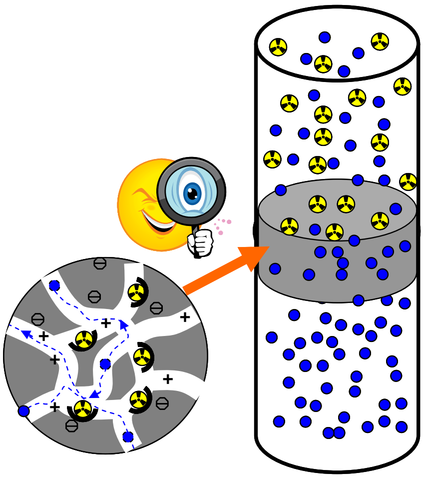
Molten salt Synthesis

Mesoporous materials in the field of nuclear industry.

F. Goettmann, X. Deschanels, G. Toquer, Ph. Makowski, H. Kaper, C. Rey, C. Delchet, S. El Mourabit, A. Merceille, A. Grandjean

Mesoporous materials are a class of materials with a specific pore size in the range of 2-50nm obtained thanks to the combination of soft matter physical chemistry and inorganic or organic sol-gel chemistry. Nevertheless, in the nuclear field, only few people interested in depollution and waste treatment have made some studies on hybrid mesoporous materials. In our opinion, many other fields within nuclear research could greatly benefit from nearly two decades of studies on mesoporous systems. Indeed: 1- the high porous volume of mesoporous materials makes them interesting materials for waste disposal. 2- the typical size of irradiation damages (dislocations) in structure materials is in the nanometer range, and mesoporous materials may thus serve as model materials for studying irradiation defects. 3- at high burn outs, nuclear fuels will produce large amounts of fission products, gases in particular. Finding new fuel forms, which can accommodate the high pressures generated by these gases, is thus of primary importance. Given this back ground, we have done this year a short review on what has already been achieved in nuclear field with mesoporous solids and which nuclear domains could present great potentialities for mesoporous solids [1].

One of the big industrial tasks in the nuclear fuel cycle is separation, *e.g.* isolating uranium from other minerals in ores, separating uranium and plutonium from fission and activation products in spent nuclear fuels (where ever recycling is the retained industrial option for waste management) and separating radionucleides from other species in the various fluxes issuing from processes involved in the fuel cycle or from dismantlement operations. Concerning the extraction of uranium from new, less concentrated, feed stocks (especially phosphates), we studied the used of mesoporous silica or carbon functionalised with specific ligand. We have also proposed functionalised mesoporous materials for the extraction of ruthenium from aqueous solutions [2], or for caesium [3] or strontium decontamination [4].



The second application of mesoporous materials in the nuclear field concerns advanced fuel forms and transmutation target. Indeed, due to the high activity of minor actinides, and in order to avoid dust during the synthesis, infiltration method is one of the most promising processes for the production of these materials. It is based on the synthesis of porous precursor ceramic and their infiltration by an actinide solution. In this context controlling the synthesis of uranium based mesoporous material with controlled pores are really attractive materials to immobilize actinides after their infiltration. Then, thirdly, we began studies of the effect of the irradiation on mesoporous materials. Indeed, by comparison with the radiation processes occurring in bulk materials, it might be expected that high surface content would play a main role in the excitation relaxation, diffusion processes and potential chemistry activation of adsorbate.

[1] Ph. Makowski, A. Grandjean, X. Deschanels, G. Toquer, D. Meyer, F. Goettmann, "**Mesoporous materials in the field of nuclear industry**" submitted to Journal of Nuclear Materials.

[2] A. Tokarev, A. Grandjean, Y Guari, J Larionova, R. lieger, C.Guérin,, **Functionalized porous glass for the removal and the confinement of ruthenium from radioactive solutions** Journal of Nuclear Materials, 400 (2010) 25-31.

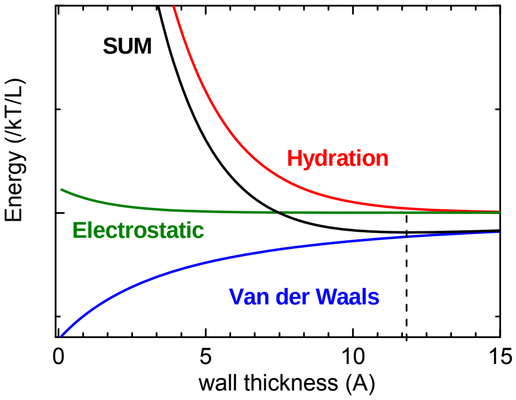
[3] A. Grandjean, J. Larionova, Y. Guari, Y. Barré, **Matériau solide nanocomposite a base d'hexa et d'octacyanomatallates, son procédé de preparation et procédé de fixation de polluants minéraux le mettant en oeuvre**., brevet. numéro d'enregistrement EN 09/53379.

[4] A. Merceille, Y. Barré, A. Grandjean, **Removal strontium ions form liquid radioactive wastes using sodium nonatitanate sorbents,** submitted to Journal of Hazardous Materials.

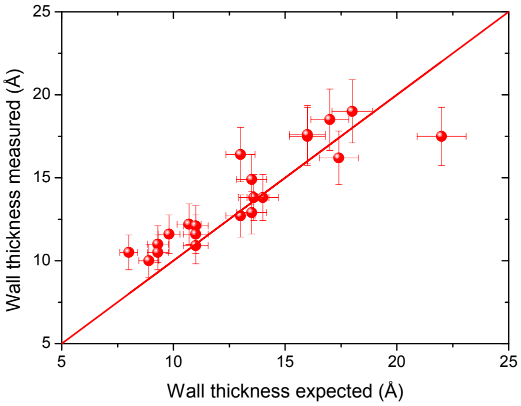
Molecular force balance allows the prediction of wall thickness of mesoporous materials.

A. Grandjean, G. Toquer, Th. Zemb

Since the discovery of mesoporous materials using micelle templates two decades ago, the booming of this field has been impressive. This kind of synthesis has been developed for diverse applications as catalysis, sensing, separation and much kind of oxides (silica, titania, zirconia). This synthesis is based on the layout of semi-rigid cylinders of surfactant in a water-phase solution. These self assembled surfactant acts as template during the sol gel process which occurs in the space left between the cylinders. Next, the wet dispersion of precursor material in the surfactant solution is aged, washed and finally calcined to remove the template. The control of surfactant geometrical parameters during the inorganic polymerisation impacts directly the properties of the final mesoporous materials. For example, the diameter of templating cylinder controls the final pore size. Nevertheless, in spite of several experiment attempts to control wall thickness, any clear and unquestionable explanation is not yet available. In this way, we develop a simple analytical model which predicts variations of wall thickness through experimental conditions. This model is free parameter and is in great agreement with experimental data available from the literature for the case of hexagonal array of cylindrical pores. The model concept consists of three main uncoupled driving forces : repulsive electrostatic, repulsive hydration and attractive Van der Waals. By adding all these supramolecular interactions and searching a minimum in potential, this latter gives then the equilibrium distance value between surfactant cylinder and consequently an expected wall thickness. The confrontation of our model with experimental data is illustrated here by several examples in order to better understand the wall thickness variation with the experimental process. This simple analytical model based on molecular force balance proposed here explains qualitatively and quantitatively in some simple cases, the wall thickness of silica-based mesoporous materials obtained via the sol-gel route.



A typical example of a force balance calculation with the dominant interactions: Hydration, Van des Waals and Electrostatic. The equilibrium interaxial distance is given by the minimum value of sum of the 3 forces.



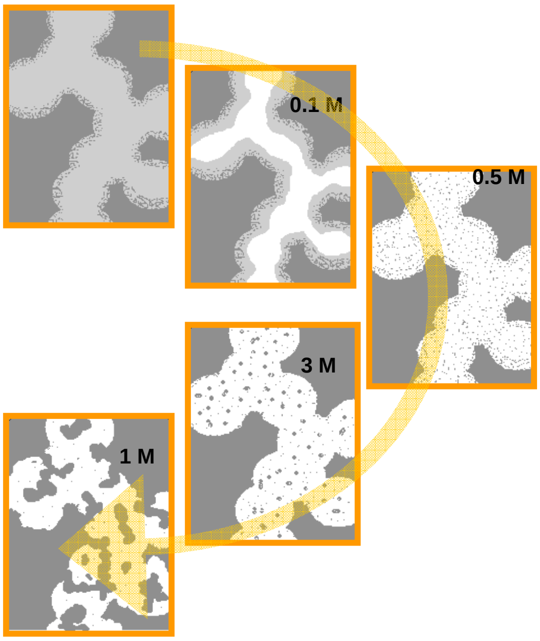
Wall thickness measurement versus wall thickness expected from force molecular balance by using several experimental data

A. Grandjean, G. Toquer, Th Zemb, **Molecular force balance allows prediction of wall thickness in precipitated precursors of mesoporous materials,** Journal of Physical Chemistry, accepted.

Effect of leaching concentration and time on the morphology of pores in porous glasses.

Guillaume Toquer, Carole Delchet, Mathieu Nemec, Agnès Grandjean

In the last decades, some interests have been devoted in high-silica porous glass from both applications and scientific standpoints. These studies deal with the fields of membrane technology, confined matter, organic/inorganic or inorganic/inorganic composites, separation sciences, biological, pharmaceutical and environmental applications. In the field of nuclear waste treatment, functional group grafted on mesopore surfaces of silica-based support is a promising way for the removal of fission product from these radioactive wastes. Porous glass was prepared by acid leaching a phase separated sodium borosilicate glasses. Effects of the HCl leaching concentration varying from 0.1M to 3M and of the leaching time varying from 2 hours to 48 hours on the pores size and shape have been studied. The porous structure was investigated using nitrogen adsorption and some glass structure has been followed using IR spectroscopy measurement. The evolution has also been analysed through small angle X-rays scattering measurements. We argue that the composition of these samples is not significantly modified with the acidic concentration of the solution and with the leaching time. However, we clearly show strong difference of porous structure. At low acid concentration, the specific area of these materials is essentially due to the small amount of colloidal silica inside the pores. Increasing the HCl concentration until about 0.7M leads to a strong increase of the specific BET area and total pore volume, which is due to the presence of silica particles in the soluble sodium rich phase borate. Still increasing the acidic concentration of the leaching solution leads to a decrease of both the specific surface area and the total pore volume. This latter point is explained by a clustering of the silica colloidal which may close some pores coming from the soluble borate phase. The effect of the leaching time is less significant than the HCl concentration one, but the same assumption can even explain both of them.



Porous glasses, prepared by acid leaching of phase separated soda borosilicate glasses, contain usually colloidal silica particles which originate from the silica content in the soluble borate phase. When the colloidal silica fills the pores of the silica porous structure, the pore volume is reduced and the diffusion through the porous glass is reduced. This figure shows a schematic view of the HCl leachong concentration effect on the morphology of pores in porous glass. Gray = silica phase, light gray : borate phase.

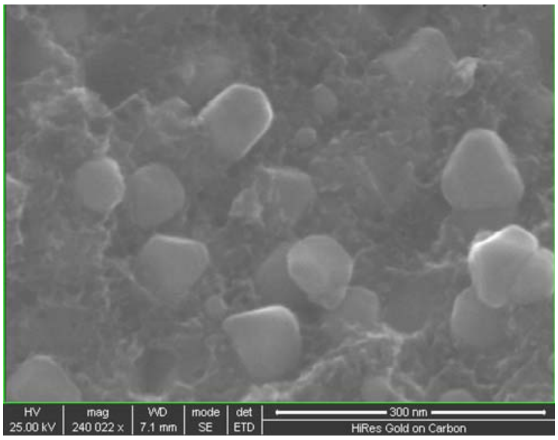
Guillaume Toquer, Carole Delchet, Mathieu Nemec, Agnès Grandjean, "**Effect of leaching concentration and time on the morphology of porous glasses**", submitted to Journal of Non Crystalline solids.
A. Grandjean, J. Larionova, Y. Guari, Y. Barré, « **Matériau solide nanocomposite a base d'hexa et d'octacyanomatallates, son procédé de preparation et procédé de fixation de polluants minéraux le mettant en oeuvre**.» FD11351, brevet, numéro d'enregistrement EN 09/53379 à la date du 20 mai 2009.

Synthesis of carbide compounds derived from colloidal oxide and carbohydrate

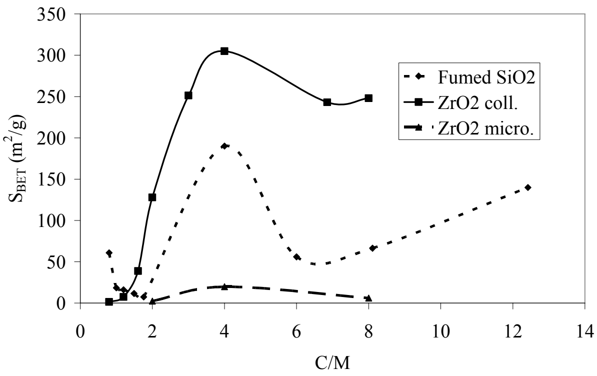
X. Deschanels, *M. El Ghazzal, C. Delchet, D. Herault*, V. Magnin, A. Grandjean, R. Podor,*
G. Cerveau, T. Zemb, R. Corriu**

* *ICG Montpellier UMR* 5253

Silicon carbide (SiC) and zirconium carbide (ZrC) powders were synthesized by the carbothermal reduction reaction of carbon and the corresponding metal oxide silica or zirconia according to the following reaction :
$MO_2 (S) + 3C (s) \rightarrow MC (s) + 2 CO (g)$
The physical and chemical properties of the final products were studied according to the nature of precursors used: colloidal or micrometric powders for the oxides, sucrose, mannitol or sorbitol for the reducing agent. The amount of carbohydrate is adjusted in a proportion ranging between 1 and 8 times the quantity needed by the reaction (1) to obtain a complete conversion of the parent compounds. The C/M ratio quantifies the deviation from stoechiometry, i.e C/M=1 means the reagents are mixed together in the proportion of the reaction (1). After mixing and freeze drying of these components, the powder was heated at temperatures ranging from 1300 and 1550°C under flowing argon to obtain the carbides. Depending on the nature of the precursors (colloidal or micrometric) an increase of more than one order in the magnitude of the surface area was observed. The highest surface area (300m²/g) was measured on a Zr+þC compound type elaborated from a colloidal precursor. The use of colloids in carbothermal reaction could be a route to control pore size in mesoporous carbides or supported porous carbon materials.



SEM micrograph of ZrC+C powders synthesized at 1550°C-4h (C/M=8).



Specific surface area (BET) of carbides elaborated from various precursors versus the ratio C/M (processing conditions 1550°C-4h under Ar).

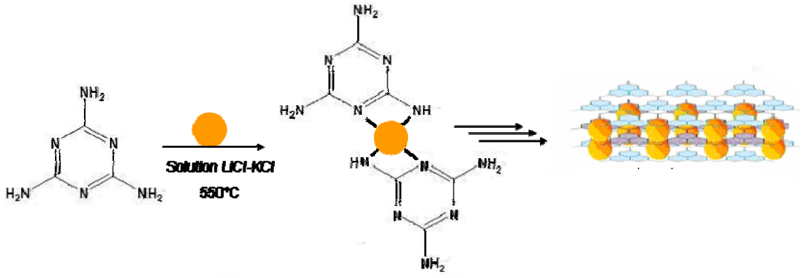
X. Deschanels., M. El Ghazzal and al., **“Synthesis of Carbide compounds derived from colloidal oxide and carbohydrate”**, Progr Colloid. Polym. Sci. 137 (2010) 47-52.

X. Deschanels., M. El Ghazzal and al. **“Synthesis of carbide compounds derived from colloidal oxide and carbohydrate”** Oral presentation - 3rd COST D43 Workshop – Antalya, Turkey – September 7-9, 2009.

Synthesis of carbonitrides in molten salt and their application to separative chemistry.

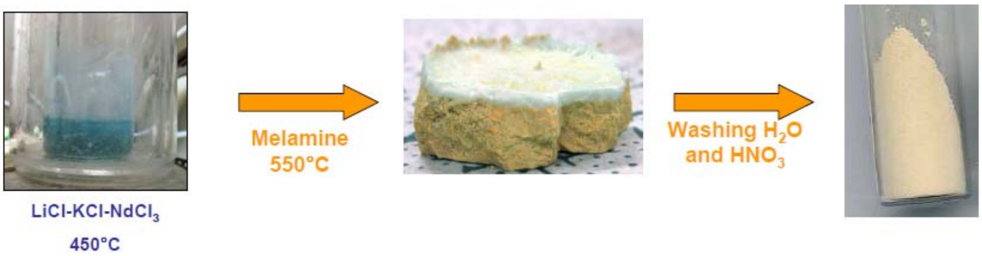
F. Goettmann, D. Meyer, A. Grandjean and A. Laplace(DRCP/SCPS)

Molten halides have often be and still are considered as possible cooling fluids for advanced nuclear reactors but also as media for the pyroreprocessing of spent nuclear fuels,[1] which prompted numerous studies on ion separation in such fluids. But molten chlorides also recently received unexpected interest from materials scientists. Indeed, Arne Thomas and co-workers show that molten chlorides were well suited as solvent to obtain highly ordered nitrogen rich polymers.[2] Building on these pioneering works we expected that the polymerisation of C_3N_4 precursors (like melamine) in molten chloride and in the presence of other metal chlorides could result in the formation of metal doped C_3N_4 compounds (Scheme 1), which could be useful as precursors for ceramic materials and/or as a mean to separate ion under pyrochemical conditions. .



Scheme 1: *A schematic view on how polymerisation of melamine in molten chlorides in the presence of metals could yield C_3N_4 intercallation compounds*

We selected lanthanides as model metals as well for their coordination chemistry as for their interest in the field of nuclear waste treatment. In a first step, the wanted lanthanide chloride was dissolved in molten LiCl/LCl mixtures at 450°C. Afterwards melamine was added to the solution and the whole crucible was heated to 550°c for two hours. After cooling down a salt block formed which trapped a yellow powder we could isolate by hydrolysis and filtration. Figure 1 shows pictures of various steps of this process. Interestingly only the powders obtained with havy lanthanides (Nd, Sm, Eu, Gd) incorporated noticeable amounts of metal (up to 30 w%), while lighter lanthanides (La and Ce) hardly precipitated. This opened a possibility to separated lanthanides in molten salts. And, indeed, when submitting a 1:1 mixutre of lanthanum and samarium chloride in LiCl/KCl to melamine we were able to precipitate a Sm enriched solid. After calcination of this solid we recovered a 90% pure samarium oxide representing 55% of the initial amount of samarium



Some steps of the synthesis of a neodymium doped C_3N_4 compound

1 J. P. Ackerman, *Ind. Eng. Chem. Res.*, 1991, ***30***, 141.

2 (a) M. J. Bojdys, J. O. Muller, M. Antonietti, A. Thomas, *Chem. Eur. J.*, 2008, ***14***, 8177(b) M. J. Bojdys, S. A. Wohlgemuth, A. Thomas, M. Antonietti, *Macromolecules,* 2010, ***43***, 6639(c) P. Kuhn, M. Antonietti, A. Thomas, *Angew. Chem.-Int. Edit.,* 2008, ***47***, 3450.

3 A. Corma, S. Iborra, A. Velty, *Chem. Rev.*, 2007, ***107***, 2411.

4 P. J. Garner, R. Jones, R. S. Airs, 1949, GB660838

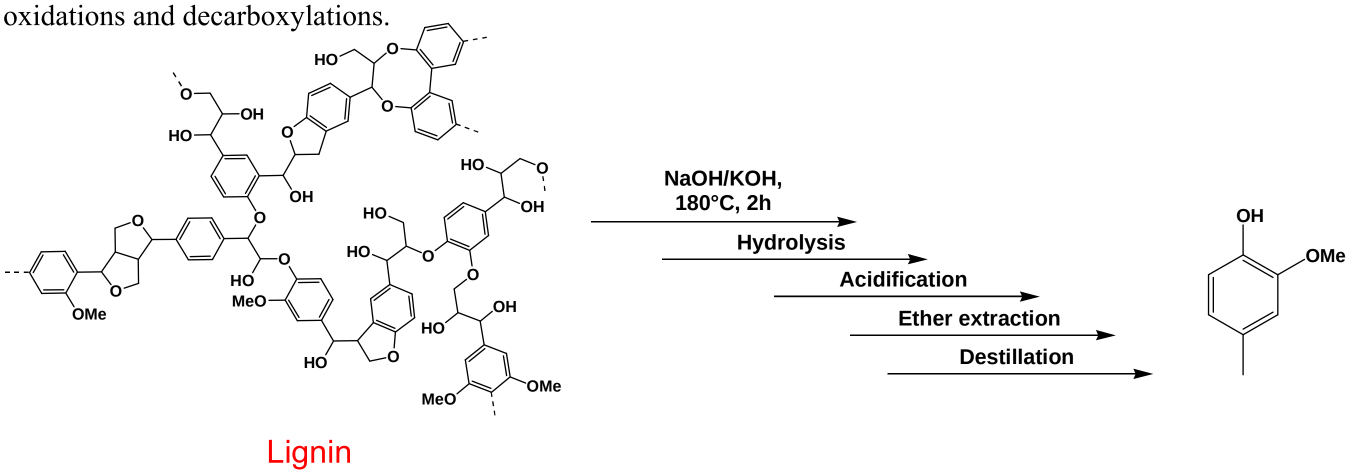
5 F. Goettmann, P. Makowski, D. Da Silva Perez, M. Petit Conil, "***Procédé de dépolymérisation de biomasse lignocellulosique***",brevet, 2010,

Molten Hydroxides for the valorisation of lignin.

F. Goettmann, Ph. Makowski, D. Da Silva Perez[‡] and M. Petit Conil[‡] (‡ Centre Technique du Papier, Domaine universitaire, 38044 Grenoble**)**

Anticipating an upcoming shortage of fossil resources available as feedstock for the production of chemical commodities, industrial as well as academic researchers are searching for renewable sources of bonded carbon. These efforts brought increased interest to the use of terrestrial vegetal biomass, which is mainly constituted of cellulose, hemicelluloses and lignins. While cellulose and hemicelluloses are relatively easy to hydrolyse and open the way to numerous, sugar chemistry based, commodity platforms, lignin proved to be much more difficult to valorise.[1] Indeed, lignin is a natural phenolic polymer, which structure is not completely solved by now. The monomeric units are held together by a combination of strong ether and C-C bonds which require harsh reaction conditions to be broken up. As a result, most attempts to convert lignin into useful small molecules yielded complicated reaction mixtures. In order to achieve a better reactivity and a higher selectivity in the depolymerisation of lignin, we wanted to combine the advantages of high temperatures and solvochemistry, which can be provided by working in molten salts. Indeed, molten inorganic salts (and the mixtures thereof) are well known to metallurgists and electrochemists (because of their high thermal resistance and their broad electrochemical window) but their potential as solvents to undertake demanding organic reactions remains largely unexplored. Despite the fact that, among all possible salt melts, molten hydroxides received no attention in this field (with the noticeable exception of a British patent dating back to 1949 reporting the activation of secondary alcohols in such media[2]), we selected them as a medium of choice to depolymerise lignin because: i- they can already melt be 180°C, ii- lignin, being a relatively acidic polymer, is partly soluble therein and iii- ether bonds are known to be openend under basic conditions.

This proved to be a successful choice. Indeed, we were able to obtain 10 mass% of methyl guaiacol from lignin (which corresponds to 50% of the maximal theoretical yield) by heating commercial lignin in molten NaOH/KOH at 180°C for only 2h (Scheme 1).[3] More interestingly when working with crude biomass (such as pine wood chips) we obtained even higher conversion yields in the same molecule. We also were able, by working with model molecules, to evidence that the depolymerisation was formally proceeding via a succession of a limited number of simple reactions including hydrolyses, oxidations and decarboxylations.



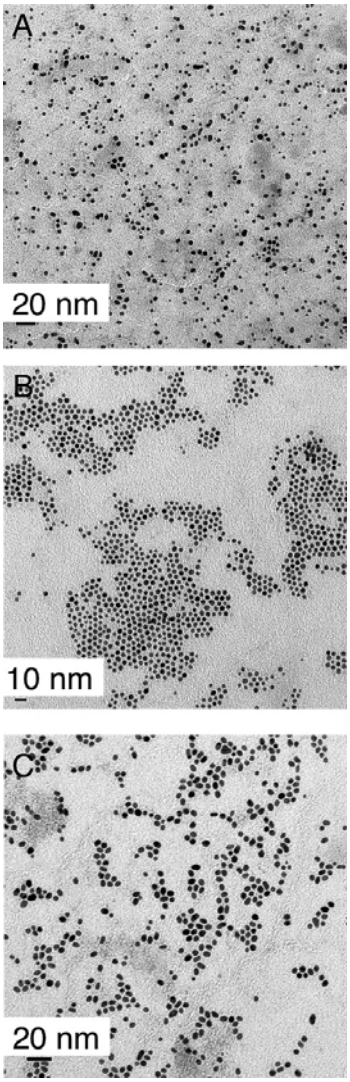
***Scheme 1:** Depolymerisation of lignin into methyl-guaiacol.*

In a second step, we except to find ways to run this reaction in a continuous process and extract the product of the reaction by liquid/liquid or liquid/gas extraction.

1 A. Corma, S. Iborra, A. Velty, *Chem. Rev.,* 2007, ***107***, 2411.
2 P. J. Garner, R. Jones, R. S. Airs, 1949, GB660838
3 F. Goettmann, P. Makowski, D. Da Silva Perez, M. Petit Conil, "***Procédé de dépolymérisation de biomasse lignocellulosique***", 2010, brevet.

Synthesis of nanoparticles using colloidal routes

Thomas Zemb, Benjamin Abécassis and Fabienne Testard (LIONS-Saclay)



Among various synthesis procedures, the use of reverse micelles is an effective route for yielding a wide range of nanoparticles of different chemical nature, size and shape. The inner core of the reverse micelles acts as a nanoreactor and the nanoparticles are obtained by mixing two microemulsions containing reacting precursors. Despite numerous theoretical studies on the formation mechanism of nanoparticles in reverse microemulsion, its elucidation is still far from being complete. Linking the size and shape of nanoparticles obtained at the end of the reaction to the shape and curvature radius of the microemulsion initially present is tempting but other parameters can also play an important role. For example, the state of the water molecules inside the water pools, the dynamics of the inter droplet exchange, and the chemical conditions are of primary importance and can prevail over the templating effect.

On the other hand, catanionic formulations of microemulsions involve surface networks of alternated positive and negative charges and produce the most rigid surfactant monolayer films known. Thus, using catanionic reverse micelles as micro-reactors, the elusive "templating" effect expected for the synthesis of monodisperse nanoparticles of controlled size as the gold nanoparticles (shown to the left) produced for the different radii of curvature of templating microstructure should be maximised.

An efficient strategy for producing small nanoparticles leading to homogeneous materials is to use stable microemulsions. For reactives are soluble in water, reverse (w/o) catanionic aggregates is the most efficient colloidal route known. Spherical gold nanoparticles are synthesized in worm-like catanionic reverse micelles, demonstrating the absence of shape templating except when the growth of the particles is slow. In situ time resolved SAXS measurements show that the microstructure of the microemulsion is conserved during the whole reaction.

The liquid–liquid phase transition of the catanionic microemulsion induced by a gentle cooling is used to recover and purify the nanoparticles in a simple manner, by using a large domain of tie-lines in the ternary phase diagram to concentrate the nanoparticles while washing away the surfactant involved [1].

The reversible separation-remixing of the dispersion before and after liquid-liquid phase instability due to long range attractive interactions between nanoreactors induced by slight temperature variations temperatures is shown to the left.

---

[1] Abecassis, Benjamin; Testard, Fabienne; Zemb, Thomas. "Gold nanoparticle synthesis in worm-like catanionic micelles: microstructure conservation and temperature induced recovery. " Soft Matter (2009), 5(5), 974-978.

6 – Surface of materials in rapid evolution

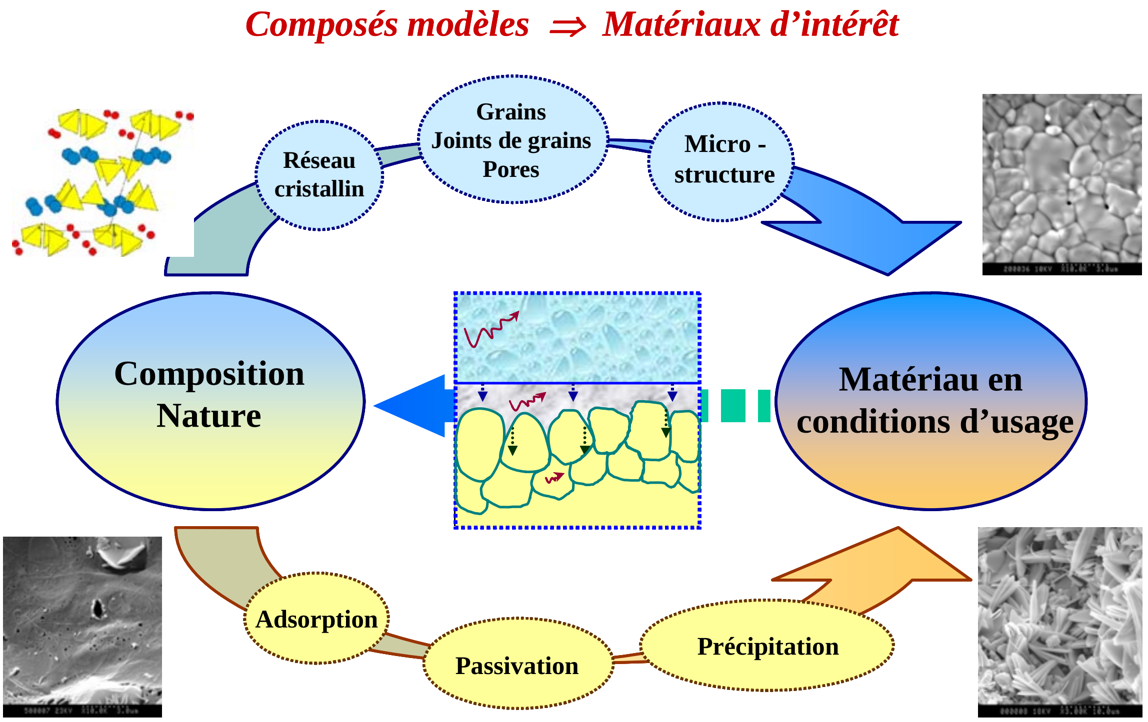
L'équipe est constituée de :
1 permanent UM2, responsable d'équipe (Pr. N. Dacheux),
1 chercheur CNRS (Dr. N. Clavier),
1 chercheur CEA (Dr. S. Szenknect),
1 post-doctorant CNRS (Dr. A. Mesbah)
4 doctorants (D. Horlait, L. Claparède, D.T. Costin, F. Crétaz)

Le laboratoire d'étude des Interfaces de Matériaux en Evolution (LIME) a pour objectif de décrire et de comprendre les phénomènes responsables de l'altération (ou de la dissolution) sous contraintes de matériaux d'intérêt pour le nucléaire du futur à travers l'étude des phénomènes physico-chimiques se déroulant aux interfaces. Il s'agit de permettre, à terme, l'optimisation des propriétés de certains matériaux utilisés (ou à utiliser) pour l'aval ou l'amont du cycle électronucléaire. Cette démarche consiste en particulier à appréhender et à comprendre les liens étroits reliant la morphologie d'un solide, d'une part, et sa propension à se dissoudre, d'autre part. Dans ce but, la première étape de l'étude a consisté à développer ou optimiser les conditions de synthèse de combustibles modèles ($Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $Ce_{1-x}Nd_xO_{2-x/2}$) en privilégiant l'usage de précurseurs cristallisés d'oxalates de manière à améliorer l'homogénéité, la réactivité et la capacité de frittage des oxydes préparés à haute température. Dans le système Th/U, une solution solide continue de formulation $Th_{1-x}U_x(C_2O_4)_2$, $2H_2O$ a été préparée puis caractérisée. La résolution structurale associée a conduit à une maille monoclinique, en désaccord avec la structure de référence orthorhombique récemment reportée dans la littérature pour $U(C_2O_4)_2$, $2H_2O$. Par ailleurs, une caractérisation *in situ* des échantillons en fonction de la température par spectroscopie μ-Raman, DRX et ESEM a démontré la présence d'une transition de phase inédite (monoclinique/orthorhombique) et la stabilisation d'une forme monohydratée. Quelle que soit la méthode employée, les précurseurs oxaliques préparés ont systématiquement conduit aux oxydes après traitement thermique au-delà de 400°C à travers une séquence réactionnelle désormais précisée. Concernant la préparation des solutions solides $Ce_{1-x}Nd_xO_{2-x/2}$, l'affinement des paramètres de maille des échantillons préparés après traitement thermique du précurseur oxalate à 1000°C a confirmé l'existence de deux domaines distincts (structures fluorine et bixbyite), résultant d'une organisation des lacunes en oxygène nécessaires à la compensation de charges. En outre, l'utilisation de méthodes de synthèse par voie humide, généralement favorables à l'amélioration de la répartition cationique au sein du solide, a permis d'étendre le domaine d'existence de telles solutions solides.

Sur la base de ces résultats, le frittage de $Th_{1-x}U_xO_2$, de $Th_{1-x}Ce_xO_2$ et de $Ce_{1-x}Nd_xO_{2-x/2}$ a été optimisé en termes de réactivité ou de conditions opératoires (pression, durée, température), ce qui a permis d'atteindre des densités voisines de 95 – 97 % des valeurs calculées. Si l'emploi des méthodes de préparation par voie humide a permis d'abaisser la température de densification sous atmosphère inerte d'environ 100°C dans le cas de solutions solides $Th_{1-x}U_xO_2$, les méthodes de préparation en conditions hydrothermales ont conduit à une amélioration significative de la répartition cationique au sein des échantillons frittés. De plus, à l'issue de ces expériences, un premier « contrôle » de la microstructure a été obtenu.

Des expériences de dissolution ont été entreprises en conditions de faible ou de fort renouvellement. Pour les solutions solides $Th_{1-x}U_xO_2$, l'amélioration de la répartition cationique au sein du solide permet de limiter l'influence de la composition, probablement du fait de la disparition de zones enrichies en uranium tandis que la réduction du nombre de joints de grains induit la diminution des vitesses de dissolution normalisées d'environ un ordre de grandeur par rapport à celles déterminées pour les échantillons préparés par précipitation directe. Cela confirme les liens forts entre la microstructure du matériau (à travers, entre autre, l'homogénéité et la réactivité de surface, …) et sa résistance à l'altération ou à la corrosion aqueuse. Enfin, la précipitation du thorium au sein de phases secondaires formées à saturation du lixiviat (telles que ThO_2, x H_2O ou $Th(OH)_4$, y H_2O) a été démontrée.

Concernant les solutions solides $Ce_{1-x}Nd_xO_{2-x/2}$, l'influence de plusieurs paramètres tels que la composition chimique, la température, l'acidité du milieu et la présence d'agents complexant sur la vitesse de dissolution normalisée a été examinée. Contrairement aux solutions solides $Th_{1-x}U_xO_2$, les premiers tests de dissolution menés sur les composés $Ce_{1-x}Nd_xO_{2-x/2}$ montrent une forte influence de la composition chimique, principalement liée à la fragilisation du réseau cristallin consécutive à la formation des lacunes en oxygène. Par ailleurs, le contrôle de la réaction de dissolution par des réactions de surface a été mis en évidence, à la fois *via* la détermination de l'énergie d'activation (voisine de 90-100 $kJ.mol^{-1}$) qu'à travers la saturation des sites actifs de surface au-delà de 2M en acide nitrique. Ces travaux sont actuellement poursuivis dans le cadre de deux thèses : Laurent Claparède (Bourse CFR, ICSM – DRCP/LCA) et Denis Horlait (Bourse MENRT sur thème prioritaire, ICSM). Un aspect particulier du travail consiste à préparer, caractériser puis entreprendre la dissolution de solutions solides $Th_{1-x}Ln_xO_{2-x/2}$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ln_xO_{2-x/2}$ et $U_{1-x}Ce_xO_2$.



Synoptic representation of the parameters considered to understand the links between chemical composition, preparation method and alteration of the interface during use of a material

Plus récemment, un second axe de recherches, en lien avec l'amont du cycle, a été initié en partenariat avec le DRCP dans le cadre de deux thèses (Dan T. Costin et Fanny Crétaz). Les premières études ont porté sur le système thorium – uranium – silicate, à travers la préparation d'échantillons d'uranothorite $Th_{1-x}U_xSiO_4$ en conditions hydrothermales. Des méthodes de purification de ces échantillons, par séparation mécanique des traces de UO_2 et/ou de SiO_2 éventuelles, ont été développées. En revanche, les tentatives de synthèses de coffinite $USiO_4$ sont demeurées infructueuses à ce jour. Le second volet de l'étude porte sur les systèmes uranium-phosphate et uranium-vanadate, plus particulièrement à travers la synthèse et la caractérisation d'autunite, de torbernite ou de carnotite. Pour ces deux volets, la démarche consiste alors à déterminer les vitesses de dissolution des échantillons (cinétique) et les données de solubilité afin d'accéder *in fine* aux données thermodynamiques (K_S, $\Delta_RH°$, $\Delta_RG°$, $\Delta_RS°$) nécessaires pour évaluer le comportement de ces phases minérales lors de leur mise en contact avec une solution. Une comparaison directe entre échantillons modèles et réels est réalisée à travers le développement de cette méthodologie parallèlement sur des minéraux et sur des échantillons synthétiques.

From oxalates to oxides: study of the thermal conversion of $Th_{1-x}U_x(C_2O_4)_2$. $2H_2O$ compounds

Nicolas CLAVIER, Nicolas DACHEUX
Murielle RIVENET, Francis ABRAHAM (UCCS – ENSC Lille)
Nicole BARRE (Groupe de Radiochimie – IPN Orsay)

Oxalate co-precipitation is currently considered as a promising way to operate the recycling of tetravalent actinides into new oxide fuel elements[1]. In these conditions, it is important to clearly understand the different reactions occurring during the heat treatment from the oxalate precursor leading to the final dioxide. Indeed, even if actinide oxalates are studied since almost 70 years[2], reliable data concerning their crystal structures and their stability range are often lacking.

A study was then focused on the system based on $Th_{1-x}U_x(C_2O_4)_2 \cdot 2H_2O$ compounds which was extensively characterized through an innovative approach combining *in situ* HT-techniques such as XRD and µ-Raman spectroscopy. First, this gave evidence of the existence of a low-temperature monoclinic form of the initial dihydrate compounds, never reported up to now, and mainly characterized by an original 2D arrangement exhibiting two types of oxalate sites as well as two distinct sets of hydrogen bonds in charge of the layer cohesion[3]. The phase transition to the well-known orthorhombic form was then observed through the modification of the µ-Raman spectra (fig. 1) and its temperature was found to vary linearly with the chemical composition of the sample.

A particular attention was then paid to the dehydration processes with the complete structural characterization of the monohydrate compounds. Here again, the temperature of formation was found to be dependent on the chemical composition as well as their stability versus rehydration. Indeed, while uranium(IV) oxalate monohydrate is quickly turned into the initial dihydrated compounds, the thorium end-member remains stable for several weeks. The possible crystallization of an anhydrous sample is also currently investigated.

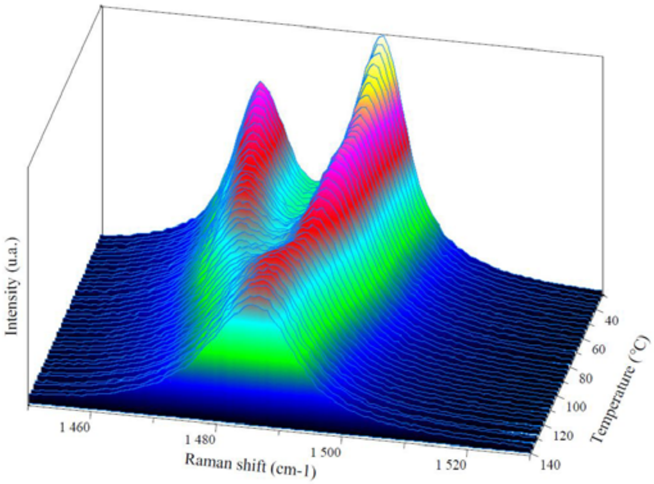


Fig.1: variation of in situ HT-µ-Raman spectra of $Th(C_2O_4)_2 \cdot 2H_2O$ during the monoclinic – orthorhombic phase transition.

Finally, the transformation of anhydrous oxalate into dioxide was investigated by TG studies and *in situ* HT-Raman in order to elucidate the eventual formation of carbonated or oxo-carbonated intermediate species, which is regularly questioned in the literature. Up to now, no characteristic vibration band associated to such entities was noticed for the thorium-uranium system, accounting for a direct transformation.

---

[1]. N. Hingant, N. Clavier, N. Dacheux, N. Barré, S. Hubert, S. Obbade, F. Taborda, F. Abraham: **Preparation, sintering and leaching of optimized uranium thorium dioxides**, J. Nucl. Mater., 2009, *385*, 400.

[2]. P.L. Günther *et al.*, Ber. Dtsch. Chem. Ges., 1938, *71B*, 1771.

[3]. N. Clavier, N. Hingant, M. Rivenet, S. Obbade, N. Dacheux, N. Barré, F. Abraham : **X-Ray diffraction and µ-Raman investigation of the monoclinic-orthorhombic phase transition in $Th_{1-x}U_x(C_2O_4)_2.2H_2O$ solid solutions**, Inorg. Chem., 2010, *49*, 1921.

Sintering of model oxides for advanced nuclear fuels from precursors: from in situ to ex situ approaches

Nicolas CLAVIER, Laurent CLAPAREDE, Nicolas DACHEUX
Renaud PODOR, Johann RAVAUX (ICSM/LME)

The recycling of minor actinides into oxide-type fuel elements or into UO_2-based transmutation matrices surrounding the core is currently considered in the framework of the fourth generation of nuclear reactors, mainly to decrease the radiotoxicity of radwaste. In these conditions, it is important to understand and anticipate the behaviour of such solids during their life-cycle, including the sintering step. The present study was then focused on $(Th,U)O_2$, $(Ce,Ln)O_2$ and $(Th,Ln)O_2$ model dioxides during their preparation as reactive powders then their densification. The sintering processes were particularly followed by dilatometry, SEM/ESEM, and pycnometric measurements.

As oxalate precipitation was used for the preparation of the final oxides, the first step lied in the optimization of the specific surface area. This latter was found to be increased by about one order of magnitude during the oxalate decomposition[1] due to the constraints generated by CO and CO_2 emissions. The resulting sub-micrometric powders were then shaped through uniaxial pressing and heated at high temperature to operate the densification. During this step, several operating parameters were studied to increase the final density of the samples including pressure (typically in the 200 – 800 MPa range), pre-heating temperature, or presence of a grinding step. The dilatometric study of $(Ce,Ln)O_2$ mixed samples (fig. 1) revealed that the incorporation of aliovalent rare earth elements led to an increase of the sintering temperature, probably through the appearance of interdiffusion phenomena competing with the sintering process itself, and of the formation of complex defects such as vacancies clusters. Nevertheless, the measured densities systematically ranged between 90 and 95 % of the calculated value after heating at 1500°C for 10 hours.

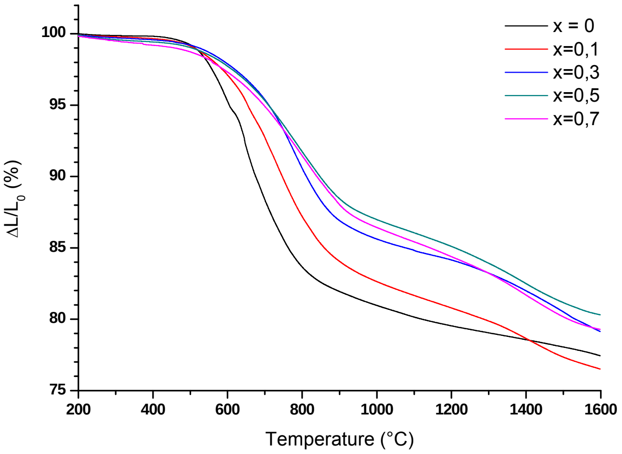


Fig.1: Dilatometric curves of $Ce_{1-x}Nd_xO_{2-x/2}$ mixed dioxides versus temperature.

Heating time and temperature could also be used to control the final microstructure of the pellet, *i.e.* average grain size, porosity distribution and grain boundary occurrence. In this framework, both *ex situ* and *in situ* ESEM observations (see also "Dynamic aspects of sintering" by Podor *et al.*) allow following the variation of the grain size during the firing step[2] while He and H_2O pycnometric measurements lead to the corresponding densities with contribution of open and closed porosities.

---

[1]. N. Hingant, N. Clavier, N. Dacheux, S. Hubert, N. Barré, R. Podor, L. Aranda : **Preparation of morphology-controlled $Th_{1-x}U_xO_2$ sintered pellets from low-temperature precursors**, Powder Tech., *in press*.

[2]. R. Podor, N. Clavier, J. Ravaux, L. Claparéde, N. Dacheux **Dynamic aspects of ceramic sintering. High temperature environmental scanning electron microscopy (HT-ESEM) in situ sintering of ceria at 1400°C**, submitted to Acta Mater.

Dissolution of $Ce^{IV}_{1-x}Ln^{III}_{x}O_{2-x/2}$ mixed dioxides

Denis HORLAIT, Nicolas CLAVIER, Stéphanie SZENKNECT, Nicolas DACHEUX
Renaud PODOR, Johann RAVAUX (ICSM/LME)

The understanding of dissolution processes of actinides dioxides has become essential for the optimization of reprocessing operations associated to the back-end of the nuclear fuel cycle. As several Gen IV reactor concepts plan to operate the simultaneous reprocessing of major and minor actinides (such as Am^{III} and Cm^{III}) in new fuel elements, we focused the study on the influence of the incorporation of trivalent lanthanide cations (namely Nd^{III} or Er^{III}) in the $Ce^{IV}O_2$ fluorite-type matrix, as model compounds before forthcoming work based on An^{IV}-Ln^{III} oxides.

In this aim, several samples were synthesized using an initial oxalic co-precipitation in order to improve the homogeneity of the final compounds obtained after heat treatment. From a structural point of view the substitution of Ce^{IV} by Ln^{III} appears to be accompanied by the formation of oxygen vacancies and generates different structures for resulting solid solutions [46]. As instance, $Ce^{IV}_{1-x}Nd_{x}^{III}O_{2-x/2}$ compounds keep the fluorite-type structure (*Fm3m*) up to about $x = 0.4$, while a cubic superstructure (*Ia-3*) appears from the ordering of oxygen vacancies for higher values. Finally, for $x > 0.7$, the formation of additional hexagonal Nd_2O_3 (space group *P3mm*) is observed.

Dissolution experiments of dioxides powders were then undertaken in 4M HNO_3 at various temperatures. The associated initial dissolution rates clearly showed that i) the dissolution of all compounds was congruent as the two cations are released in the solution with close normalized dissolution rates, ii) the fraction of trivalent cations (and therefore the oxygen vacancies) strongly enhanced the dissolution rate, iii) the temperature (activation energy of about 80 $kJ.mol^{-1}$) did not influence the dissolution mechanism and iv) normalized dissolutions rates were found to follow the lanthanides series (La-doped dissolving faster than Yb-doped compounds). Conversely, the crystalline structure-type did not seem to have any significant influence on the dissolution rate.

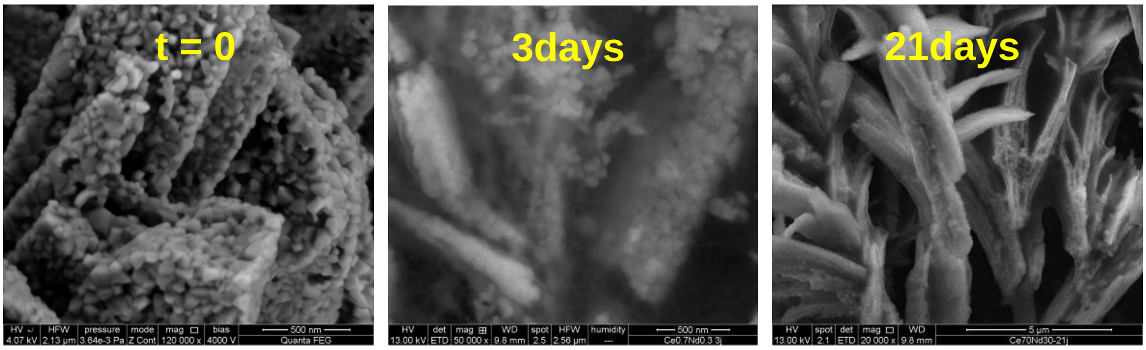


Fig. 1. ESEM micrographies of $Ce_{0.7}Nd_{0.3}O_{1.85}$ samples leached in 4M HNO_3 at 60°C.

Environmental SEM and BET studies were then undertaken on several samples to follow the modifications of the samples morphology throughout the dissolution process. We observed in the first times of the dissolution a strong increase of the specific surface area, correlated to the breakaway of nanometric crystallites (fig. 1). For longer leaching times, the formation of a gelatinous layer was observed and was linked to the decrease of dissolution rate after few hours. Similar experiments were then carried out on sintered pellets. The material appeared preferentially altered through the formation of corrosion pits randomly dispersed onto the surface of the grains and along the grain boundaries. Moreover, the alteration of the grains surface was only observable after several days. Additionally, sintered samples were more rapidly dissolved within the grain boundaries and surface local defects.

---

[46]. D. Horlait, L. Claparède, S. Szenknect, N. Clavier, N. Dacheux, R. Podor, J. Ravaux, V. Magnin: **Characterization by µ-Raman and XRD of $Ce_{1-x}Ln_{x}O_{2-x/2}$ mixed-oxides prepared via oxalic precipitation**, submitted to *Chem. Mater.*

Influence of crystallization state and microstructure on the chemical durability of mixed dioxides

<u>Laurent CLAPAREDE</u>, Nicolas CLAVIER, Stéphanie SZENKNECT, Nicolas DACHEUX
Renaud PODOR, Johann RAVAUX (ICSM/LME)
Philippe MOISY, Stéphane GRANDJEAN (DEN/DRCP/SCPS/LC2A)

The recycling of actinides into new fuel elements has emerged to economise uranium resources, reduce long-term radiotoxicity of waste, and increase resistance to proliferation. Such a strategy, initiated with the recycling of uranium and plutonium into MOX fuel obtained through dry chemical processes, could be improved by the initial precipitation of cations as low-temperature precursors such as oxalates. In this context, it appears important to evaluate the consequences of these changes on the microstructure of the final sintered dioxide pellets and on the subsequent modifications concerning dissolution processes. Consequently, this study aims to highlight the links between the crystallization state and the microstructure of dioxide materials and their ability to dissolve since several studies already showed that parameters such as density, porosity, grain size or density of grain boundaries could have a significant impact on the normalized dissolution rates.

As a first approach, model compounds with general formula $Ce_{1-x}Nd_xO_{2-x/2}$ were synthesized from oxalic precipitation then fired to obtain the corresponding oxides (300°C < T < 1100°C). The variation of the crystallization state of cerium dioxide versus the heating temperature was then evidenced through the average FWHM and was found to decrease strongly between 300°C to 700°C before it stabilized up to 1100°C. The dissolution of these solids was then studied in 2M HNO_3 at 60°C [47]. Whatever the temperature of the heat treatment, the variation of the normalized dissolution rates (R_L) exhibited two tendencies (fig. 1). First, the initial dissolution rate decreased inversely with temperature as a consequence of the progressive sample crystallization, thus of the increase of the cohesion energy. Conversely, the R_t value was not affected, subsequently to the formation of the gel at the solid/liquid interface.

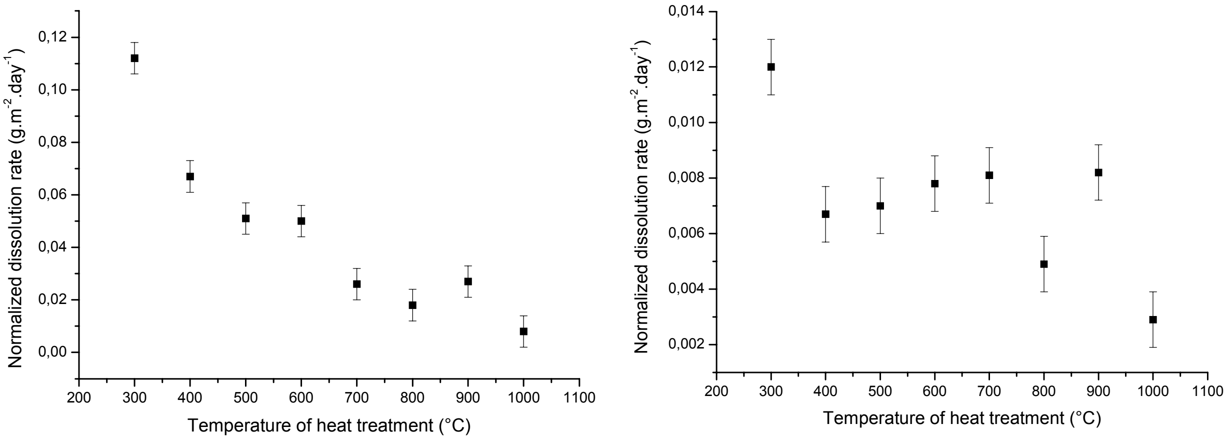


Fig. 1 : Variation of R_0 (left) and R_t (right) versus heating temperature

Several studies were then focused on the influence of the density of the pellets. Besides the normalization of the dissolution rates by the reactive surface, it appears that the less the density, the higher the normalized dissolution rate. These two results confirm that microstructure influences the chemical durability of the samples and should be considered carefully for the design of optimised mixed dioxides.

---

[47]. L. Claparède, N. Clavier, N. Dacheux, P. Moisy, R. Podor, J. Ravaux : **Influence of crystallization state over chemical durability of (Ce,Nd)O_2 mixed dioxides**, submitted to Acta Mater., 2010.

Thermodynamic of uranium/thorium-bearing mineral phases involved in the nuclear fuel cycle

Nicolas CLAVIER, Dan COSTIN, Fanny CRETAZ, Stéphanie SZENKNECT,
Nicolas DACHEUX
Christophe POINSSOT (DEN/DRCP – CEA Marcoule)

Uranium and thorium-bearing mineral phases, mainly including phosphates, vanadates and silicates, are of great importance for the nuclear fuel cycle[48]. On the one hand, new natural resources must be exploited with sustainable processes: it is thus essential to improve the knowledge concerning the thermodynamics describing the field of stability of such mineral phases, and to acquire the necessary kinetic data to optimize the ore treatment processes. On the other hand, thermodynamic equilibria are expected to control the concentration of released uranium in the field of the underground repository of spent fuel, particularly through the precipitation of silicate based phases, including $USiO_4$ coffinite.

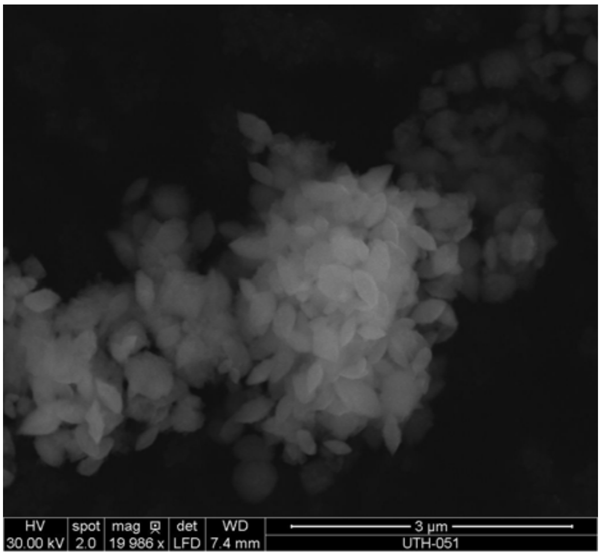


Fig.1 : SEM observation of $Th_{0.5}U_{0.5}SiO_4$ solid solution.

Our first work deals with the synthesis of thorium-uranium silicates *via* original hydrothermal methods. Several parameters such as pH, temperature, heating time or chemical composition were studied and allowed reporting for the first time optimal operating conditions for the synthesis of coffinite, as well as accurate unit cell parameters[49]. This experimental setup was also applied to the preparation of $Th_{1-x}U_xSiO_4$ ($0 \leq x \leq 0.75$) solid solutions (fig. 1). Since residual UO_2 and/or SiO_2 were frequently observed, the current studies aimed to prepare pure samples in order to investigate the behaviour of these solids *versus* temperature and to access the corresponding thermodynamic data such as K_S, $\Delta_R H°$, $\Delta_R S°$ and $\Delta_R G°$.

Such values were already determined in the case of phosphate-based phases involved in the front end of nuclear fuel cycle, *i.e.* autunite and torbernite through comparative approach investigating synthetic and natural samples. As an example, the solubility constant of torbernite was evaluated, either by under- or over-saturation methods, between 3×10^{-51} and 4×10^{-48} in the 20-90°C range, which corresponds to a standard enthalpy variation of about 100 $kJ.mol^{-1}$. Alteration tests are also undertaken to determine the dissolution rates of these solids as a function of various parameters such as temperature, pH, or complexing agent.

---

[48] M. Cuney et al.: Recent and not-so-recent develoments in uranium deposits and implications for exploration, 2009, Mineralogical Association of Canada Eds.

[49]. V. Pointeau, A.P. Deditius, F. Miserque, D. Renock, U. Becker, J. Zhang, N. Clavier, N. Dacheux, C. Poinssot, R.C. Ewing: **Synthesis and characterization of coffinite**, J. Nucl. Mater., 2009, *393*, 449.

7 – Scattering and diffraction

L’équipe est constituée de :
1 permanent CEA responsable d’équipe (O. Diat),
1 enseignant chercheur ENSCM (J. Cambedouzou)
1 technicien (B. Corso, CEA)

Deux équipements de diffusion de rayons X ont été mis en place dans le laboratoire transverse diffusion/diffraction à l'ICSM: un diffractomètre BRUKER (D8 Advance) multi-usage et un banc de diffusion aux petits angles assemblé par la société XENOCS.

Le premier est un équipement que l’on trouve sur catalogue ; il est utilisé avec une source au cuivre et un ensemble de collimation échangeables permettant d’accéder à une large gamme d'analyse structurelle à l'échelle atomique : l’identification de phases et la détermination de leur fraction volumique (composition chimique), la mesure de paramètres de maille, l’analyse de structure atomique en utilisant la méthode de Rietvelt, la détermination de taille de cristaux, des mesures en fonction de la température (four MRI pouvant atteindre 1600°C). Les géométries d’analyse peuvent être adaptées en fonction de l’échantillon (son absorption et sa quantité) pour travailler en réflexion ou transmission. Il est possible d’effectuer également des mesures de réflectivité afin de déterminer des profils de densité électronique perpendiculairement à des surfaces de couches minces. Toute cette instrumentation a été calibrée et optimisée pour répondre déjà à un nombre important d’analyses principalement dédiées à l’ICSM (600 échantillons mesurés). En effet, cet équipement a été mis en place au CEA début 2008, car il nous a été livré avant la construction du laboratoire et à ensuite été transféré au laboratoire fin 2009.
C’est un équipement qui est fortement exploité soit par les chercheurs de l’institut mais aussi par les équipes du centre de Marcoule. La demande dépasse largement l’offre et il est donc convenu de le doubler avec un équipement de diffraction soit du même type qui couvrerait principalement les demandes d’analyse en incidence rasante soit par une instrumentation de cristallographie de paillasse permettant de couvrir la simple demande de caractérisation d’échantillons.

Pour des études plus spécifiques et qui concernent des analyses structurales de systèmes colloïdaux, de fluides complexes, de couches minces absorbantes, de matériaux mésoporeux, tous ayant en commun la particularité de contenir des espèces à haut Z, un dispositif de diffusion aux petits angles non conventionnel et recouvrant petits et grands angles de diffusion (> à deux ordres de grandeur en vecteur d’onde) en une seule acquisition a été spécifié par l’équipe et réalisé par une société française XENOCS, ceci pour la première fois.
Ce dispositif utilisant une source au Molybdène (17 keV), entièrement automatisé et permettant de réaliser des expériences relativement simplement est opérationnel depuis le mois d’avril 2009. La mise en place de fentes anti-diffusantes de dernière génération (avec cristaux clivés en bord de fentes) simplifie considérablement l’alignement de ce type de montage et permet d’atteindre aisément $1.8.10^{-2}$ $Å^{-1}$ en q_{min}. En ce qui concerne l’environnement échantillon, nous avons mis en place un équipement porte capillaire thermostaté pouvant couvrir une gamme de température continue de -15 à 120°C, l’ensemble étant automatisé. Toutes les mesures en solution sont traduites en échelle absolu et peuvent être analysées en utilisant un logiciel gratuit et suivi par PSI et HMI : SASfit.

Un développement vers des expériences de diffusion aux petits angles en incidence rasante est possible et sera développé dés que possible.

Ces deux équipements complémentaires sont intégrés à une plateforme technique de Montpellier afin de pouvoir offrir un service à un maximum de scientifiques.

SAXS-WAXS @ 17keV

B. Corso, J. Cambedouzou, O. Diat

This exemple illustrated below shows the advantage of using the molybdenium wavelength; indeed SAXS/WAXS scattering data can be collected simultaneously on a large detector and give us some interesting results. As presented, lamellar phases are suitable multi-interfaces phases for studiing the amphiphilic properties of an extractant. And it was the objective of the A. Banc work for malonamide molecules (DIAMEX process) within an ACSEPT European project. These non ionic lamellar phases in which the extractant was inserted, were characterized by X-ray scattering. Spectra (Figure 1b) display the first and second order Bragg peaks at q_0 and $2q_0$, characteristic of the lamellar phase. Moreover, a wide peak observed at large Q-vector is analysed using two Gaussian signals roughly centred at q_w=19.8 nm^{-1} and q_b=14.4 nm^{-1} (see inset of Figure 1). Both contributions can be assigned to the correlation distances characteristic of the liquid order in the aqueous phase, and within the bilayers, respectively. The former is constant whatever the dilution.

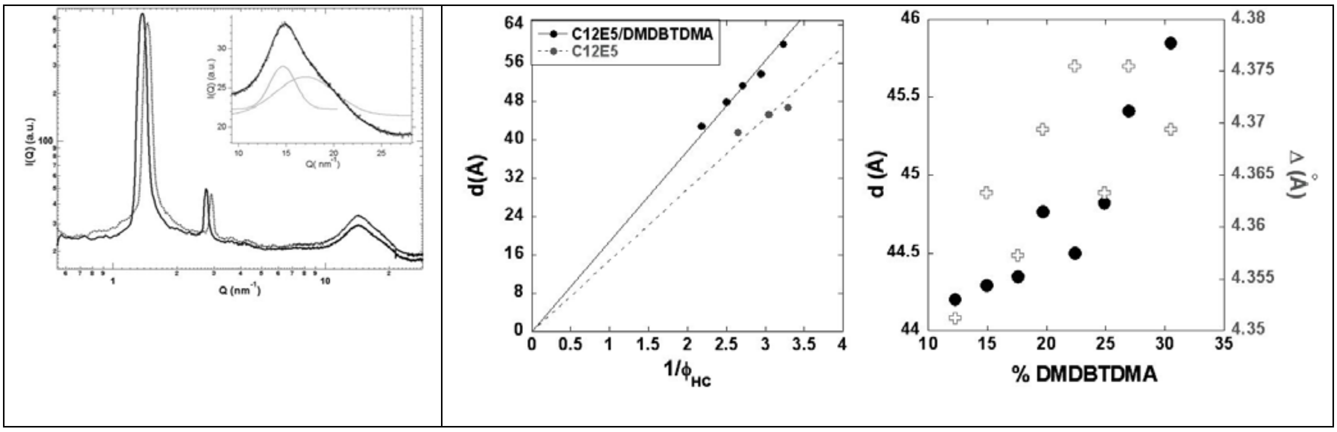


Figure 1. left: X-ray scattering spectra of the 80/20 (full line) and the 100/0 (dashed line) lamellar phases at $C_{12}E_5$/DMDBTDMA weight fraction ϕ=70% (inset: decomposition of the wide angle scattering part). Right: (a) Dilution laws of $C_{12}E_5$/DMDBTDMA 80/20 and 100/0 systems fitted according to equation 1. The range of ϕ_{HC} is fixed by the stability phase boundaries and shows that the lamellar phase containing the extractant molecule can be slightly more diluted. (b) Evolution of the lamellar periodicity (full dots) and the characteristic distance of the bilayer liquid order (empty crosses) versus the molar percentage of DMDBTDMA into the bilayers of a lamellar phase at ϕ=70%.

Defining *d* the periodicity of the lamellar phase obtained with the position of Bragg peaks $d=2\Pi/q_0$, ϕ_{HC} the volume fraction of DMDBTDMA and alkyl chains of $C_{12}E_5$ into the sample, and ϕ_{HC}. the hydrocarbon thickness of bilayers, figure 2a displays the evolution of lamellar periodicities as a function of the inverse of ϕ_{HC}. As polyoxyethylene groups were considered to be in the aqueous region of the phase, we fitted our data using the following dilution law - $d=\tilde{\delta}_{HC}\phi_{HC}$. For the $C_{12}E_5$/DMDBTDMA 80/20 system, the evolution of *d* appears more linear than for the 100/0 system. It attests to a more classical behaviour of the dilution law characterizing a lamellar phase with a constant thickness of the bilayers and weak bilayer undulations. Slopes of the linear fits in Figure 2 indicate the average hydrocarbon bilayer thicknesses: δ_{HC}= 14.0 Å for $C_{12}E_5$ (100/0), and δ_{HC}=18.8 Å for $C_{12}E_5$/DMDBTDMA 80/20. The polar head area of $C_{12}E_5$ deduced from the geometrical relationship $A_{C12E5}=2*V_{HC}/\delta_{HC}$ is 50.1 Å²/molecule, which is consistent with the data from the literature. On figure 1b, the increase in the lamellar periodicity and in the averaged distance within the bilayers ($\Delta=2\Pi/q_b$) with the extractant molar fraction are displayed for ϕ=70%. Both evolutions confirm the insertion of DMDBTDMA into the bilayers. The Δ values range from that of pure surfactant (Δ_S=4.35Å) towards that of pure extractant (Δ_E=4.58Å) in their liquid state respectively.

Ionic charge dynamics in hydrated functionnalized SBA-15 mesoporous silica investigated by solid state NMR.

Nicolas Bibent with S. Devautour-Vinot, G. Silly A. Mehdi , P. Gaveau, F. Henn, C. Reye, R.J.P. Corriu (Institut Charles Gerhardt, Montpellier), T. Charpentier (Laboratoire Claude Fréjacques, CEA Saclay)

Thanks to soft chemistry and more particularly to the Sol-Gel route, it is possible to obtain functionalized and organized mesoporous materials by direct synthesis [R.J.P Corriu & al, J. Mater. Chem. 12 (2002) 1355]. These new materials have received considerable attention regarding their numerous potential applications including catalysis and gas or liquid adsorption [A.Corma & al, Chem. Rev. 97 (1997) 2373; C. Sanchez & al, J. Chem. Rev 102 (2002) 4093]. From this point of view, we recently showed from conductivity measurements that water dynamic in hydrated functionalized SBA-15 is influenced by the nature of the groups at the pore surface (i.e -$C_3H_6PO(OX)_2$, X= Et, H, Li, Na, K, Rb), due to preferential interactions between the adsorbate and the functional walls of the porous silica [N. Fekkar-Nemmiche & al, *Eur. Phys J. Special Topics* 141 (2007) 45]. In this work, our aim is to obtain a better description of this phenomenon by investigating the dynamic of the functional groups linked at the pore surface of the hydrated SBA-15, using different NMR techniques. Solid-State NMR on various nuclei (^{7}Li, ^{23}Na, ^{1}H, ^{29}Si, ^{13}C and ^{31}P) demonstrated that the Sol-Gel route is fruitful to prepare expected functionalized SBA-15. Morover it is evidenced that when samples are subjected to water adsorption there is an increase of the mobility of organics groups (see figures).

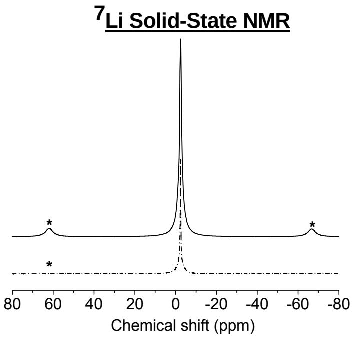


Fig1: (-) dried SBA-15 with -$C_3H_6PO(OLi)_2$, (...) hydrated SBA-15 with -$C_3H_6PO(OLi)_2$.

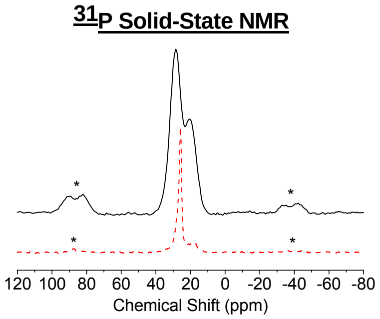


Fig2: (-) dried SBA-15 with -$C_3H_6PO(OLi)_2$, (...) hydrated SBA-15 with -$C_3H_6PO(OLi)_2$.

^{7}Li and ^{31}P (1D) MQ MAS NMR spectra of dried and hydrated SBA-15 with -$C_3H_6PO(OLi)_2$ groups are shown in figures 1 and 2, respectively. The disappearance of the spinning side bands points out that the anisotropy of the system decreases with water adsorption and a decrease of bands width is connected either to a complete hydration of the Li^+ ions or to an increase of the organic chains mobility or likely both phenomena.

This work will focus on a better knowledge of the role of surface functions on the trapping and transport of alkaline cations in the mesoporous silica.

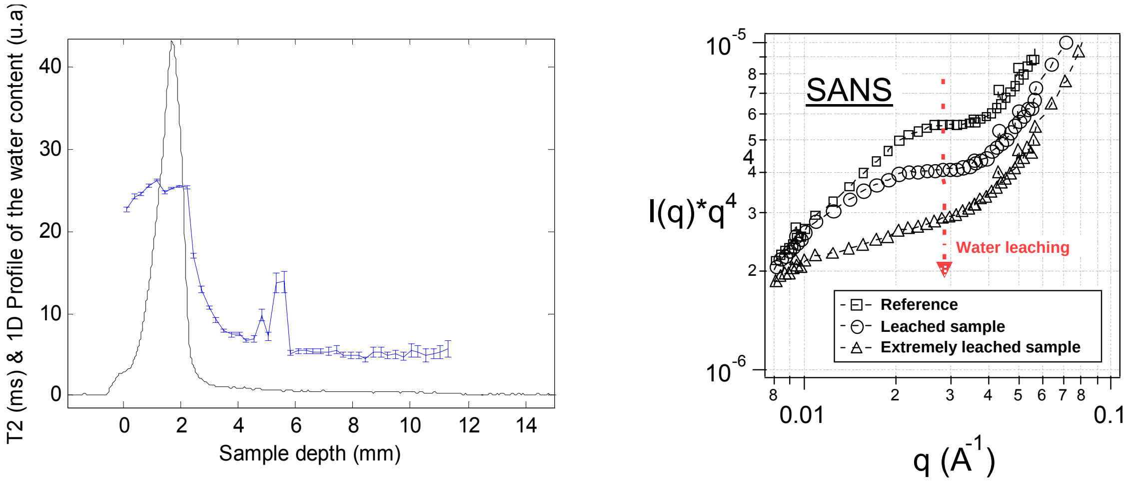
Bitumen matrix under lixiviation stresses: Study of the evolution the multiscale porosity

S. Le Feunteun, O. Diat – Collaboration A. Guillermo (UMR 5819 SPrAM, CEA Grenoble),
A. Poulesquen (DEN/L2ED CEA-Marcoule), A. Ledieu (DEN/LM2C CEA-Marcoule)

The main objective of this project is to characterize the evolution of porosity in inactive bituminized waste products (BWP) caused by variable exposures to external radiations or water. In France, bitumen is used since 4 decades as a container material for low/intermediate activity and long lifetime radionuclides. Industrial BWP are produced by continuous extrusion of 60 %w. of bitumen and 40%w. of salts (volumic ratio ~3:1), in which a very small fraction is lastly radioactive. The prediction of long term behaviour, needed for a sustainable management of BWP, is usually achieved by studying non radioactive-model materials in various conditions of ageing, mainly due to radiolysis and water leaching stresses.

Recent works have focused on the need for a better understanding on the impact of the swelling (and subsequent porosity), developing in both radiolytic and leaching conditions [Sercombe, C. et al, J. Nucl. Mat. 349 (2006) 96-106]. Our current aim is to refine the ageing modelling with a multiscale characterization of the relationship between the porosity evolution (e.g. the swelling) and the transport properties at the bitumen-salt interfaces, at the early stages of the alteration as well as the longer ones.

Low and high field ^{1}H-NMR are non-invasive techniques are used to provide global information on the leaching kinetics and on the topology of the porous zone at a micrometer scale by studying the water properties (e.g. quantity, relaxation times and diffusion properties) as it progresses through BWP. Moreover, 1D NMR-imagery is used in a similar approach to provide a spatial characterization of the samples structure along the depth of BWP. Such types of study constitute an original and promising approach to enhance our understanding on the creation and the evolution of the porous network as a function of ageing time. In parallel, SAS studies are conducted in order to relate the structural variations observed by NMR techniques to the specific surface and the topology of the interfaces at a smaller scale. Main results are (i) the strong effect of the initial matrix composition (i.e. soluble and/or insoluble salts) on the microstructure of the porosity and (ii) the evolution of water properties according to the leaching duration and the sample depth, which can be related to different scales of porous networks.



*Left: NMR 1D-profile of water and its transverse relaxation time as a function of sample depth. Right: Porod representation I(q)*q^4 versus q of the intensity of three samples of bitumen matrix as function of the leaching stages.*

1. “NMR imaging of water infiltration into mesoporous matrices”, S. Le Feunteun, O. Diat, A. Guillermo, R. Podor, in press.

What can we learn from combined SAXS and SANS measurements of the same sample?

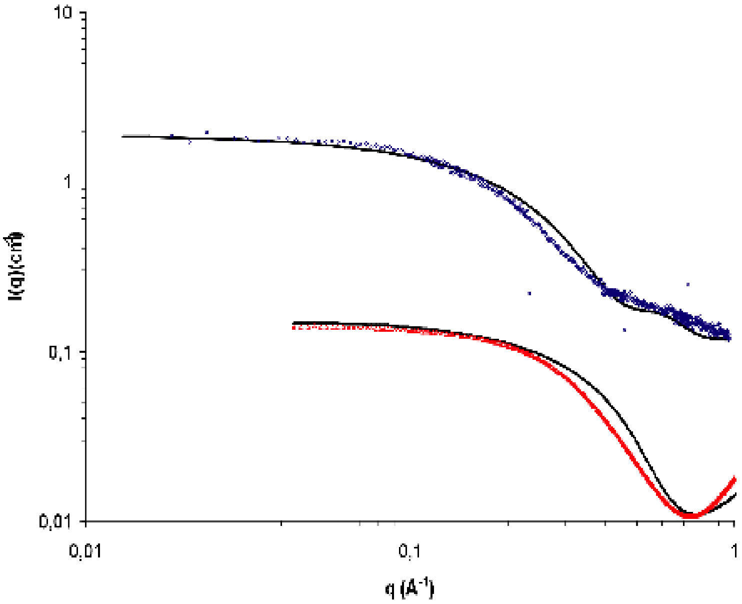
Thomas Zemb, Olivier Diat

An enormous increase in the micro-structural information is gained when one studies the same sample by SANS and SAXS on the *same* sample. Unique information of chemical systems or nanoreactors or heterogeneous solids can be obtained if intensities I(q) are determined and used on absolute scale as well as over a large q-window, thus extending to the « Porod limit » asymptotic range.

Comparing SAXS and SANS peak positions (when present) shifts versus volume fraction variation allows unambiguous identification of structure factors separated from underlying form factors. Absolute scale refers to scattering cross-section while resolution relates to the qmax/qmin ratio. Taking into account ”external” knowledge of molecular volumes in constrained fitting from explicit models gives better results on aggregation numbers as well as on interfacial thickness than considering only Patterson functions.

This general methodology applies to adsorption isotherms on surfactant films as well as equations of state quantifying colloidal interactions. Identification of the topological origin of swelling behaviour are made possible by using combined SAXS and SANS on the largest possible q-range. Best results using this general methodology up to now were obtained by considering data separated from background up to q_{max}= 0.6 Å-1 - 0.8 Å-1[1].

Fig.1: Scattered intensity in log-log and absolute scale in SANS (top) and SAXS (bottom) spectrum of the same reverse micelle, as obtained with a triple chain amphiphilic molecule, compared to models using simultaneous fitting with only one parameter, the area per molecule and the average aggregation number of the small w/o reverse micelles in thermodynamic equilibrium with monomers[2]. Solvent is deuterated heptane. Co-solubilized water contained in the core is determined separately by titration.



If osmotic coefficients and partial molecular volumes, this method is the only method to obtain parameter free aggregation numbers, areas per head-group and curvature of a molecular aggregate, including those responsible for ion separation in hydro-metallurgy.

---

[1] Thomas Zemb and Olivier Diat, Journal of Physics IOP: Conference Series 247 (**2010**) 012002

[2] *Erlinger C et al. , 1998 Solvent Ext. Ion Exch. 16 707 and Y. Meridiano, phD thesis 2010*

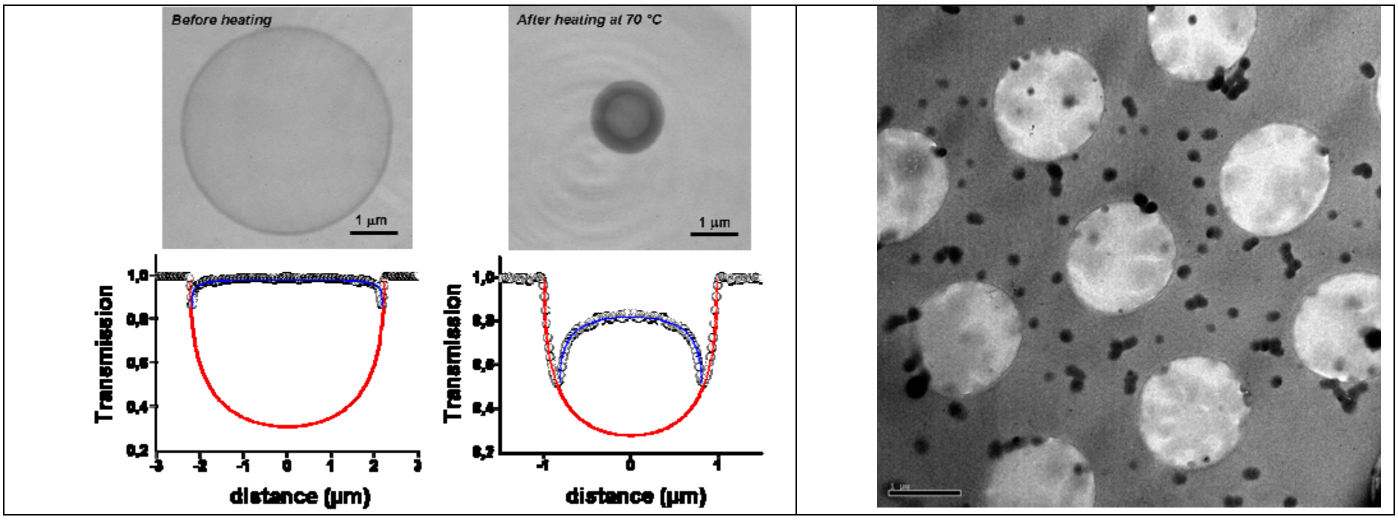
8 - Microscopies

L’équipe est constituée de :
1 permanent CNRS responsable d’équipe (Dr. Renaud Podor),
2 ingénieurs d’études CNRS (Sandra Maynadié, Johann Ravaux),
1 technicien CEA (Henri-Pierre Brau).

Les activités scientifiques réalisées dans le cadre du LME ont été menées par le biais de collaborations scientifiques. Les principaux résultats portent sur la caractérisation de la matière molle par des techniques classiques ou très innovantes, toutes délicates à mettre en œuvre, de part les difficultés de préparation des échantillons ou d’accès aux moyens expérimentaux. Ces objets sont caractéristiques des matériaux élaborés dans l’Institut, en vue de développement de nouvelles techniques de séparation.

Différents systèmes auto-organisés en solution aqueuse ont été caractérisés par microscopie électronique à transmission après congélation rapide de l’échantillon afin de figer l’ordre liquide, en collaboration avec le CSIC de Barcelone (laboratoire ICMAB). Les résultats ont permis de mettre en évidence l’auto-organisation de complexes de cobalt amphiphiles sous forme de nano-objets à différentes échelles ainsi que l’existence d’équilibres thermodynamiques entre ces objets. Ces résultats sont à ce jour inédits.

Par ailleurs, la mise en œuvre, inédite dans le domaine de la matière molle, de la microscopie de rayons X mous à transmission (technique associée aux grands instruments permettant l’observation directe d’objets en solution aqueuse avec une résolution de 20nm) a permis la caractérisation quantitative de microcapsules creuses à membrane polyélectrolyte. Ces objets présentent un fort potentiel dans le domaine du transport de principes actifs, des matériaux ou de la chimie séparative. Les résultats obtenus ont mis en évidence la façon dont ces objets se condensent lors d’un traitement thermique modéré. Lors du chauffage, la réduction du diamètre des capsules s’accompagne d’un épaississement des parois et de l’exclusion d’environ 50% de l’eau d’hydratation. Après chauffage à 90°C, des sphères pleines sont obtenues.



Left: Images obtained from microcapsules using soft X-ray microscopy. Together with the experimental transmission coefficient measured pixel by pixel. Modelisation (in blue, allows for the first time local analysis of water content in the walls at 10 nm scale (BESSY, Berlin, collaboration MPI-KG Potsdam). Right: Supramolecular aggregates produced by cobalt complexed by self-assembling molecules (COSAN), observed as dispersed by cryo-TEM (collaboration CSIC-Barcelona).

L’un des principaux faits marquant le début des activités du LME au sein de l’ICSM a été la réflexion menée autour de la définition du cahier des charges du MEB à acquérir. Les besoins des chercheurs de l’ICSM et les activités de recherches à mener en propre au LME, combinés avec les dernières innovations techniques dans le domaine de la microscopie électronique à balayage, ont conduit à opter pour l'acquisition d'un microscope électronique à balayage environnemental, équipé de 5 modules spécifiques :

- une chambre haute température couvrant la gamme 25-1500°C,
- un module dit STEM, de microscopie électronique à transmission,
- un étage Peltier permettant l'observation d'échantillons hydratés dans la gamme de température -20°C à 25°C, $0 < PH_2O < 4000$Pa,
- un module dit Wet-STEM permettant la réalisation de microscopie en transmission en mode environnemental,
- et un analyseur X à fort taux de comptage de technologie SDD.

Cet appareillage est opérationnel depuis le mois de février 2009 à l'ICSM. Les premières expériences qui ont été menées ont conduits à des résultats très innovants, d'ores et déjà valorisés par plusieurs publications scientifiques.

Autonomic Self-Repairing Glassy Materials

Renaud Podor
Daniel Coillot, François O. Méar, Lionel Montagne (Unité de Catalyse et Chimie du Solide - UMR-CNRS 8181 -Université Lille Nord de France)

A new process that enables glassy materials to self-repair from mechanical damage is presented in this paper. Contrary to intrinsic self-healing, which involves overheating to enable crack healing by glass softening, this process is based on an extrinsic effect produced by vanadium boride (VB) particles dispersed within the glass matrix. Self-repair is obtained through the oxidation of VB particles, and thus without the need to increase the operating temperature. The VB healing agent is selected for its capacity to oxidize at a lower temperature than the softening point of the glass. Thermogravimetric analyses indeed show that VB oxidation is rapid and occurs below the glass transition temperature. Solid-state nuclear magnetic resonance spectroscopy indicates that VB is oxidized into V_2O_5 and B_2O_3, which enable the local formation of glass. The autonomic self-healing effect is demonstrated by an in situ experiment visualized using an environmental scanning electron microscope. It is shown that a crack could be healed by the VB oxidation products.[1].

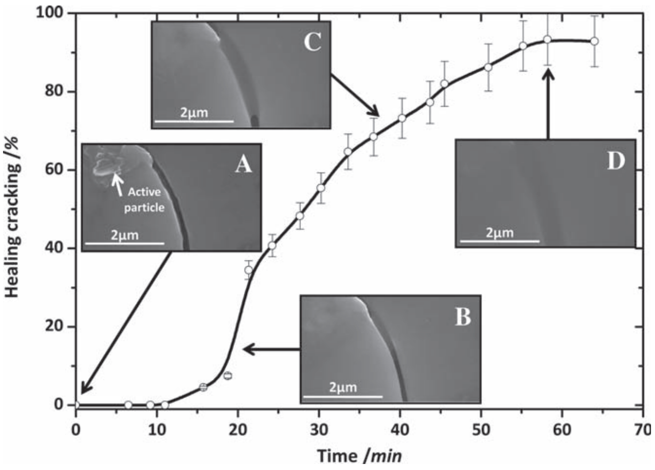


Fig.1: Healing ratio plotted as a function of heat-treatment duration and ESEM images of a glass + VB composite. A crack (0.5 µm wide, 15 µm long) was generated by Vickers indentation. An isothermal treatment at 700°C in air led to the oxidation of VB and formation of V2O5 and B2O3, which flowed and filled the crack. ESEM images (magnification × 7,500) were taken after: A) 0 min; B) 20 min; C) 40 min; and D) 60 min.....

In situ high-temperature healing of cracks in composites made of glass and vanadium boride (VB) particles was observed using an environmental scanning electron microscope equipped with a high-temperature chamber (HT-ESEM). HT-ESEM is an adequate tool for studying the self-healing property of these materials. The change in crack length as a function of redox atmospheric conditions is reported. No self-healing behaviour was observed under reducing conditions, while a complete and rapid healing of the cracks was measured under oxidizing conditions. HT-ESEM image analyses enabled the monitoring of the healing effect. The self-healing mechanism was identified as a consequence of the VB active particles oxidation and subsequent pouring of fluid oxides into the cracks. These innovative composites offer an interesting potential in the domain of solid oxide fuel cell sealants[2].

---

[1] D. Coillot, F. O. Méar, R. Podor, L. Montagne **Autonomic Self-Repairing Glassy Materials**, Adv. Funct. Mater. 2010, In press.

[2] D. Coillot, R. Podor, F.O. Méar, L. Montagne **Characterisation of self-healing glassy composites by high-temperature environmental scanning electron microscopy (HT-ESEM)**, J. Electron Microsc., 201059(5) 359-366

Dynamic aspects of ceramic sintering

<u>Renaud Podor,</u> Nicolas Clavier, Johann Ravaux, Laurent Claparéde and Nicolas Dacheux

The solid state sintering involves two major phenomena occurring simultaneously: pore shrinkage and grain growth. The microstructure evolution of a solid during sintering is related to the kinetics of change in the grain size and pore distributions. The modifications of these distributions are directly linked to atom and pore mobilities (and more generally mass transfer) that generates grain boundary, intergranular pores and intragranular pores displacements. Even if numerous models were developed to predict these processes on the basis of diffusion equations and energy minimisation, there is a lack of experimental data in this domain. The recent development of the environmental scanning electron microscope (ESEM) equipped with a high temperature device offers the possibility to directly observe in situ the sintering mechanisms of ceramics at the sub micrometer scale[1].

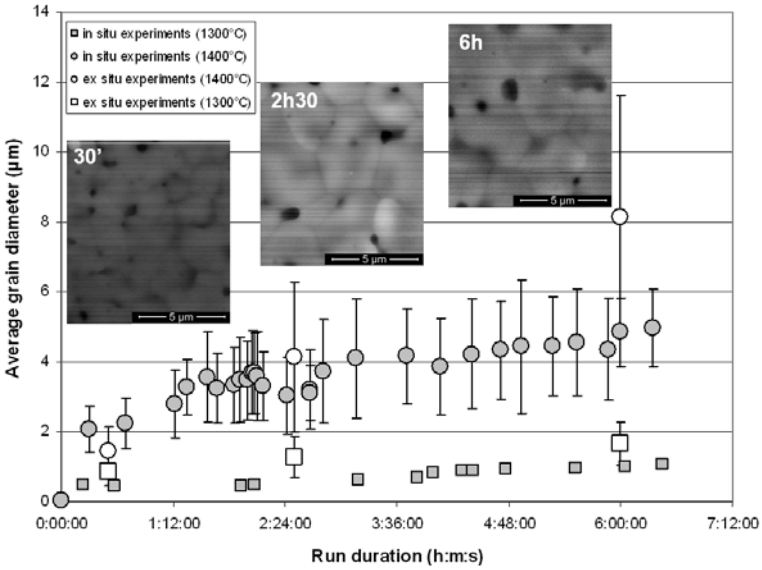


Fig.1: Mean grain diameters determined at 1300°C and1400°C from 25µm X 25µm in situ HT-ESEM images compared to the data obtained from ex situ experiments. Corresponding in situ images recorded at T=1400°C for 30', 2h30 and 6h heat treatment are also reported.

The CeO_2 sintering was studied directly in the ESEM chamber from 1000 to 1400°C. The morphological modifications of a single grain population were observed for 6 hours and good quality images were recorded. Kinetic parameters are extracted from the obtained image series. The local grain growth determined from the single population studied in situ was compared to the general grain growth obtained by the classical ex situ technique in order to validate the use of HT-ESEM for sintering study (Fig. 1). From the image series recorded at T=1400°C, kinetic parameters are derived. The grain boundary velocities were determined. They are ranging between 0 and 110µm.h^{-1}, with a mean value of 7µm.h^{-1}. The intra-granular velocities are ranging between 0.4 and 1.2µm.h^{-1} and strongly depend on pore diameters: the smaller the pore diameter, the faster the pore velocity. The time that is necessary to fill a pore that arises at the sample surface was determined as a function of pore diameter. The obtained values are ranging between 12 and 210 minutes. Their dependence with the pore diameters is established.
This theme is developed with the LIME team.

---

[1] R. Podor, N. Clavier, J. Ravaux, L. Claparède, N. Dacheux **Dynamic aspects of ceramic sintering. High temperature environmental scanning electron microscopy (HT-ESEM) in situ sintering of ceria at 1400°C**, J. Eur. Ceram.Soc. 2011, Submitted.

Study of cement phases for radionuclide wastes conditioning

Johann Ravaux, Adel Mesbah, Jean-Baptiste Champenois, Céline Cau-dit-Coumes (CEA DEN/DTCD/SPDE Bagnols sur Cèze)

Cement phases are potentially good candidates to conditioning radionuclide's wastes (as ^{36}Cl and ^{14}C) occurring from the old nuclear power reactors "UNGG". The scientific collaboration between both laboratories has been focused on two themes : the analysis of particular cement phases and the study of hydration of calcium sulfoaluminate cement by in situ ESEM experiment.

Two cement phases of the AFm family (that is known to present good capacities to bind chloride anions) have been particularly studied by XRD and EDS for structural and compositional determinations. The crystal structure of Kuzel's salt with general formula $3CaO\cdot Al_2O_3\cdot ½CaSO_4\cdot ½CaCl_2\cdot 11H_2O$ has been successfully determined. It belongs to the layered double hydroxide (LDH) large family. Its structure is composed of positively charged main layer $[Ca_2Al(OH)_6]^+$ and negatively charged interlayer $[Cl_{0.50}\cdot(SO_4)_{0.25}\cdot 2.5H_2O]^-$.[1]. Chloride to carbonate substitution in AFm phase of general formulae $[Ca_2Al(OH)_6]\cdot[Cl_{1-x}(CO_3)_{x/2}.(2+x/2)H_2O]$ has been characterized by studying 12 powdered samples. It forms one stable rhombohedral $[Ca_2Al(OH)_6]\cdot[Cl_{1-x}.(CO_3)_{x/2}.(2+x/2)H_2O]$ solid solution with $0.25 \leq x \leq 0.95$. A second metastable monoclinic $[Ca_2Al(OH)_6]\cdot[Cl_{1-x}\cdot (CO_3)_{x/2}\cdot (2+x/2)H_2O]$ solid solution has also been identified in a less extended x domain[2].

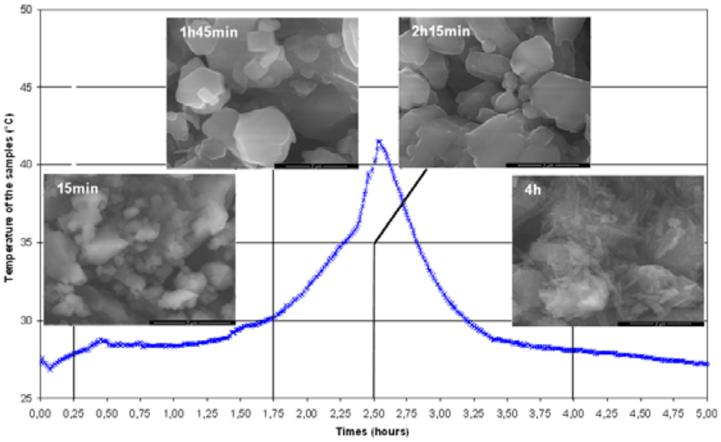


Figure 1: morphologic evolution of a CSA cement paste linked to the temperature elevation among the paste during its hydration

Calcium SulfoAluminate cements (CSA) are of great interest since their production needs less energy and emits less CO_2 than traditional Portland cement. Moreover, the two main hydration products of CSA cements, ettringite and calcium monosulfoaluminate, can incorporate numerous ions into their crystal structures, making it an ideal candidate for nuclear waste immobilisation. To further understand the hydration mechanisms of these new hydraulic binders, *in situ* ESEM study was carried out. CSA clinker, mixed with 10% of gypsum, was hydrated with a w/c ratio of 0.8 under stirring conditions to exhibit phenomena. Under these conditions, important changes of morphology were observed during the first fifth hours after the beginning of hydration. It was clearly observed that a transitory phase precipitates first and then re-dissolves to give mainly ettringite and amorphous aluminium hydroxide. This step of re-dissolution is responsible in this case for the second elevation of temperature observed during CSA hydration.[3]

---

[1] A. Mesbah, M. François, C. Cau-dit-Coumes, F. Frizon, Y. Filinchuk, F. Leroux, **J. Ravaux** and G. Renaudin **Crystal structure of Kuzel's salt 3CaO•Al2O3•½CaSO4•½CaCl2•11H2O determined by synchrotron powder diffraction** *Cement and Concrete Research* Submitted.

[2] A. Mesbah, C. Cau-dit-Coumes, F. Frizon, F. Leroux, J. Ravaux and G. Renaudin **A new investigation of the Cl^--$CO3^{2-}$ substitution in AFm phases**, J Am. Ceram. Soc.. 2010, In press

[3] J.B. Champenois, C. Cau Dit Coumes, F. Bart, J. Ravaux – to be published

Quantitative soft X-ray microscopy at the 10 nm scale

Ch. Dejugnat, Th. Zemb,
K. Kohler and H. Moehwald (Max Planck Potsdam), P. Guttman (BESSY II, Berlin)

Quantifying chemical content of water, i.e. access to local osmotic pressures indepedently of the Laplace terms is of major importance in order to be able to model supramolecular assemblies[1]. We have demonstrated that images obtained by soft X-ray microscopy of spherically symmetric objects can be desmeared in order to obtain the water content in pixels of the order of 10 nm.

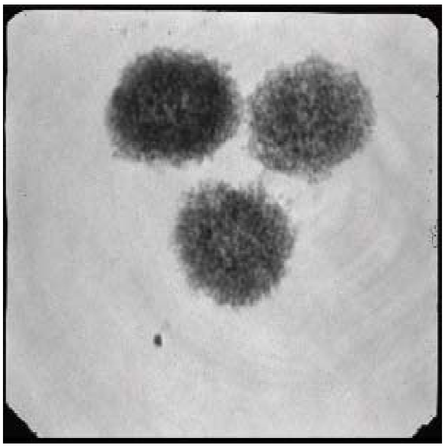


Fig.1: Raw image obtained with a 16bit depth detector in the image plane of the soft X-ray microscope at BESSY. The objects observed in situ at 20 nm resolution are hollow capsules of PSS/PHH containing metallic nanoparticles which have been synthetized in the walls

This radically new analytic tool has been used to follow the local water content of microcapsules. of polyelectrolyte complexes for the first time a non invasive analysis of the water content in loose supramolecular assemblies of polyelectrolytes. The water content has not been measured *inside* the capsules but the amount of water contained in the wall has been measured, following the polyelectrolyte wall ageing under controlled conditions.[2]

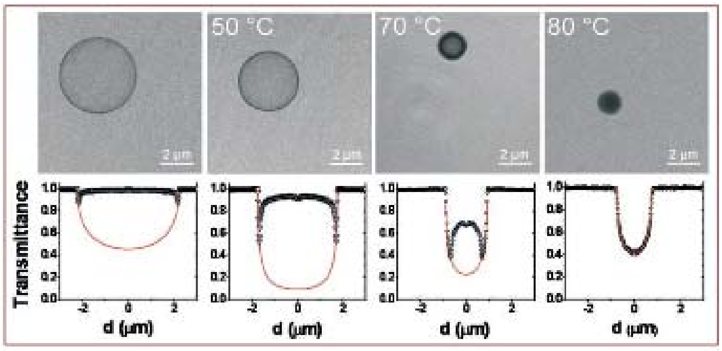


Fig.1: Soft X-ray transmission micrographs of differently shrunk (PDADMAC/PSS)4 capsules after heating for 20 min in water and the corresponding fitted transmittance profiles giving access to quantitive values of the water content decreasing during ageing; This ageing is the key for controlling the permeability of capsules used for controlled encapsulation.

---

[1] Zemb, Th.; Blume, A. "Self-assembly weak long-range interactions at work." Current Opinion in Colloid & Interface Science (2007), 12(3), 99-100.

[2] Koehler, Karen; Dejugnat, Christophe; Dubois, Monique; Zemb, Thomas; Sukhorukov, Gleb B.; Guttmann, Peter; Moehwald, Helmuth. " Soft X-ray Microscopy To Characterize Polyelectrolyte Assemblies. " Journal of Physical Chemistry B (2007), 111(29), 8388-8393.

9 - Mesoscopic Modelling and Theoretical Chemistry

The objectives of the emerging theory group of ICSM are modelling of complex systems at the intermediate "nano" or "meso" scale.

At the microscopic scale, atomic modelling can describe the molecular properties. Unfortunately, the latter cannot be applied directly for numerous multi-scales materials because they are too heavy to be applied at intermediate scales. Thus, the theoretical treatment of such systems is especially challenging. Mesoscopic modelling provides an alternative method to bridge the gap between macroscopic descriptions and the microscopic world. Thanks to specific coarse-graining procedures, it is possible to model complex systems by taken into account the complex structure by averaging step by step the complex structure of the material.

In the context of ICSM chemistry, such mesoscopic descriptions can be applied to many open issues:

- Modelling of liquid-liquid extraction. The latter can be seen as the dehydration and transfer of cations from a concentrated ionic solution to the core of reverse micelles. The various free energy contributions can be estimated at different level of modelling.
- Modelling of ions adsorbed on a macroscopic interface, *i.e.* as ions adsorbed on emulsion droplets. These emulsions are made from oil-rich micro-emulsion and excess dispersed on concentrated ionic solutions (or the reverse).
- Modelling of ions adsorbed in the pores of mesoporous silica. This mesoscopic approach is especially relevant because of the complex porosity.

Altogether, at least for some selected particular systems, a multiscale approach will lead to an uninterrupted chain of parameters inferred from atomic scale first-principles modelling (in which the electronic structure is taken into account) to macroscopic descriptions of engineering. This justifies the role and the significance of mesoscopic and multi-scale modelling.

Furthermore, even if mesoscopic descriptions are by themselves unable to get from first-principles particular features, they can handle them whenever useful input from microscopic models or experimental observation is provided. Mesoscopic models are of first importance in the description of extraction / separation and storage / migration processes of actinide or nuclear wastes.

Hydrophobic to hydrophilic transition in a realistic model of porous amorphous silica

B. Siboulet, J.-F. Dufrêche,
P. Turq (Université Pierre et Marie Curie et ICSM),
B. Coasne (Institut Charles Gerhardt)

Realistic models of amorphous silica surfaces with different silanol densities are built using MonteCarlo simulated annealing. Water silica interfaces are studied in terms of energy interaction maps, adsorption isotherms, self-diffusion coefficients, and Poiseuille flows. Results exhibit a hydrophilic to hydrophobic transition as the amorphous surfaces vary from highly hydroxylated to purely siliceous.

Porous silicas are both of fundamental and practical interests as they exhibit a large specific surface and a porosity network that can be tuned precisely (pore size and morphology). Moreover, their surface can be functionalized with a variety of molecules and groups. As a result, porous silicas find important industrial applications in catalysis, phase separation, storage and separation of radionuclides, nanofiltration, drug delivery, medical diagnosis, etc. An important parameter that controls most of these processes is the silanol surface density. Such polar groups are hydrophilic and control the adsorbate/ surface interaction strength and the adsorbate mobility. The silanol density can be tuned by different procedures such as heating or irradiating the silica sample. For instance, the observed release of hydrogen from irradiated silicates is attributed to the radio-induced emission of protons from the surface silanol groups. Understanding the role played by these groups in the hydrophilic or hydrophobic nature of silica requires estimating the thermodynamics and dynamics of water adsorbed or confined in realistic models.[1]

Our realistic slit pore models of amorphous silicas allow connecting the surface chemistry of materials and their affinity for water. The thermodynamics and dynamics of water confined in the materials with various surface chemistries show a hydrophobic to hydrophilic transition as the silanol density increases. The results provide a consistent picture of the hydrophobicity and hydrophilicity of siliceous materials. Silanol free surfaces are hydrophobic. This indicates that the hydrophilicity of real amorphous silica is due to its defects and not to its amorphous nature. On the other hand, in agreement with experiments, amorphous surfaces with non negligible silanol densities are hydrophilic. Such differences could be evidenced in the case of irradiated glasses by experimental techniques based on electrokinetic phenomena or dielectric spectroscopy.

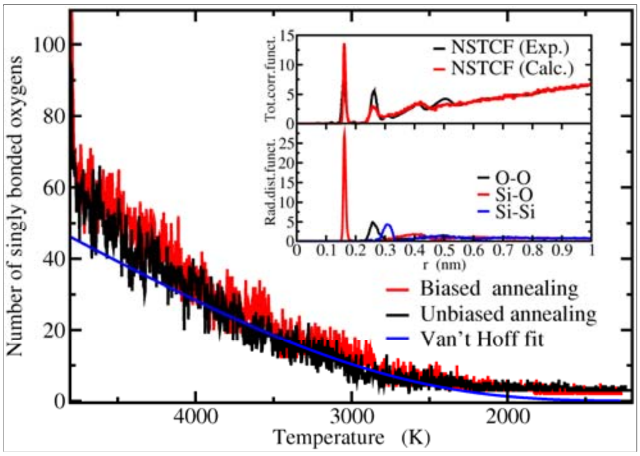


Figure 1. We build a silica slit pore with Monte Carlo annealing. Defects are singly bonded oxygen atoms. They appear on surface and are highly hydrophilic. For this reason, their number should be reduced to minimum; if a hydrophobic surface is to be found. Indeed, as temperature decreases, the number of defects decreases to 0. We use BKS potential for this surface preparation. Neutron Scatering Total Correlation Functions, calculated and experimental, are in fair agreement. (there are no silanol at this point.)

---

[1] Hydrophobic to hydrophilic transition in a realistic model of porous amorphous silica, Siboulet B., Dufrêche J.-F., Turq P., Coasne B. (Insitut Charles Gerhardt)

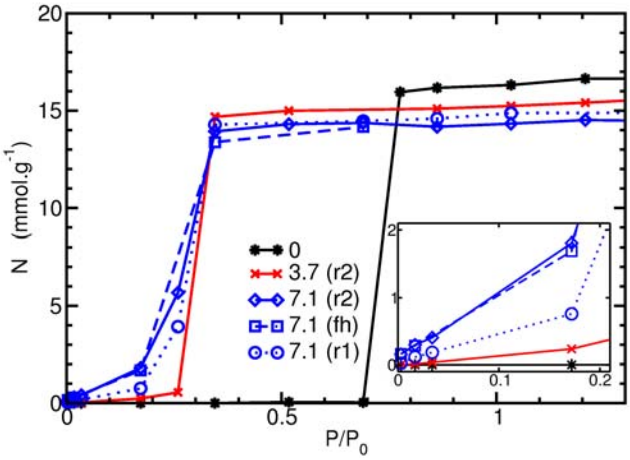
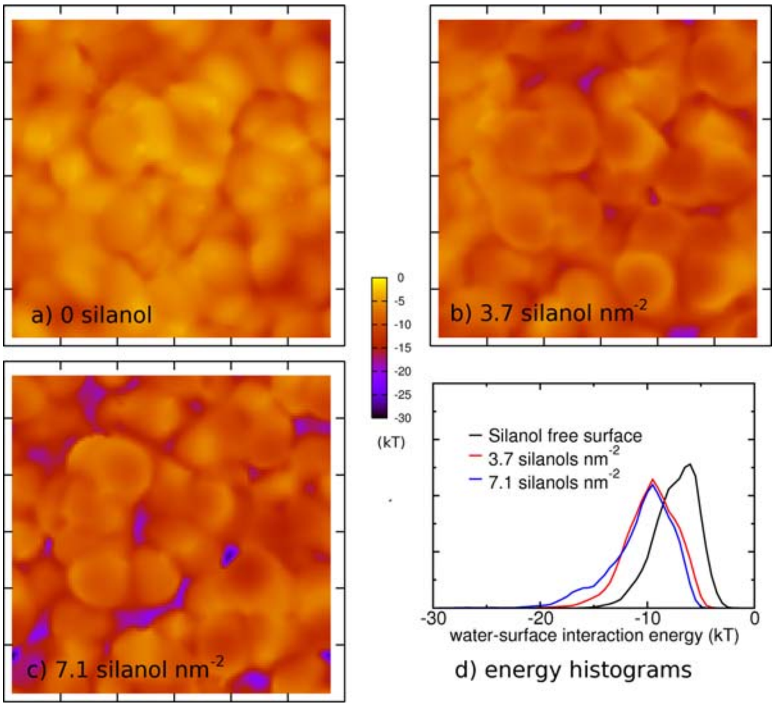


Figure 2. The number of silanols is varied from 0 to 7.1. nm^{-1}. (This surface density is very high). Silanols are progressively added on the silanol free surface. For each addition, the surface is relaxed so that atoms take natural positions. The structure results in tetrahedra. We use two types of relaxation, r1 and r, r2 being specially tailored so as to reduce the number of inter-silanol H-bonds, which are unphysical. The hydrophobic to hydrophilic transition occurs between 0 and 3.7 silanols nm^{-2}, and is spectacular.

Figure 3. The interaction of a single water molecule with surface is mapped with the 3 silanol surface concentrations. As the silanol density increases, the interaction increases. On the above adsorption plots, the transition from hydrophobic to hydrophilic appears between 0 and 3.7 silanols nm^{-2}. Consistently, water surface interaction comes below -17 kT, which is the water vaporization energy, within the same silanol density range. Adsorption (figure 2), water surface interaction (this figure), diffusion coefficients and Poiseuille flows (figure 4) give a consistent image of this transition



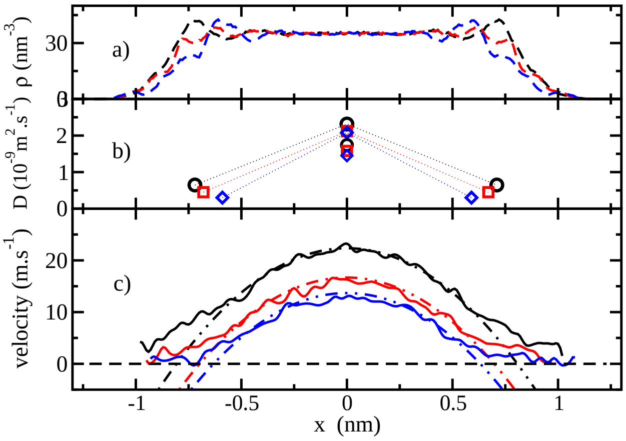


Figure 4. Density, diffusion coefficients and Poiseuille flows for all surfaces. As the silanol density increases (black: 0, red: 3.7, blue: 7.1 silanols nm^{-2}), diffusion coefficients reduce by a factor 2.2. Slippage appears for hydrophobic surface, with a slip length estimated to 0.3 nm. Observed differences have an impact on surface driven phenomena and can lead to dramatic enhancement of Darcy flows and electrokinetic phenomena.

Multi-Scale modelling of electrolyte solutions

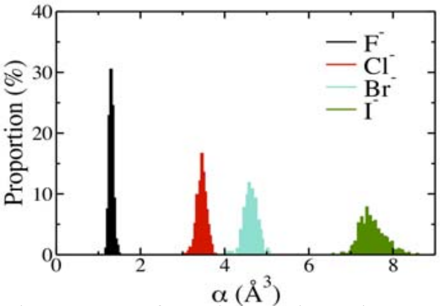
Jean-François Dufrêche, John Molina, Pierre Turq, Mathieu Salanne (PECSA/Paris 6)
Magali Duvail (DEN/DRCP-Marcoule), Ph. Guilbaud (DEN/DRCP-Marcoule)

The study of electrolytes in solution has relied heavily on computer simulations, which have allowed us to better understand the microscopic and macroscopic properties of these systems, complementing the available experimental techniques. The different length and time scales that need to be considered, in order to obtain a complete description of electrolyte solutions, require distinct levels of description: from ab-initio quantum calculations, to classical molecular dynamics simulations, and finally to simple implicit solvent descriptions. We attempt to develop a unified (consistent) muli-scale description of electrolyte solutions:

1. Classical polarizable force fields, suitable for ions in aqueous solution, were parametrized using results obtained from quantum ab-initio calculations.
2. Integral equation theories were used to derive solvent averaged potentials from the structural information obtained from classical Molecular Dynamics simulations. These solvent averaged potentials were then used in implicit solvent Monte-Carlo simulations to determine the ion activities.
3. Liquid perturbation theory was used to determine the best implicit solvent description in terms of charged hard-sphere type models, for which approximate (but accurate) analytical solutions for the thermodynamic and structural properties are known.

Until recently, most polarizable potentials were parametrized by adding a polarization term to existing non-polarizable classical force fields, using scaled gas phase values for the polarizabilities of the ions. In order to adequately represent the dipole polarizabilites of ions in condensed phases, we have studied the linear response of the Maximally Localized Wannier Functions, obtained from ab-initio calculations (within density functional theory) for a trajectory of an ion in water. For most of the monoatomic cation considered (Na+, K+, Rb+, Mg2+, Ca2+, Sr2+), the condensed phase polarizabilities are the same as those for the gaseous phase; however, for Cs+ and a series of anions (F-, Cl-, Br-, I-) environmental effects considerably reduce their polarizabilities in aqueous solutions[1]. Once the values of the polarizabilities are known, a force-fitting technique can be used to parametrize more accurate polarizable potentials to be used in classical Molecular Dynamics simulations.

Figure 1: Distribution of the isotropic polarizabilities of halide ions in liquid water, obtained from ab-initio simulations by studying the linear response of the Maximally Localized Wannier Funcions to an applied external electric field.



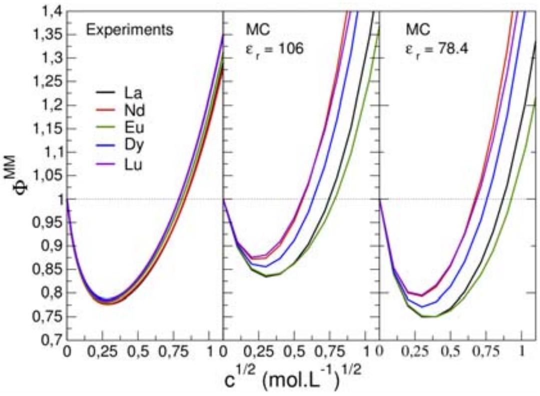
Classical Molecular Dynamics simulations provide a convenient way of studying the microscopic properties of ions in solution, but obtaining macroscopic thermodynamic properties, such as activities and osmotic coefficients is notoriously difficult. To reduce the complexity of the system, coarse-grained, implicit solvent models are derived from the microscopic structure of the fluid. We use the hypernetted-chain integral equation to obtain solvent averaged effective potentials that accurately describe the ion-ion interactions in solution, without any explicit reference to the solvent. These effective potentials are then used in implicit-solvent Mont-Carlo simulations to study the thermodynamic and structural properties of the fluid. This coarse-grained technique has been applied

---

[1] Molina, John; Lectez, Sébastien; Tazi, Sami; Salanne, Mathieu; Dufrêche, Jean-François; Roques, Jérôme; Simoni, Eric; Madden, Paul; Turq, Pierre. "Ions in solutions: determining their polarizabilities from first-principles". *Journal of Chemical Physics* (2010), 133 (accepted for publication).

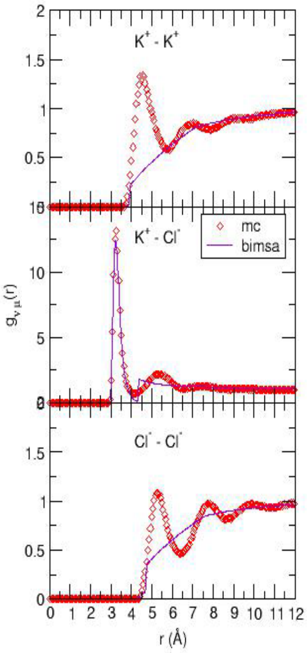
to study simple 1-1 electrolytes in solution, as well as more complicated 3-1 electrolytes such as lanthanoid-chloride aqueous solutions. The agreement with the atomic and coarse-grained descriptions is found to be excellent[1,2].; however, considerable discrepancies are found when comparing to experimental data, due to the fact that the underlying atomic force-fields are generally parametrized to reproduce ion-water properties, and the ion-ion correlations are not necessarily properly described. Thus, the use of coarse-grained models provides an efficient method for fine-tuning atomic force-fields to experimental data.

Figure 2: Osmotic coefficients in the McMillan-Mayer frame of referenced obtained from coarse-grained atomistic simulations of a series of lanthanoid-chloride solutions as a function of the square root of the concentration. The correction of the dielectric permittivity (from 106 to 78) of the water model improves the agreement.



While the use of implicit-solvent models in Monte-Carlo simulations reduced the complexity considerably, with respect to an atomistic description of both solvent and solute particles, it still requires a relatively costly numerical solution. When an explicit expression for the properties of the fluid (thermodynamic, structural, or dynamic) is needed, these methods cannot be used. In these cases, one resorts to the use of some simple physical model for which the solution is known. For electrolyte solutions this is the primitive model, which describes the system in terms of charged hard-spheres moving in a dielectric background. The MSA solution (and its improvements) to this model has been extensively used, but the parameters of the model have usually been fitted to reproduce some experimental data. We have shown that it is possible to use Liquid Perturbation theory to derive the best possible representation from just the effective ion-ion potentials[3]. Thus, we are able to go from an explicit solvent atomistic description, to an implicit solvent description for which exact results are available. It is important to note that no fitting parameters are used, the outputs at one level of our multi-scale modelling are used as inputs for the next level.

Figure 3: Radial distribution functions for a solution of K+ - Cl- at c=0.5 mol/L obtained from Monte-Carlo simulations using coarse-grained ion-ion potentials and from the BIMSA solution for a system of sticky hard-spheres given by Perturbation Theory calculations. The MC results take days to compute, the BIMSA results only require a few minutes.



---

[1] Molina, John; Duvail, Magali; Guilbaud, Philippe; Dufrêche, Jean-François. "Coarse-grained lanthanoid chloride aqueous solutions". *Journal of Molecular Liquids* (2010), 153, 107-111.

[2] Molina, John; Dufrêche, Jean-François; Salanne, Mathieu; Bernard, Olivier; Jardat, Marie; Turq, Pierre. "Models of electrolyte solutions from molecular descriptions: The example of NaCl". *Physical Review E* (2009), 80, 06513.

Weak adsorption of salts and oil-water buyancy of peptides: Is the concept of amino-acid intrinsic hydrophilicity self-consistent?

Ch. Déjugnat, Thomas Zemb et Jean-François Dufrêche

We show that an amphiphilic hexapeptide has been used as a model to study how specific ion effects can tune the hydrophilic/hydrophobic balance and induce phase diagram modifications. N-merisation of the peptide has been studied in water and octanol as well as its water/octanol partition: role of H-bonds and adsorbed ions are evidenced. In the presence of electrolytes, competitive interactions are involved: "battle for hydration water" makes the peptide more hydrophobicdue to salt addition in the water phase, whereas charging via chaotropic ion adsorption can increase hydrophilicity. These interactions also strongly affect phase separation upon heating (cloud point). These effects can be rationalized considering the salt-decorated peptide as a van der Waals fluid. Weak salt adsorption is the motor of oil-water buoyancy, in the thermodynamic approach of "hydrophilicity", as proposed by Tanford.

Increasing further the salt concentration induces a phase separation by coacervation. This coacervation can be modelled as due to dispersion force, partially quenched by adsorption of ionic species. The energy associated to adsorption of chaotropic ions is measured and compared to the buoyancy effect. The result questions the concept of intrinsic hydrophilicity, which should be dependent of the nature of the salt dissolved in the water, i.e. the nature of the "buffer".

In summary, the weak interaction responsible of salt adsorption leads to charges of the order of one par peptide and energy associated is of the same order than water-solvent transfer of this type of amphiphilic peptide considered as a bio-inspired "extractant" [1].

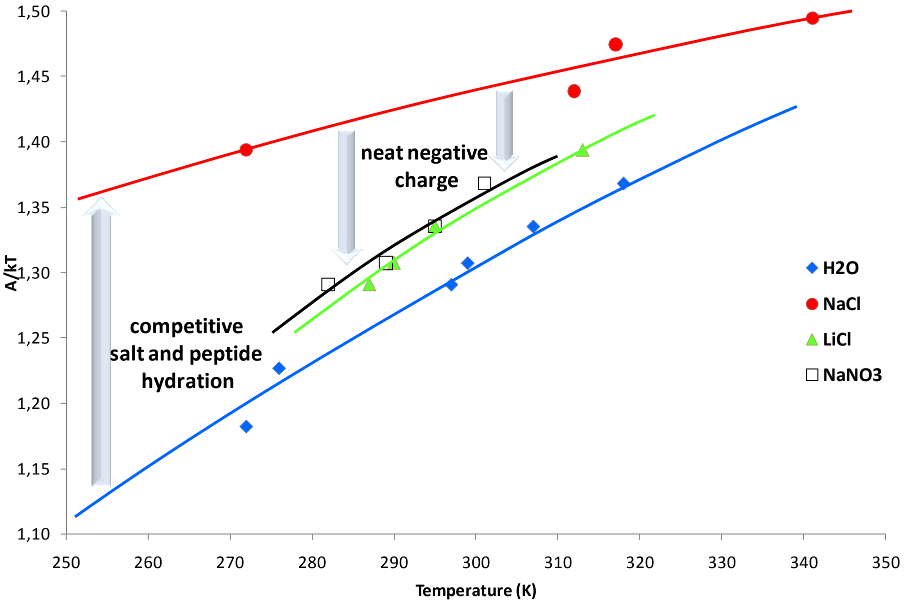


Figure 1: Figure: The apparent Hamaker A/kT constant driving towards coacervation decreases with temperature; due to weak adsorption of salt. The "neutral" salt is always salting-in, while specific ion adsorption-desorption induces partial quenching of the attraction due to electrostatic repulsion: Hydrophilicity of this hexapetide is in this "buffer" dependant.

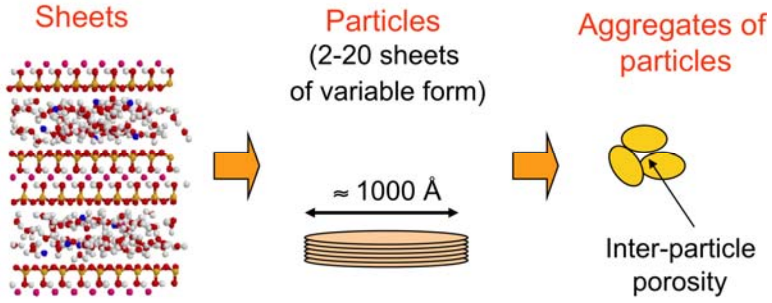
---

[1] Ch. Déjugnat, Jean-François Dufrêche andThomas Zemb " Ion-driven hydrophilic/hydrophobic balance of a short amphiphilic peptide in water and in octanol ", submitted.

A multi-scale approach to ion transport in clays.

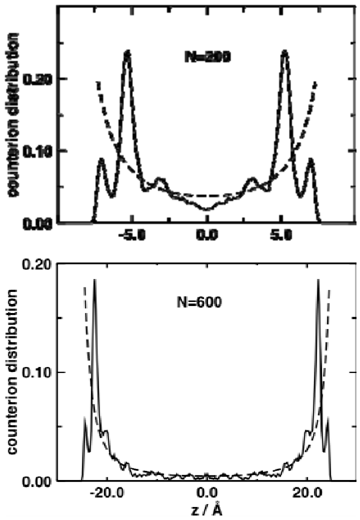
P. Turq (UPMC), in collaboration with B. Rotenberg, V. Marry, E. Giffaut and J-F Dufrêche (LI2C- Paris)

A multi-scale approach has been developed for the diffusion of ions in montmorillonite clays. This media is microscopically a charged lamellar system for which water molecules and ions are confined between charged sheets. Nevertheless, at the macroscopic scale this structure does not hold anymore and the system is made of different porosities.



Schematic description of montmorillonite clays from the (lamellar) atomic scale to the macroscopic media with various porosities.

A multiscale study has been carried out for the transport of ions in such a system. At the atomic level of description, Monte-Carlo simulations and molecular dynamics have been used. These results have been compared to the continuous description, based on hydrodynamics and non-equilibrium thermodynamics for hydrated clays. The results for the ion distributions represented in the figure show a good agreement even for small intersheets distances



Ion distributions between two sheets obtained from atomic (solid line) and mesoscopic (Poisson-Boltzmann, dashed line) models for two interlayer distances, 17 Å (upper) and 52 Å (bottom). The difference comes from oscillations, which are reminiscent of the molecular structure of water. Similar comparisons have been performed for the hydrodynamics, and they reveal a good agreement if corrects boundary conditions are taken into account

An alternative study has been made for dehydrated clays. The adsorption constants Kd have been calculated and the results have been compared to broadband dielectric spectroscopy. It should be noted that the method is quite general and independent on the nuclear waste storage issue.

References

- B. Rotenberg, J.-F. Dufrêche, B. Bagchi, E. Giffaut, J.-P. Hansen, P. Turq *Ion dynamics in compacted clays: Derivation of a two-state diffusion-reaction scheme from the lattice Fokker-Planck equation*, *J. Chem Phys.* **124**, 154701 (2006)
- B. Rotenberg, V. Marry, J.-F. Dufrêche, N. Malikova, E. Giffaut, P. Turq *Modelling water and ion diffusion in clays: A multiscale approach*, *Compt. Rend. Chimie* **10**, 1108 (2007)

Dispersion of lipid bilayers: separation without complexation induced by selective weak long range attractive interactions

Th. Zemb, A. Aroti, M. Leontidis (University of Nicosia, Cyprus)

Long range forces (LRI), i.e. non covalent interactions beyond the first neighbour are extremely important in modern chemistry of surfaces, for instance in the domain of self-assembly in water on in non-conventional fluids.[1] A review of their influence in functional materials as well as complex fluids has been recently made available.[2]

Aiming to improve understanding of the long range interactions in specific anion separation effects in biological systems, we have studied the effects of sodium salts of simple monovalent anions belonging to the Hofmeister series on the bilayers of the zwitterionic lipid 1,2-dipalmitoyl-sn-glycero-3-phosphocholine using small-angle x-ray scattering and the osmotic stress technique. NaCl, NaBr, $NaNO_3$, NaI, and NaSCN were used. The electrolytes were found to swell the bilayers and to increase the area per lipid headgroup at each value of the osmotic pressure, suggesting the assocn. of anions with the bilayer-lipid interfaces. The effects follow the so-called "Hofmeister" series. "Ion competition" expts. with mixed NaI/NaCl solns. at total salinity 0.1 and 0.5 M revealed that the effect of ions on the lipid equation-of-state is roughly linear at low concns., but strongly nonlinear at high concns. "binding" or "partitioning" constants of anions in the lipid bilayers by intruducing the concept of "active interface".[3]

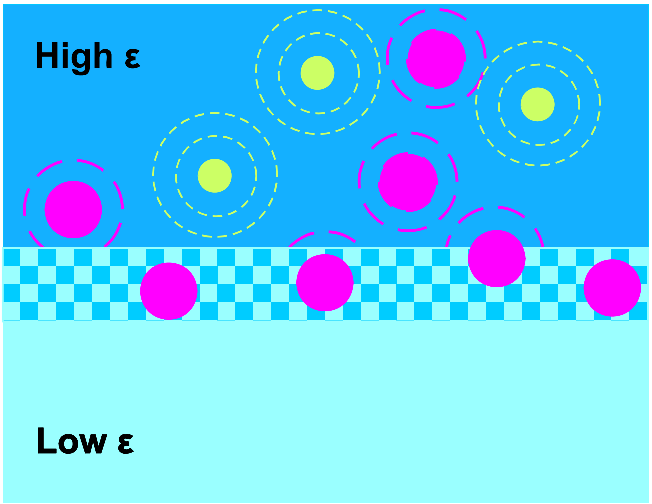


Figure 1: The concept of active interface: ions are partitioned between "bulk" and interface". The interface here is the location where the symmetry of hydration shell is broken, along with definition by Jungwirth-Kunz-Netz theory. For any ion, anion or cation, there is a free energy gain/loss when moving from bulk to the interface. In entropic terms, chaotropic/cosmotropic nature of ions favour Interface/bulk. For the enthalpic term, the volume and cohesion energy of the solvent as well as the "active" interface has to be considered.

Chaotropic/cosmotropic ions are considered in equilibrium between bulk and the active interface. The active interface is in contact with lipid monolayers. "Perpendicular" as well as in-plane equations of state linking osmotic pressures to distances have been established separately for the first time to our

---

[1] Zemb, Th.; Blume, A. "Self-assembly weak long-range interactions at work." Current Opinion in Colloid & Interface Science (2007), 12(3), 99-100.

[2] French R G, Parsegian V A, Zemb, Th. et al., "Long range interactions in nanoscale science" *REVIEWS OF MODERN PHYSICS* (2010) , vol. 82

[3] Aroti, A.; Leontidis, E.; Dubois, M.; Zemb, T, "Effects of monovalent anions of the Hofmeister series on DPPC lipid bilayers part I: swelling and in-plane equations of state". Biophysical Journal (2007), 93(5), 1580-1590.

knowledge for a common lipid. The effects of Hofmeister anions on the perpendicular and lateral equation-of-state (EOS) of the dipalmitoylphosphatidylcholine lamellar phase are here examd. using appropriate free energy models for the intra- and interbilayer interactions. Minimizing the free energy with respect to the two basic geometrical parameters of the lamellar phase, which are the interbilayer water thickness, dW, and the lipid headgroup area, aL, provides the perpendicular (osmotic pressure balance) and lateral EOS. Standard models are used for the hydration, undulation, and Van der Waals attractive force between the bilayers in the presence of electrolytes whereas two alternative treatments of electrostatic interactions were used to obtain "binding" or "partitioning" constants of anions to the lipid bilayers both in the absence and in the presence of sodium binding.

The computed binding constants depend on anion type and follow the Hofmeister series, but were found to increase with electrolyte concentration, implying that the local binding approximation cannot fit bilayer repulsion data. Hovwever, estimates of the free energy of transfer from bulk to the active interface near the monolayer could be derived for all anions investigated[1].

The same approach was conducted in three different geometries, i.e. Langmuir monolayers, bilayers and micelles, which differ by area per mol. and radius of curvature. The zwitterionic lipids DPPC (1,2-dipalmitoyl-phosphatidylcholine) and DPC (Dodecylphosphocholine) were used to form the three geometries. The salt solutions used were NaCl, NaBr, NaNO3, NaI, NaBF4, NaClO4, and NaSCN. Various interfacial and bulk exptl. techniques were used to study the effect of the anions on the amphiphiles in the 3 geometries. The interfacial techniques used were surface pressure-area isotherms, Brewster angle microscopy (BAM), Grazing incidence x-ray diffraction (GIXD), IR reflection absorption spectroscopy (IRRAS). The bulk sensitive techniques used were small-angle x-ray scattering (SAXS), osmotic stress (OS), and light scattering. The exptl. results obtained from the 3 model systems indicate that the interfaces become charged through lipid-ion association. The results were fitted with appropriate models to provide "binding" or "partitioning" constants of anions in the head-group region of the lipid molecules. The analysis strongly suggests that the anions do not associate with the lipid molecules through a local chemical interaction with first neighbour, but rather that they partition inside the disordered lipid interfaces[2].

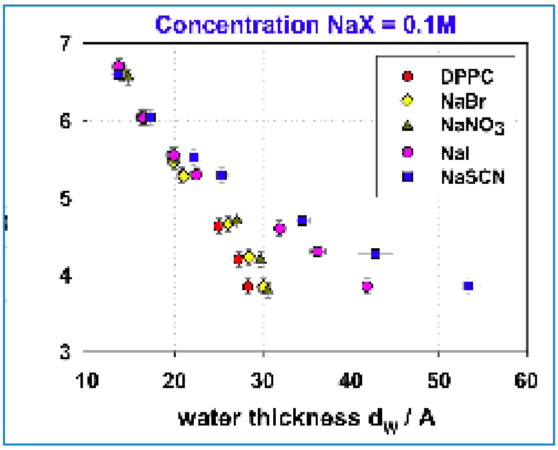


Figure 2: Typical "perpendicular" equation of state linking the logarithm of the osmotic pressure to the interbilayer distance for neutral bilayers in the presence of several monovalent salts. Chaotropic anions are expelled from bulk, gain energy in coming into the "active" interface. Once absorbed, they induce a concomitant increase of the area per molecule as well as a decrease in the bilayer thickness which is measured and modelled as the "lateral" equation of state linking osmotic pressure with are per molecule.

---

[1] Leontidis, E.; Aroti, A.; Belloni, L.; Dubois, M.; Zemb, T" Effects of monovalent anions of the Hofmeister series on DPPC lipid bilayers part II: modeling the perpendicular and lateral equation-of-state." Biophysical Journal (2007), 93(5), 1591-1607.

[2] Aroti, A.; Leontidis, E.; Dubois, M.; Zemb, T.; Brezesinski, G " Monolayers, bilayers and micelles of zwitterionic lipids as model systems for the study of specific anion effects." in Colloids and Surfaces, A: Physicochemical and Engineering Aspects (2007), 303(1-2), 144-158.

Towards "ionics": a generic model of liquid-liquid extraction

Thomas Zemb and Jean-François Dufrêche,
Fabienne Testard (LIONS, Saclay),
Philippe Guilbaud and Laurence Berthon (DRCP, Marcoule)

We develop a general model of competing salt equilibria between a concentrated solution of mixed salts containing charged, hydrated and polarisable ions and a oil phase containing small reverse aggregates solubilized by an amphiphilic "complexing" agent. This is the generic situation at meso-scale of all liquid-liquid extraction technology.

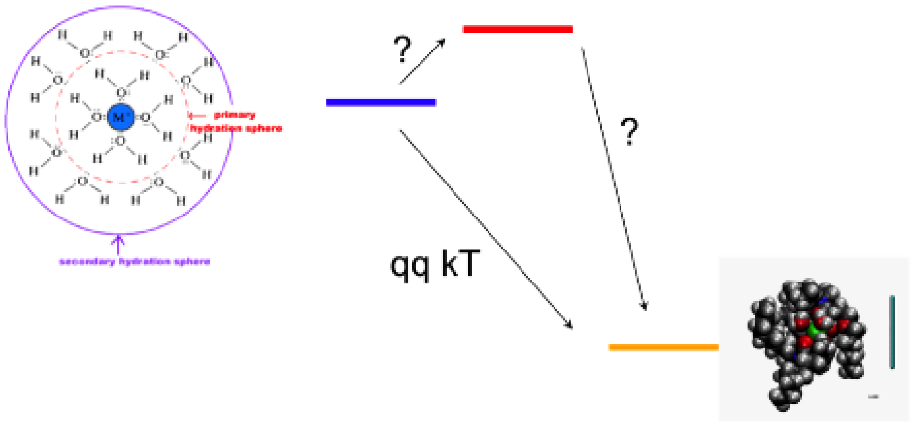


Figure 1: schematic representation of the chemical potentials levels of ions in coexisting water (left) and "oil" phase at the left. In the case of metals, differences of complexation in water with mainly oxygen atoms and with the complexing agent in the polar core of reverse aggregates are the motor for extraction. However, terms related to long range interactions, such as elastic deformation of the extractant film making the reverse aggregate and also van der Waals terms can be dominant in the difference between "blue" and "yellow" level of free energy. Identifying the intermediate state, i.e. when ion is in the Gouy-Chapman layer attracted to the macroscopic oil-water interface is the key of the control in kinetics[1].

Formulation may be driven in the future by predictive modelling. In order to achieve this, one needs to make an evaluation of all interactions involved, beyond the classical complexing with first neighbour. This can be done only after supra-molecular speciation, i.e. identification of amounts of coexisting monomers, small reverse aggregates as well as precursors of liquid crystals are identified. This is possible since a few years only, since osmometry, small angle X-ray and small angle SAXS/WAXS must be combined. However, once this is done jointly with determination of activity coefficient in the water phase, all long-range terms coming in the free energy balance shown in the figure can be predicted.

---

[1] Olivier Diat, Jean-François Dufrêche, Daniel Meyer, Stéphane Pellet-Rostaing, Pierre Turq et Thomas Zemb, "Cinétique de l'extraction liquide-liquide en hydrométallurgie", Note technique ICSM **2010**-2

The first results clearly show that selectivity "anomalies" of selectivity with concentration are not unexplained "curiosities" but necessary experimental facts and differences of one order of magnitude in partition coefficients of ions in liquid-liquid extraction are obtained when complexation wit first neighbour only is taken into account, i.e. when long range interactions, van der Waals interactions and elastic free energy of complexing film are neglected [1].

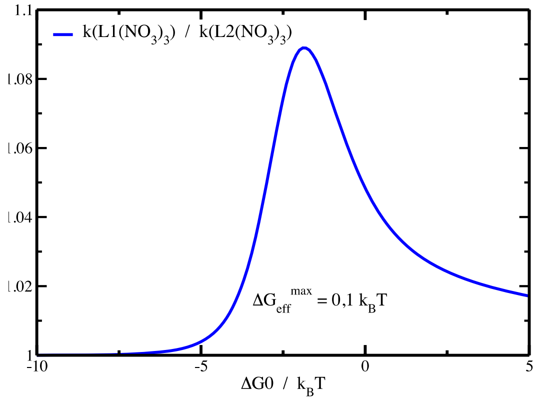


Figure 2: Apparent selectivity variation versus complexation energy difference simulated in cases of reverse aggregates of diamides in the case of Europium versus Dysprotium at constant concentration of extractant. With classical theories, the selectivity between two coexisting metals should be independent of concentration, and only depend on complexation free energy difference between ions and ligands.

On a more general point of view, equilibrium of ions between an organic and an aqueous phase must be considered not only as a balance of complexation in wtar and a complextion inan organo-mettalci oil-soluble complex. All the other interactions, i.e. the weak interactions beyond the first neighbour must be considered: these must encompass the van der Waals forces, the electrostatics within the polar core and the forces related to image charges, the elasticity of the monolayer of complexing amphiphiles and its wetting by the solvent (typical configuration of an extracting aggregate is shown on external page of this booklet shown on cover. Consequences of the exclusion of these dominant terms as in classical treatment of ion separation in hydrometallurgy is illustrated in the figure 2 below.

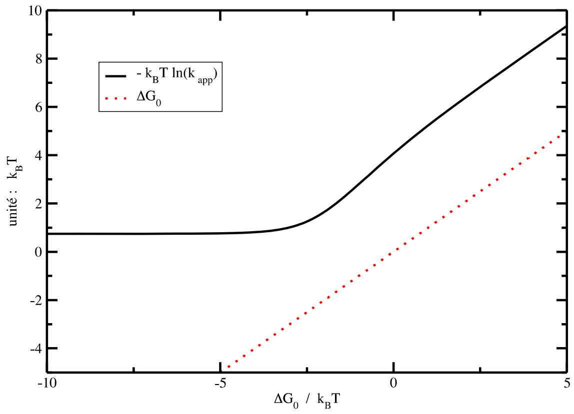


Figure 2: The ordinate represents the quantity RT ln(kd) which corresponds to the partition coefficient of a typical extracted cation in hydrometallurgy. If Kd= 50, then this quatity is 4 kT. Classical treatment in organo-metallic chemistry associates a difference in complexation also to 4kT (dashed lie). Treatment at colloidal scale (shown in continuous line) associates to this value of 4kT on the Y-axis a negligible complexation balance DG_0*. This situation explains the puzzling complexation free selective extraction as observed by H. Petrache et al. (PNAS 2004).*

As was done for *neutronics* in order to model neutron fluxes in the core of a nuclear reactor fifty years ago "*ionics*" in emulsified complex fluids remains to be build up for the nuclear fuel cycle of the future. ***This is a major goal in separation chemistry where ICSM has to intervene as world-class institute in the next ten years.***

---

[1] Jean-François Dufrêche and Thomas Zemb "Ion-driven hydrophilic/hydrophobic balance of a short amphiphilic peptide in water and in octanol", first workshop on modelling in chemistry at CEA, Saclay, July 2010.

Teaching activities linked to ICSM

In cooperation with ENSCM, UM2, ED 459
and
Institut National des Sciences et Techniques Nucléaires
INSTN – antenne de Marcoule (Pr M.-H. Hengé)

ICSM develops teaching activities in three directions: the master "**Chimie Séparative, Matériaux et Procédés: application au cycle du combustible nucléaire**", the annual practical separation chemistry summerschool and the "Thursday Lectures on separation chemistry".

The master was launched in 2005 together by UM2, ENSCM and INSTN. The training is followed by 16 students plus 8 students from ENSCM for the M1 level and 12 students plus 8 from ENSCM for the M2 level. The number of students increases from year to year, despite of a strong selection at M2 level. Teaching will progressively be done in English in the next years.
Teaching is aimed at the diffusion of critical knowledge on chemistry, radiochemistry, intefaces chemistry, conception and synthesis of new materials for nuclear purpose and process. Teaching on the separation chemistry used in the "amont" of nuclear cycle and basis on safety rules and nuclear right will be added to the training, starting in 2011

The **European practical summerschool of Marcoule in separation chemistry** was created in Marcoule jointly by ICSM, INSTN and SBTN with the support of ACTINET program. Twenty hours of teaching chemistry at cutting edge level are complemented by practicals (2 half days) devoted to the application of the theoretical courses.
The 2007 school on "fluid interfaces: separation of species at the nanometer scale" and the 2008 edition were build around lectures given by Helmuth MOhwald Möwald and Pr Christian Amatore.
In 2009, the school was devoted to "Analytical and separation chemistry" together with CETAMA. The 2010 edition was mainly organised by ACTINET on nuclear and analytical chemistry.

From year to year, the school is becoming more and more attractive for foreign students.

The **Thursday lectures on separation chemistry** are aimed to the 45 PhD students active in Marcoule and are devoted to modern aspects of chemistry, in all specialities, with a focus on nanosciences. "Theoretical "and "Experimental" lectures are coupled to an invited seminar on a topic related to the lectures.

Outlook...

Initial period of the growing of our institute since inauguration in June 2009 has been based on the objectives summarized in the paper following.

After four years as an embryonic and young organism, we are now at 75% of final planned size. The nine teams have started to take their position on international level of discussion and advancement of modern chemistry.

In 2010, a project for the period 2011-2014 has been proposed to the Agency AERES. We were extremely happy that project of ICSM, evaluated as whole as *one* team got the highest grade "A^+".

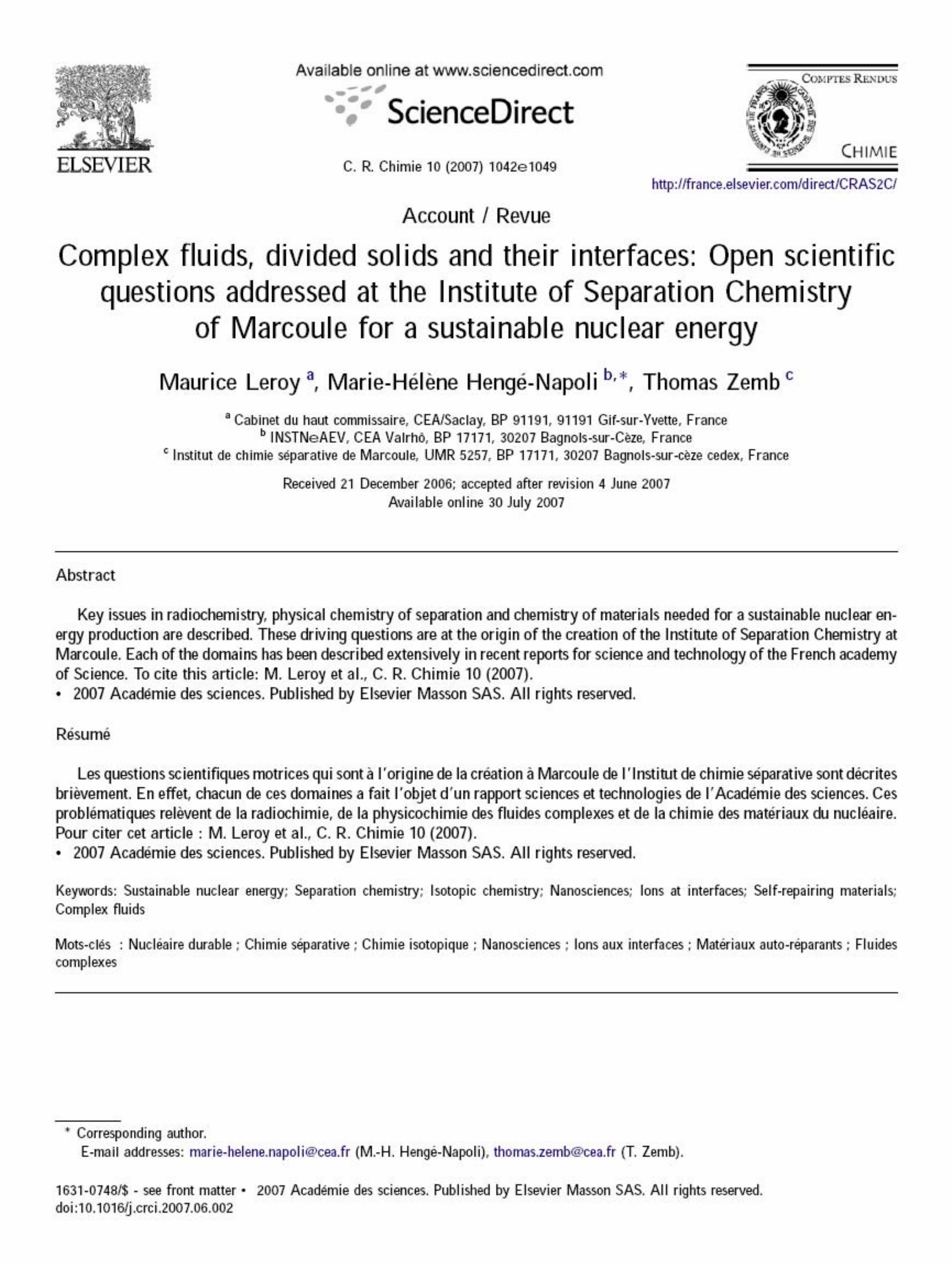
ICSM, UMR 5257, considered as *one* united team, together with the 25 other identified research teams from “Pole de Chimie Balard du Languedoc-Roussillon”, Service de Biologie et de Toxicologie Nucléaire de Marcoule (CEA/DSV), the group working on "Matériaux de grande diffusion" at the Ecole des Mines d' Alès and the soft matter group of the LCVN in Montpellier has prepared and proposed the creation of a laboratoire d'excellence "CheMISyt", i. e. chemistry of systems.

We hope that this LABEX project will be accepted in the strong competition announced for 2011. The overview of the project extending over the period 2011-2020 can be found in the Appendix.

T Zemb

Stéphane Pellet-Rostaing

Thomas Zemb



Available online at www.sciencedirect.com
ScienceDirect
C. R. Chimie 10 (2007) 1042e1049

COMPTES RENDUS
CHIMIE
http://france.elsevier.com/direct/CRAS2C/

Account / Revue

Complex fluids, divided solids and their interfaces: Open scientific questions addressed at the Institute of Separation Chemistry of Marcoule for a sustainable nuclear energy

Maurice Leroy [a], Marie-Hélène Hengé-Napoli [b,*], Thomas Zemb [c]

[a] Cabinet du haut commissaire, CEA/Saclay, BP 91191, 91191 Gif-sur-Yvette, France
[b] INSTNeAEV, CEA Valrhô, BP 17171, 30207 Bagnols-sur-Cèze, France
[c] Institut de chimie séparative de Marcoule, UMR 5257, BP 17171, 30207 Bagnols-sur-cèze cedex, France

Received 21 December 2006; accepted after revision 4 June 2007
Available online 30 July 2007

Abstract

Key issues in radiochemistry, physical chemistry of separation and chemistry of materials needed for a sustainable nuclear energy production are described. These driving questions are at the origin of the creation of the Institute of Separation Chemistry at Marcoule. Each of the domains has been described extensively in recent reports for science and technology of the French academy of Science. To cite this article: M. Leroy et al., C. R. Chimie 10 (2007).

Résumé

Les questions scientifiques motrices qui sont à l'origine de la création à Marcoule de l'Institut de chimie séparative sont décrites brièvement. En effet, chacun de ces domaines a fait l'objet d'un rapport sciences et technologies de l'Académie des sciences. Ces problématiques relèvent de la radiochimie, de la physicochimie des fluides complexes et de la chimie des matériaux du nucléaire. Pour citer cet article : M. Leroy et al., C. R. Chimie 10 (2007).

Keywords: Sustainable nuclear energy; Separation chemistry; Isotopic chemistry; Nanosciences; Ions at interfaces; Self-repairing materials; Complex fluids

Mots-clés : Nucléaire durable ; Chimie séparative ; Chimie isotopique ; Nanosciences ; Ions aux interfaces ; Matériaux auto-réparants ; Fluides complexes

---

* Corresponding author.
E-mail addresses: marie-helene.napoli@cea.fr (M.-H. Hengé-Napoli), thomas.zemb@cea.fr (T. Zemb).

1631-0748/$ - see front matter • 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.crci.2007.06.002

1. Maintaining and acquiring competence in separation chemistry

For the future use of fission technology in a long-term perspective, it is crucial to maintain and develop competence for the safe and economic operation of the present and future nuclear power plants, including waste management and decommissioning. Advanced reactor systems and fuel cycle modeling projects should help attract the bright young professionals needed not only to keep the fission option open, but also to maintain the high level of scientific competence for development and safety of new concepts for energy production.

Market forces work to reduce industry support to long-term R&D at universities and other research institutions serving as a training and recruitment base. Today, the priorities of the scientific community regarding basic research lie elsewhere than in nuclear sciences. Taken together, these circumstances create a significantly different situation from three to four decades ago when much of the present competence base was in fact generated. Also, many of the highly competent engineers and scientists, who helped create the present nuclear industry and its regulatory structure, are approaching retirement age. These competence issues need to be addressed at national level and the ''Institut de chimie séparative'' is one element of the strategy to be deployed for acquiring knowledge and for building expertise.

This will be done by tightening links between the nuclear research centers and the scientific community and giving access to installations, especially Atalante. The present paper deals with illustrations on key issues for modern chemistry, and with the way problems will be tackled, leading to the creation of seven research teams planned to operate at the Institute of Separation Chemistry.

Any technological problem solving or improvement process requires a thorough understanding of the basic phenomena. Typically an evolution from macroscopic to meso- and microscopic investigation is required and a coupling between the different disciplines and scales of research within one institute is of vital importance. A good knowledge of fundamental physical, chemical and materials science data on actinides and actinide-containing products, i.e. nuclear fuels and nuclear waste, is the basis for addressing nuclear issues at ICS. More knowledge is needed in chemistry at the ''nano'' scale, concerning the chemical evolution in complex fluids (alias fluids containing ''nanoreactors'' and materials with large specific surface, alias ''nanomaterials'') and the processes associated, such as dissolution, separation and cohesive aggregation.

Acquiring knowledge on actinide behavior is of interest for the whole scientific community. For instance, the recent identification and characterization of the superconductivity of $PuCoGa_5$ can be taken as a revolution, challenging new progresses, since none of the currently accepted descriptions of the 5f orbitals can be used to model these experimental findings. This means that the study of oxides containing actinides may open new routes in the understanding of superconductivity. Here as in other aspects of physical chemistry, the 5f electrons cannot be described by an extrapolation of theories developed for 4f electrons. The study of actinides in this case can result in returns not directly linked to energy production.

The needs for knowledge in the prediction of the evolution of active materials, as well as in separation chemistry have been summarized in the report edited by the French Academy of Sciences [1] in 2000; core of the recommendations is to focus on the mesoscale species of materials separating from the bulk under the action of radioactivity: colloids created under irradiation, ill-defined by extremely present surface activation under radioactivity, coupled reactions by synergy between defects and radicals left along a unique trace due to a radioactive decay.

Extending the questions from the concentrated radioactive material ''in ponderal quantity'' and the usage materials needed for handling active material in the fuel cycle, another report points to important need in knowledge of material in contact with active fluids. The report by Zaoui and Blanzat points out that these effects can only be modeled efficiently by a multi-scale approach. Interactions between atoms and molecules, including not only the covalent or complexing bond implying an actinide, but also long range interactions not restricted to first neighbour, such as van der Waals have to be considered. This implies that it is crucial to consider the ''meso'' scale, the scale relevant when a network of cracks and defects has to be modeled with some predictive power [2].

The mesoscale, when active species are linked by weak bonds only, when fluids organize at a supramolecular or colloidal scale, is the modern aspects of chemistry as a nanoscience. As pointed out by Corriu [3], the «nanoscience» alias «colloidal» approach of chemistry is relevant when reactive species are not implied via a simple stoichiometry, but atoms or molecules react as nano-objects, with stoichiometric quantities from ten to millions. Moreover, concepts developed in solid-state chemistry, with crystallographic-plane dependent reactivity, are also not relevant to colloidal chemistry dealing with nano-objects, since «weak interactions» are at work in the chemical transformation of nanoparticles or nanodroplets. Effect of radioactivity is always to produce large amounts of fluid–fluid or fluid–solid or solid–solid interface, typically hundreds of square meter per gram. Therefore, chemistry of radioactive solids or fluids most of the time deals with submicron sizes of materials or droplets: these are nano-objects, the new word for colloids. It is remarkable that the first French Nobel prize in chemistry was obtained by Jean Perrin for investigating colloids and that his son, Francis Perrin, was the leading scientist in the early development of science at the "Commissariat à l'énergie atomique".

Even nowadays, colloidal aspects are still crucial for the nuclear fuel cycle. For instance, it has been shown less than 10 years ago that efficiency and selectivity of tributylphosphate, the ubiquitous extractant used to separate uranium and plutonium from nitric acid solutions since the Manhattan project, are only because molecules which are being extracted in apolar solvents aggregate in small "water in oil" micelles. This means that each extracted ion is in interaction not only via complexation with one given complexing molecule, but with all molecules in a micellar aggregate. When this aggregate is present in solution, activity of the extractant is highly non-linear and the extraction is largely enhanced [4]. Phase transition and stability of these extracting fluids, such as those used in columns at the La Hague nuclear plant, can only be understood and predicted once it is realized that these micelles, considered as individual nano-objects, are the actors of liquid–liquid phase transitions driven by weak attractions. This "nanoscience" approach, for which each micelle is a nanomachine, allows making bridges and similarities with other micelles, used in detergency or assisted extraction of petrol. The instability recently identified in nuclear fluid extraction is equivalent to "Winsor II–Winsor III" equilibriums identified in the early 1950s in the field of formulation and emulsification by Winsor [5].

These "nanomachines" are nucleated around polar nanometre-sized cores, with specific properties, and the equilibrium between this core and the hydrated ions in aqueous solution controls selectivity (Fig. 1). The situation is reminiscent to the core of water channels, in the proton pump of photosynthetic transmembrane protein systems, or other membrane channels. In these biological systems, selectivity and efficiency, as well as control of separation of species are orders of magnitude higher than in ion extraction-desextraction using complexing molecules. It is not only in electronics or mechanical engineering that there is still "a large room at the bottom", to remind the prediction of Richard Feynman.

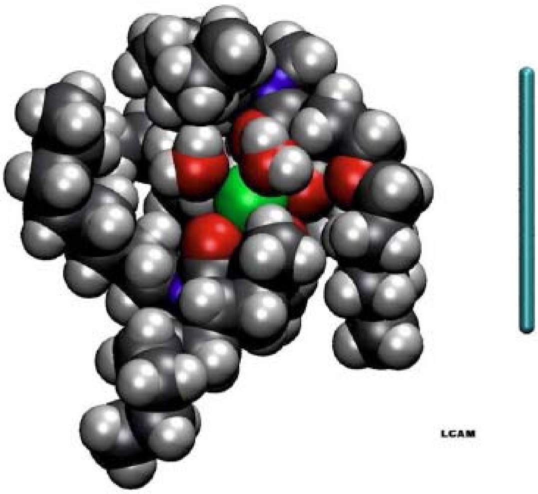


Fig. 1. Synergeic localization of complexing molecules around an ion, seen as a reverse micelle formed by four complexing molecules, around the polar core containing the ions to be extracted as well as the co-extracted water molecules. The bar is 1 nm (thanks to Philippe Guilbaud).

2. Selected topics and teams

In relation with these questions, linked to various sub-fields of physical chemistry, three axes of research need to be developed for the needs of a sustainable nuclear energy.

A – Combination of nanostructure and thermodynamic aspects in the physical chemistry of complex fluids used for extraction, decontamination, precursor solution for nanomaterials, or matrices for interim storage.

B – Characterization and modeling at the nanometre supramolecular chemistry level, which is the scale relevant to "colloidal science", now more widely designed as «nanoscience»'. Solid–liquid as well as liquid–liquid interfaces have to be characterized and modeled when chemical separation occurs through the interface (simple transfer, corrosion or oxido-reduction).

C – Modern solid-state chemistry of nanomaterials and hierarchically based materials, including bio-inspired hybrid materials with controlled shape at sub-micronic levels. This includes characterization by structural methods of all scales involved for materials at the preparation stage as well as during the corrosive evolution at high temperature or in extremely ''corrosive'' situations, enhanced by the presence of radioactivity and high fluxes of ionizing radiation.

More specifically, seven fields need to be urgently addressed.

Soft condensed matter chemistry of complex fluids, weak long range forces such as dispersion/van der Waals forces are at work in liquid–liquid extraction, with its application in hydrometallurgy. In order to develop predictive models of the water–solvent equilibrium of ions, the explicit distribution of ions in the first nanometre near the monolayer of extractant present at the water–oil interface needs to be measured and taken into account. By analogy with kinetics of chemical reactions, it is clear that the transient excited limiting step is the ion adsorption on the macroscopic monolayer. These ions present in the ''excited transient state'' are in kinetic equilibrium with ions in water as well as in reverse micelles. The extraction yield depends on the free energy difference between water and reverse micelles, while the kinetics of transfer depends on the activation energy, which is the difference of the energy between the aqueous bulk and the excited state of ions. The interaction between the transient fluctuations reminiscent of liquid crystals and the macroscopic water–solvent interface must be characterized and their microstructure as well as dynamics needs to be elucidated. Modeling kinetics at the liquid-liquid interface is crucial to predict extraction yields for a given chemical engineering strategy including continuous emulsification of microemulsions. This needs to be understood in terms of a balance three possible states of the ions: hydrated, adsorbed at the macroscopic interface and embedded in small micelles. Similar situation occurs in the corrosion process of surface layer; it has to be quenched for waste-conditioning material or enhanced for efficient solubilisation of solids: development of predictive models of reactants' distributions (mainly ions and charged species) in the last nanometre and in the diffuse cloud of reactive species present at the interface is needed. These models should provide a description beyond the DLVO theory, i.e. they should take into account the Hofmeister effect, surface charge regulation, dispersion forces and molecular protrusion [6]. This will be the central paradigm of the interfacial chemistry under reactive conditions (team 3).

Synergeic effects often attributed to self-assembly at supramolecular scale as well as colloidal scale require better understanding of the extractant self-assembly, at the origin of extracting power. Moreover, the ''solvent'' used by chemical engineers often contains solvo-surfactants, hydrotropes which induce long-range order in the solvent, as well as co-surfactants, with deep implication in the cohesion density and liquid–liquid surface tension. Most effective and selective processes able to perform reversible selective adsorption/desorption of specific ions in a mixture involve synergic effects in the interaction between recognized ''target'' ions and a self-assembled nano-object, contained in either a droplet or a solid nanoparticle; therefore peptides containing extractant groups as well as surfactants with grafted complexing groups will be used as model systems. The methods of combinatory chemistry using self-assembled peptides or modified peptides will be used to compare self-assembly and selective ion recognition capacity. Modeling at supramolecular level to develop predictive models required for process development will be an important task. These topics will constitute the central paradigm of the team dealing with ion separation using bio-inspired supramolecular self-assembled colloids (team 2) working in close cooperation with the team devoted to ions at interfaces.

Using chemistry induced mechanically by sound requires combining physical chemistry of liquid surfaces (as in teams 2 and 3 just described) and sonochemistry and could potentially cross-fertilize recent advances in both fields – using the physical chemistry of colloids such as controlling intermolecular forces by the presence of salt, solvo-surfactants or charged surface active crystalline nanoparticles by possibilities offered by sonochemistry. We will characterize and model phase transitions such as nucleation and coalescence of bubbles from gases dissolved in liquids as well as chemical reactivity under high temperature, high pressures and ultrasonic speed of reactant molecules during the implosion of the micron-sized bubbles coming from gas dissolved in the liquid.

Surface of bubbles appearing in liquids under ultrasonic excitation are by definition absolutely clean, and the density of ions and solutes at the liquid–vapor interface can be controlled and finely tuned by formulation of the fluid (chaotropic versus cosmotropic salts, hydrotropes and surface active partially hydrophobic colloids). Chemical study requires time-resolved (nano- to microsecond range) spectrophotometry of the light emitted, as well as the electrical field radiated by ions associated to the interface.

The initial direction of research is to measure and develop predictive models of the light emitted by the bubble during implosion, depending on the solutes present, and use this knowledge to develop new separative physical processes such as sound-induced flotation or new ''green chemistry'' processes, such as selective destruction, oxidation of toxic species, or peptization of flocculates containing heavy ions or even actinides.

Sonochemistry, i.e. chemical reactions triggered by thermal and pressure ultra-short transient peaks of temperature, is potentially the source of a vast emerging ''green chemistry'' technology based on nanometric to micrometric bubbles which can be generated via ultrasound. Under hydrostatic oscillating pressure, dissolved gas nucleates in the form of bubbles. The coalescence of bubbles is controlled by salt-specific effects, surface dilation modulus and by adsorption of colloidal semi-hydrophobic species. However, the relative importance of these three mechanisms is not known. The ''test tube'' of the sonochemist is a sub-micronic bubble and the reagents are the molecules present at the interface, between the compressed vapor bubbles till the implosion of the bubble [7]. No predictive model exists yet about the most direct manifestation of sonochemistry: sonoluminescence produced during bubble implosion, and the effect of solutes present in the liquid submitted to ultrasonic excitation.

Reacting species are the liquid vapor, the gases initially dissolved in the fluid and also all species specifically adsorbed at the interface such as salts including a structure-breaking (''chaotropic'') ion or hydrotropes able to rearrange within milliseconds at the liquid–vapor interface. During formation of the bubble, surface active materials as well as any partially hydrophobic colloids adsorb on the bubble and concentrate reagents in the bubbles. The timescales involved in temperature and pressure spikes are comparable with self-assembled structures in soft matter and complex fluids. Also, bubbles produced via ultrasound can nucleate easier in the presence of rough powders, which are degraded in corrosive conditions at a much larger rate in the presence of cavitations induced by vaporization/degassing provoked by ultrasound.

Bubbles induced by ultrasounds may be stabilized by surface active molecules and polymers, and hence may be the core of a whole technology transposing the flotation process – the biggest colloidal process by tonnage on mankind – from macroscopic bubbles to microscopic bubbles produced by ultrasound in water solutions saturated by gas. Since the bubbles produced by ultrasound are smaller than those used in standard technology via a ''frit'', their Laplace pressure is much larger. Thus more possibilities are offered by ultrasound produced bubbles flotation than classically, as obtained via blowing gas into a solution through a porous solid. New separation processes could come from the control of sonochemical processes, treated by analogy with detonics of fast reactions (Fig. 2).

Fig. 2. Sonoluminescence produced in a liquid under ultrasound excitation.

The micron-sized bubble resulting from nucleation of initially molecularly dissolved gas and vapor is indeed an ultra-high temperature and pressure transient chemical reactor, with high power for disrupting and finally new ways of solubilizing cohesive nanohybrids, as required by the fuel cycle. The reactants in interaction are molecules mainly located at the solid–liquid interface. This type of chemistry minimizes secondary waste for different reasons, including the absence of a permanent ''container'' where high T–P takes place. Progresses in the comprehension of the simplest cases (sonoluminescence or sonication of dispersed solids) require conjunction of competence in physical chemistry of multiphase systems, acoustics in droplets and also chemistry of interfaces. This furtive chemistry, studying sonochemical processes in complex fluids will be the scientific domain of expertise of one team at ICSM (team 4).

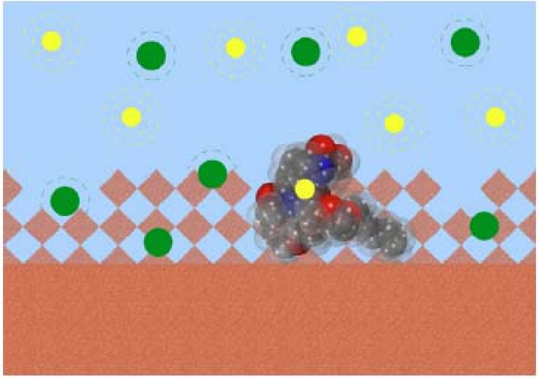


Fig. 3. An "active" molecule adsorbed at an interface, compared to the counter-ion cloud (thanks to Sylvain Prévot).

Two mainstreams for waste materials are well understood, as a result of intense fundamental research since 20 years: the family of borosilicate glasses including engineered modifiers with its star "R7T7" and microcrystalline ceramic material with a large amount of intergranular amorphous material known as SYNROC inspired by geochemical observations. Whatever be the microstructure, no solid material can be engineered in order to reduce to undetectable values the release of complex fractal-like colloids created by energy release in the material. The key property of glass is the local reformation of the glassy network. These inorganic complex "polymers" are released at the macroscopic interface of the confinement material, and are one vehicle for transport of cations. However, the complex fractal colloids could be considered as the precursor of a secondary material, for example by ion exchange within an ionic solid. The mechanical or leaching performance of the ionic solid could be improved after solid-state reaction with radiolytically produced species (Fig. 3).

Using modern progresses of hybrid multi-scale nanomaterials, there is a large class of possibilities of multi-scale nanomaterials. For instance, colloidal silica could be engineered for initial storage of active species, but these could be embedded at the micron-scale in an ionic solid. The latter would be reactive towards the species released at the interface of this hybrid nanomaterial in order to form a slowly forming "secondary phase" with better usage properties than the initial material. Application of this strategy is not limited to the nuclear industry. For example developing paints that self-heal slowly under the influence of atmospheric carbon dioxide would also be possible by concentrating in the same institute competence in synthesis, characterization of evolution and modeling of this type of nanomaterials. The knowledge about nanomaterials, their synthesis, the chemical reactivity and modeling of long-term usage properties will be the driving force for the team Self-repairing of hybrid nanomaterials with hierarchical structure (team 5). Of course, if one of the nanomaterials designed is of interest for specific storage application after separation of species, this team will be working with teams already active in Marcoule outside the Institute of Separation Chemistry involved in development of these materials and that involved in program-oriented projects.

Long-term usage with a high level of confidence and known safety margins of materials at high temperature, in the presence of corrosive fluids such as molten salts or concentrated ionic solutions requires also better experimental knowledge of the "interface". Characteristics of the latter to be determined are thickness, own internal structure as well as speciation of atoms involved. Each of the atoms or molecules near the interface under stress (high temperature, oxidative stress) can be characterized by a coefficient of diffusion. From there, they are two types of "extreme cases". Corrosion of the interface is dominated by the "disappearance" of atoms or molecules near the interface and hence displacement of the interface towards the bulk material, with instability of shapes associated to defects or local re-crystallisation. The opposite extreme is the case where the diffusion of species is faster than the speed of interface displacement. The first case is the case of ceramics in mild conditions. The second case is typical for fluids in boiling conditions. Complex gels or nanomaterials close from the melting transition lie probably in the intermediate case, when neither diffusion of atoms nor the speed of dissolution can be neglected. Acquisition of experimental data on selected model systems requires an effort in measurement of solid-state diffusion, characterization of interface and evaluation of surface reactivity in extreme conditions. The selected model systems will be preferably relevant to generation IV of nuclear plants, because fuel will be used at the highest possible "safe" temperature, but could also be chosen as confinement materials under very aggressive chemical stress, and the problems related linked to re-dissolution of materials, since dissolution of materials or uncontrolled solubilisation is the main "enemy" of efficient separation chemistry.

Successful predictive modeling of evolution of a solide fluid interface will require a subtle dosage between approach involving diffusion of atoms, diffusion of defects as well as evolution of the interface defined by a distribution of curvatures. Evolution of surface structure in real cases and the kinetics associated have to be described along several mechanisms, since the corresponding morphology of the surface is present in several forms, ranging from simple uniform ablation to formation of dendrite cracks or even autogenic build-up of fractal structures. Associating surface and bulk characterization methods on model systems selected with our colleagues from applied research with sufficient precision to allow successful predictive modeling is the initial direction of research of the team Interface of materials under rapid evolution (team 6).

Most of the scientific challenges in separation chemistry as well as in sonochemistry described up to this point may involve actinides as frequently as possible; natural uranium and thorium as well as depleted uranium will be handled in the institute within the French regulation. All experiments involving other actinides, for which security and safety requirements need the usage of chemical and physical instrumentations in ''zones surveillées'' will be done at the adequate installation ''Atalante'' in cooperation with teams managing this large experimental facility. Actinides will therefore be studied as ions in fluids, up to ions embedded in micelles and liquid crystals. For the teams working on porous solids, interfaces and nanomaterials, actinides will be chemically bound to solids, such as oxides, nitrides or carbides.

The first target here is to improve knowledge about thin layers of actinides, i.e. their reactivity and dissolution from the metallic or oxide form in the presence of oxygen peroxide . This simple way of introducing highly reactive species in a known concentration will be studied in detail. The knowledge of the behavior of actinides in the presence of radical produced by an ionizing particle along a track needs to be largely improved. For example the relative importance of the covalence or the ionicity of the bond between atoms in a solid, as well as in a salt, molten salt or highly concentrated solution is not known. Moreover, it is known qualitatively that metallic or oxide-type layers synthesized through different routes have extremely different behaviors. Two known routes of synthesis of well-defined thin films are either assembling ''secondary building units'' or small nanoparticles usually containing 1–10 actinide atoms, or using vapor phase deposition process which produces the deposit layer by layer from the gas phase. Therefore, in a joint research program with teams at the ITU-Joint Research Centre, Karlsruhe, dissolution kinetics and morphological evolution will be studied on ''thin'' layers – thin meaning here 1 nm to 1 mm – in the presence of oxygen peroxide, and later, in the presence of minor actinides so as to study quantitatively the effect of self-irradiation.

These scientific targets will be addressed by the team Chemical and physical properties of massive actinides (team 1). Especially strong scientific links with teams 1 and 2 will lead to common publications about classifying actinide-based anions or cations in the Hofmeister chaotropic/cosmotropic series. Implication of the interaction of actinides with red cell membranes or model membranes made of polyelectrolyte or actin filaments adsorbed on bilayers will be studied in collaboration with the other fundamental research laboratory in Marcoule: the ''Service de biologie et de toxicologie nucléaire'' and proposals will be submitted to the ACTINET network. Properties related to oxido-reduction, as well as solubility and corrosion will be studied in conjunction with team 6. Interaction with the sonochemists will involve separation by flotation of actinide-based colloids. Nanomaterials prepared by team 5 will of course include actinides, while the experimental methods developed for characterization of surface by team 6 will of course be used by the scientists dealing with actinides.

Finally, there is also a strong need for in situ isotropic imagig in materials containing active species. Looking back at what has been achieved after 20 years of effort in imaging ice cores extracted in polar regions, one realizes that characterization of materials which have been for long period in high radiation environment possibly reveals interstitial hydrogen or other isotopes which could be studied using localized nuclear magnetic resonance. Their 3D cartography using new solid-state imaging techniques would be probably an invaluable information for models of long-term usage – long term meaning here 10–50 years – of materials in an active environment. Even in cases where 3D imaging is not possible, the simple chemical characterization such as via the shift of silicium according to coordinence with oxygen atoms, is already important, if possible in an active environment containing paramagnetic species, and with ''imaging'' coming from polarization transfer at a fluid-solid interface. The recent giant leap of possibility offered by ex situ NMR techniques [8], much easier to nuclearise than conventional high field NMR machines limited to low levels of activity (typically less than 1 MBq per sample), will be used by the team devoted to isotopic chemistry and NMR imaging. This team will work very closely with a team in project-oriented research already present in Marcoule.

Availability of large quantities of the appropriate isotopes would allow the studies of solids and liquids by NMR: the labeling of an essential or a toxic element in a sample containing enzymes or active membrane-based biochemical systems would provide useful information on fate and species of a given element in living systems.

This type of applications is possible only by conjunction of two factors: availability of isotopically pure samples, liquid- and solid-state NMR in controlled environment. These goals can therefore only be tackled by association of a production line of pure isotopes in CEA, associated with teams in basic research of materials and fluids, and biochemistry and biology.

As a more ambitious long-term target, it is important to share instrumental and methodological developments of ''analytical'' instrumentation, either spectroscopic or based on scattering or cartography of local properties, as a generalization of imaging with non-radioactive instrumental developers. This has been done in the field of mass spectrometry. A national effort has been taken in the frame of the GDR ''NOMADE'' as well as in European networks to start feasibility experiment of solid-state NMR including magic angle spinning of samples containing several percent per mass of actinides. These experimental techniques based on NMR adapted to high levels of activity would be relevant also in applied programs aimed at designing new conditioning of nuclear waste, substrate for incineration of minor actinides as well as for nuclear fuels. All these experiments could be done also at high temperature, if the design of a sample cell can be certified.

There are even more attractive objectives in physical chemistry of isotopically pure materials, that could only be developed within CEA. Considering again the case of $PuCoGa_5$, it appears that the transition temperature towards the superconductive state depends on the isotope used to prepare the sample. If these could be precisely measured, the relevant data would be the most crucial knowledge, as this isotopic effect challenges description of superconductivity. Even more ''simpler'' effects, such as thermal conductivity, can depend by factors up to 50% on the isotopic composition. Coherent phonon propagation, perturbed by minor isotopes seen as a mechanical defect in the lattice, is dominant in the thermal conductivity measured. This is the case with samples containing yttrium, barium and cobalt. More understanding of the underlying phenomena is needed before evaluation of the improvement of performance such as that of semi-conductor chip using isotopically pure ^{29}Si, making profit of its low calorific capacity, in order to produce chips working in extreme environment, a possible contribution of the isotopic chemistry e both knowledge and controlled in-house production lines e to the electronic industry.

References

[1] R. Guillaumont, B. Blanzat (Eds.), Radiochimie e Matière radioactive et rayonnements ionisants, Académie des sciences, Paris : Rapport sur la science et la technologie n° 4, Tec et Doc Lavoisier, Paris, juillet 2000.

[2] A. Zaoui, B. Blanzat (Eds.), Matériaux du nucléaire, Académie des sciences, Paris : Rapport sur la science et la technologie n° 5, Tec et Doc Lavoisier, Paris, juillet 2000.

[3] R. Corriu, P. Nozières, C. Weisbuch (Eds.), Nanosciences e Nanotechnologies, Académie des sciences, Paris : Rapport sur la science et la technologie n° 18. Réalisé avec l'Académie des technologies, tec et Doc Lavoisier, Paris, avril 2004.

[4] S. Nave, C. Mandin, L. Martinet, L. Berthon, F. Testard, C. Madic, T. Zemb, Phys. Chem. Chem. Phys. 6 (4) (2004) 799.

[5] C. Erlinger, L. Belloni, T. Zemb, C. Madic, Langmuir 15 (1999) 2290.

[6] See the special issue devoted to Non-electrostatic long-range effects between ions, Curr. Opin. Colloid Interface Sci. 9 (1e2) (2004).

[7] J. Bercoff, M. Tanter, M. Fink, Appl. Phys. Lett. 84 (12) (2004) 2202.

[8] C.A. Meriles, D. Sakellariou, H. Heise, A.J. Moulé, A. Pines, Science 293 (5527) (2001) 82;
D. Sakellariou, C.A. Meriles, A. Pines, C. R. Physique 5 (3) (2004) 337;
B. Blümich, F. Casanova, J. Perlo, S. Anferova, V. Anferov, K. Kremer, N. Goga, K. Kupferschläger, M. Adams, Magn. Reson. Imaging 23 (2) (2005) 197;
J. Perlo, V. Demas, F. Casanova, C.A. Meriles, J. Reimer, A. Pines, B. Blümich, Science (Washington, D.C., United States) 308 (5726) (2005) 1279.

Appendix A

Liste des publications

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
2010				
French, RH; Parsegian, VA; Podgornik, R; Rajter, RF; Jagota, A; Luo, J; Asthagiri, D; Chaudhury, MK; Chiang, YM; Granick, S; Kalinin, S; Kardar, M; Kjellander, R; Langreth, DC; Lewis, J; Lustig, S; Wesolowski, D; Wettlaufer, JS; Ching, WY; Finnis, M; Houlihan, F; von Lilienfeld, OA; van Oss, CJ; Zemb, T	Long range interactions in nanoscale science	REVIEWS OF MODERN PHYSICS	2010, 82, 2, 1887-1944	33,145
Zech, O; Bauduin, P; Palatzky, P; Touraud, D; Kunz, W	Biodiesel, a sustainable oil, in high temperature stable microemulsions containing a room temperature ionic liquid as polar phase	ENERGY & ENVIRONMENTAL SCIENCE	2010, 3, 6, 846-851	8,500
Chave, T; Nikitenko, SI; Scheinost, AC; Berthon, C; Arab-Chapelet, B; Moisy, P	First Synthesis of Uranyl Aluminate Nanoparticles	INORGANIC CHEMISTRY	2010, 49, 14, 6381-6383	4,657
Clavier, N; Hingant, N; Rivenet, M; Obbade, S; Dacheux, N; Barre, N; Abraham, F	X-Ray Diffraction and mu-Raman Investigation of the Monoclinic-Orthorhombic Phase Transition in Th1-xUx(C2O4)(2)center dot 2H(2)O Solid Solutions	INORGANIC CHEMISTRY	2010, 49, 4, 1921-1931	4,657
Virot, M; Chave, T; Nikitenko, SI; Shchukin, DG; Zemb, T; Mohwald, H	Acoustic Cavitation at the Water-Glass Interface	JOURNAL OF PHYSICAL CHEMISTRY C	2010, 114, 30, 13083-13091	4,224
Toquer, G; Zemb, T; Shchukin, D; Mohwald, H	Ionic physisorption on bubbles induced by pulsed ultra-sound	PHYSICAL CHEMISTRY CHEMICAL PHYSICS	2010, 12, 43, 14553-14559	4,116
Demir-Cakan, R; Makowski, P; Antonietti, M; Goettmann, F; Titirici, MM	Hydrothermal synthesis of imidazole functionalized carbon spheres and their application in catalysis	CATALYSIS TODAY	2010, 150, 01-févr, Sp. Iss. SI, 115-118	3,526
Michina, Y; Carriere, D; Charpentier, T; Brito, R; Marques, EF; Douliez, JP; Zemb, T	Absence of Lateral Phase Segregation in Fatty Acid-Based Catanionic Mixtures	JOURNAL OF PHYSICAL CHEMISTRY B	2010, 114, 5, 1932-1938	3,471
Borrini, J; Bernier, G; Pellet-Rostaing, S; Favre-Reguillon, A; Lemaire, M	Separation of lanthanides(III) by inorganic nanofiltration membranes using a water soluble complexing agent	JOURNAL OF MEMBRANE SCIENCE	2010, 348, 01-févr, 41-46	3,203
Lin, Y; Espinas, J; Pellet-Rostaing, S; Favre-Reguillon, A; Lemaire, M	Stereochemistry effect of dicyclohexano-18-crown-6 on zinc isotope separation	NEW JOURNAL OF CHEMISTRY	2010, 34, 3, 388-390	3,006
Kannappan, R; Bucher, C; Saint-Aman, E; Moutet, JC; Milet, A; Oltean, M; Metay, E; Pellet-Rostaing, S; Lemaire, M; Chaix, C	Viologen-based redox-switchable anion-binding receptors	NEW JOURNAL OF CHEMISTRY	2010, 34, 7, 1373-1386	3,006
Nikitenko, SI; Venault, L; Pflieger, R; Chave, T; Bisel, I; Moisy, P	Potential applications of sonochemistry in spent nuclear fuel reprocessing: A short review	ULTRASONICS SONOCHEMISTRY	2010, 17, 6, Sp. Iss. SI, 1033-1040	2,993
Romieu, A; Tavernier-Lohr, D; Pellet-Rostaing, S; Lemaire, M; Renard, PY	Water solubilization of xanthene dyes by post-synthetic sulfonation in organic media	TETRAHEDRON LETTERS	2010, 51, 25, 3304-3308	2,660

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Banc, A; Bauduin, P; Diat, O	Tracking an ion complexing agent within bilayers	CHEMICAL PHYSICS LETTERS	2010, 494, 04-juin, 301-305	2,291
Khedim, H; Katrina, T; Podor, R; Panteix, PJ; Rapin, C; Vilasi, M	Solubility of Cr2O3 and Speciation of Chromium in Soda-Lime-Silicate Melts	JOURNAL OF THE AMERICAN CERAMIC SOCIETY	2010, 93, 5, 1347-1354	1,944
Tokarev, A; Grandjean, A; Guari, Y; Larionova, J; Pflieger, R; Guerin, C	Functionalized porous glass for the removal and the confinement of ruthenium from radioactive solutions	JOURNAL OF NUCLEAR MATERIALS	2010, 400, 1, 25-31	1,933
Dacheux, N; de Kerdaniel, ED; Clavier, N; Podor, R; Aupiais, J; Szenknect, S	Kinetics of dissolution of thorium and uranium doped britholite ceramics	JOURNAL OF NUCLEAR MATERIALS	2010, 404, 1, 33-43	1,933
Papaiconomou, N; Estager, J; Traore, Y; Bauduin, P; Bas, C; Legeai, S; Viboud, S; Draye, M	Synthesis, Physicochemical Properties, and Toxicity Data of New Hydrophobic Ionic Liquids Containing Dimethylpyridinium and Trimethylpyridinium Cations	JOURNAL OF CHEMICAL AND ENGINEERING DATA	2010, 55, 5, 1971-1979	1,695
Berthon, L; Testard, F; Martinet, L; Zemb, T; Madic, C	Influence of the extracted solute on the aggregation of malonamide extractant in organic phases: Consequences for phase stability	COMPTES RENDUS CHIMIE	2010, 13, 10, 1326-1334	1,58
Molina, JJ; Duvail, M; Guilbaud, P; Dufreche, JF	Coarse-grained lanthanoid chloride aqueous solutions	JOURNAL OF MOLECULAR LIQUIDS	2010, 153, 02-mars, 107-111	1,278
Dufreche, JF; Rotenberg, B; Marry, V; Turq, P	Bridging molecular and continuous descriptions: the case of dynamics in clays	ANAIS DA ACADEMIA BRASILEIRA DE CIENCIAS	2010, 82, 1, 61-68	1,074
Bauer, C; Bauduin, P; Diat, O; Zemb, T	Ion Extractant as Cosurfactant at the Water-Oil Interface in Microemulsions	TENSIDE SURFACTANTS DETERGENTS	2010, 47, 5, 307-311	0,329
2009				
Nikitenko, ST; Martinez, P; Chave, T; Billy, I	Sonochemical Disproportionation of Carbon Monoxide in Water: Evidence for Treanor Effect during Multibubble Cavitation	ANGEWANDTE CHEMIE-INTERNATIONAL EDITION	2009, 48, 50, 9529-9532	11,829
Makowski, P; Thomas, A; Kuhn, P; Goettmann, F	Organic materials for hydrogen storage applications: from physisorption on organic solids to chemisorption in organic molecules	ENERGY & ENVIRONMENTAL SCIENCE	2009, 2, 5, 480-490	8,500
Makowski, P; Rothe, R; Thomas, A; Niederberger, M; Goettmann, F	Chlorine borrowing: an efficient method for an easier use of alcohols as alkylation agents	GREEN CHEMISTRY	2009, 11, 1, 34-37	5,836
Yao, WT; Makowski, P; Giordano, C; Goettmann, F	Synthesis of Early-Transition-Metal Carbide and Nitride Nanoparticles through the Urea Route and Their Use as Alkylation Catalysts	CHEMISTRY-A EUROPEAN JOURNAL	2009, 15, 44, 11999-12004	5,382
Abecassis, B; Testard, F; Zemb, T	Gold nanoparticle synthesis in worm-like catanionic micelles: microstructure conservation and temperature induced	SOFT MATTER	2009, 5, 5, 974-978	4,869

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
	recovery			
Carriere, D; Belloni, L; Deme, B; Dubois, M; Vautrin, C; Meister, A; Zemb, T	In-plane distribution in mixtures of cationic and anionic surfactants	SOFT MATTER	2009, 5, 24, 4983-4990	4,869
Abou-Hassan, A; Dufreche, JF; Sandre, O; Meriguet, G; Bernard, O; Cabuil, V	Fluorescence Confocal Laser Scanning Microscopy for pH Mapping in a Coaxial Flow Microreactor: Application in the Synthesis of Superparamagnetic Nanoparticles	JOURNAL OF PHYSICAL CHEMISTRY C	2009, 113, 42, 18097-18105	4,224
Gracia, S; Cazorla, C; Metay, E; Pellet-Rostaing, S; Lemaire, M	Synthesis of 3-Aryl-8-oxo-5,6,7,8-tetrahydroindolizines via a Palladium-Catalyzed Arylation and Heteroarylation	JOURNAL OF ORGANIC CHEMISTRY	2009, 74, 8, 3160-3163	4,219
Jardat, M; Dufreche, JF; Marry, V; Rotenberg, B; Turq, P	Salt exclusion in charged porous media: a coarse-graining strategy in the case of montmorillonite clays	PHYSICAL CHEMISTRY CHEMICAL PHYSICS	2009, 11, 12, 2023-2033	4,116
Nave, S; Testard, F; Coulombeau, H; Baczko, K; Larpent, C; Zemb, T	Ternary phase diagrams of a thermoreversible chelating non-ionic surfactant	PHYSICAL CHEMISTRY CHEMICAL PHYSICS	2009, 11, 15, 2700-2707	4,116
Kunz, W; Testard, F; Zemb, T	Correspondence between Curvature, Packing Parameter, and Hydrophilic-Lipophilic Deviation Scales around the Phase-Inversion Temperature	LANGMUIR	2009, 25, 1, 112-115	3,898
Liu, LP; Bauduin, P; Zemb, T; Eastoe, J; Hao, JC	Ionic Liquid Tunes Microemulsion Curvature	LANGMUIR	2009, 25, 4, 2055-2059	3,898
Michina, Y; Carriere, D; Mariet, C; Moskura, M; Berthault, P; Belloni, L; Zemb, T	Ripening of Catanionic Aggregates upon Dialysis	LANGMUIR	2009, 25, 2, 698-706	3,898
Zech, O; Thomaier, S; Bauduin, P; Ruck, T; Touraud, D; Kunz, W	Microemulsions with an Ionic Liquid Surfactant and Room Temperature Ionic Liquids As Polar Pseudo-Phase	JOURNAL OF PHYSICAL CHEMISTRY B	2009, 113, 2, 465-473	3,471
Metay, E; Duclos, MC; Pellet-Rostaing, S; Lemaire, M; Kannappan, R; Bucher, C; Saint-Aman, E; Chaix, C	Synthesis and conformational analysis of redox-active ferrocenyl-calixarenes	TETRAHEDRON	2009, 65, 3, 672-676	3,219
Dahirel, V; Jardat, M; Dufreche, JF; Turq, P	Two-scale Brownian dynamics of suspensions of charged nanoparticles including electrostatic and hydrodynamic interactions	JOURNAL OF CHEMICAL PHYSICS	2009, 131, 23	3,093
Chave, T; Nikitenko, SI; Granier, D; Zemb, T	Sonochemical reactions with mesoporous alumina	ULTRASONICS SONOCHEMISTRY	2009, 16, 4, 481-487	2,993
Li, LN; Chang, L; Pellet-Rostaing, S; Liger, F; Lemaire, M; Buchet, R; Wu, YQ	Synthesis and evaluation of benzo[b]thiophene derivatives as inhibitors of alkaline phosphatases	BIOORGANIC & MEDICINAL CHEMISTRY	2009, 17, 20, 7290-7300	2,822

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Gracia, S; Metay, E; Pellet-Rostaing, S; Lemaire, M	Synthesis of 8-Oxo-3-acetylenic-5,6,7,8-tetrahydroindolizines via Sonogashira Coupling	SYNLETT	2009, 16, 2617-2620	2,718
Carrignon, C; Makowski, P; Antonietti, M; Goettmann, F	Chloride ion pairs as catalysts for the alkylation of aldehydes and ketones with C-H acidic compounds	TETRAHEDRON LETTERS	2009, 50, 34, 4833-4837	2,660
Molina, JJ; Dufreche, JF; Salanne, M; Bernard, O; Jardat, M; Turq, P	Models of electrolyte solutions from molecular descriptions: The example of NaCl solutions	PHYSICAL REVIEW E	2009, 80, 6	2,400
Garcia, J; Meyer, DJM; Guillaneux, D; Moreau, JJE; Man, MWC	Investigation of titanium-catalysed dehydrogenative coupling and hydrosilylation of phenylhydrogenosilanes in a one-pot process	JOURNAL OF ORGANOMETALLIC CHEMISTRY	2009, 694, 15, 2427-2433	2,347
Schelero, N; Lichtenfeld, H; Zastrow, H; Mohwald, H; Dubois, M; Zemb, T	Single particle light scattering method for studying aging properties of Pickering emulsions stabilized by catanionic crystals	COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS	2009, 337, 01-mars, 146-153	1,988
Diop, I; David, N; Fiorani, JM; Podor, R; Vilasi, M	Experimental investigations and thermodynamic description of the PbO-Bi2O3 system	JOURNAL OF CHEMICAL THERMODYNAMICS	2009, 41, 3, 420-432	1,966
Pflieger, R; Malki, M; Guari, Y; Larionova, J; Grandjean, A	Electrical Conductivity of RuO2-Borosilicate Glasses: Effect of the Synthesis Route	JOURNAL OF THE AMERICAN CERAMIC SOCIETY	2009, 92, 7, 1560-1566	1,944
Pflieger, R; Lefebvre, L; Malki, M; Allix, M; Grandjean, A	Behaviour of ruthenium dioxide particles in borosilicate glasses and melts	JOURNAL OF NUCLEAR MATERIALS	2009, 389, 3, 450-457	1,933
Wintergerst, M; Dacheux, N; Datcharry, F; Herms, E; Kapusta, B	Corrosion of the AlFeNi alloy used for the fuel cladding in the Jules Horowitz research reactor	JOURNAL OF NUCLEAR MATERIALS	2009, 393, 3, 371-380	1,933
Hingant, N; Clavier, N; Dacheux, N; Barre, N; Hubert, S; Obbade, S; Taborda, F; Abraham, F	Preparation, sintering and leaching of optimized uranium thorium dioxides	JOURNAL OF NUCLEAR MATERIALS	2009, 385, 2, 400-406	1,933
Pointeau, V; Deditius, AP; Miserque, F; Renock, D; Becker, U; Zhang, J; Clavier, N; Dacheux, N; Poinssot, C; Ewing, RC	Synthesis and characterization of coffinite	JOURNAL OF NUCLEAR MATERIALS	2009, 393, 3, 449-458	1,933
Metay, E; Duclos, MC; Pellet-Rostaing, S; Lemaire, M; Schulz, J; Kannappan, R; Bucher, C; Saint-Aman, E; Chaix, C	Conformational analysis and anion-binding properties of ferrocenyl-calixarene receptors	SUPRAMOLECULAR CHEMISTRY	2009, 21, 01-févr, 68-80	1,885
Manara, D; Grandjean, A; Neuville, DR	Advances in understanding the structure of borosilicate glasses: A Raman spectroscopy study	AMERICAN MINERALOGIST	2009, 94, 05-juin, 777-784	1,859
Lacquement, J; Boussier, H; Laplace, A; Conocar, O; Grandjean, A	Potentialities of fluoride-based salts for specific nuclear reprocessing: Overview of the R&D program at CEA	JOURNAL OF FLUORINE CHEMISTRY	2009, 130, 1, Sp. Iss. SI18-21	1,730

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Zemb, T	Flexibility, persistence length and bicontinuous microstructures in microemulsions	COMPTES RENDUS CHIMIE	2009, 12, 01-févr, 218-224	1,580
Testard, F; Berthon, L; Zemb, T	Liquid-liquid extraction: An adsorption isotherm at divided interface?	COMPTES RENDUS CHIMIE	2007, 10, 10-nov, 1034-1041	1,580
Lenoir, M; Grandjean, A; Poissonnet, S; Neuville, DR	Quantitation of sulfate solubility in borosilicate glasses using Raman spectroscopy	JOURNAL OF NON-CRYSTALLINE SOLIDS	2009, 355, 28-30, 1468-1473	1,252
Manara, D; Grandjean, A; Neuville, DR	Structure of borosilicate glasses and melts: A revision of the Yun, Bray and Dell model	JOURNAL OF NON-CRYSTALLINE SOLIDS	2009, 355, 50-51, 2528-2531	1,252
Meridiano, Y; Berthon, L; Crozes, X; Sorel, C; Dannus, P; Antonio, MR; Chiarizia, R; Zemb, T	Aggregation in Organic Solutions of Malonamides: Consequences for Water Extraction	SOLVENT EXTRACTION AND ION EXCHANGE	2009, 27, 05-juin, 607-637	1,163
Prevost, S; Coulombeau, H; Baczko, K; Berthon, L; Zorz, N; Desvaux, H; Testard, F; Zemb, T; Larpent, C	Thermo-responsive Metal-chelating Surfactants: Properties and Use in Cloud Point Extraction of Uranyl Nitrate	TENSIDE SURFACTANTS DETERGENTS	2009, 46, 2, 100-104	0,329
2008				
Diat, O; Gebel, G	Proton channels	NATURE MATERIALS	2008, 7, 1, 13-14	29,504
Morel, AL; Nikitenko, SI; Gionnet, K; Wattiaux, A; Lai-Kee-Him, J; Labrugere, C; Chevalier, B; Deleris, G; Petibois, C; Brisson, A; Simonoff, M	Sonochemical approach to the synthesis of Fe_3O_4@SiO_2 core-shell nanoparticles with tunable properties	ACS NANO	2008, 2, 5, 847-856	7,493
Makowski, P; Cakan, RD; Antonietti, M; Goettmann, F; Titirici, MM	Selective partial hydrogenation of hydroxy aromatic derivatives with palladium nanoparticles supported on hydrophilic carbon	CHEMICAL COMMUNICATIONS	2008, 8, 999-1001	5,504
Thomas, A; Goettmann, F; Antonietti, M	Hard templates for soft materials: Creating nanostructured organic materials	CHEMISTRY OF MATERIALS	2008, 20, 3, 738-755	5,368
Thomas, A; Fischer, A; Goettmann, F; Antonietti, M; Muller, JO; Schlogl, R; Carlsson, JM	Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts	JOURNAL OF MATERIALS CHEMISTRY	2008, 18, 41, 4893-4908	4,795
Fischer, A; Makowski, P; Mueller, JO; Antonietti, M; Thomas, A; Goettmann, F	High-surface-area TiO_2 and TiN as catalysts for the C-C coupling of alcohols and ketones	CHEMSUSCHEM	2008, 1, 5, 444-449	4,767
Veilly, E; de Kerdaniel, ED; Roques, J; Dacheux, N; Clavier, N	Comparative Behavior of Britholites and Monazite/Brabantite Solid Solutions during Leaching Tests: A Combined Experimental and DFT Approach	CHEMSUSCHEM	2008, 47, 23, 10971-10979	4,657
Hubert, S; Heisbourg, G; Dacheux, N; Moisy, P	Effect of inorganic ligands and hydrogen peroxide on ThO_2 dissolution. Behaviour of $Th_{0.87}Pu_{0.13}O_2$ during	INORGANIC CHEMISTRY	2008, 47, 6, 2064-2073	4,657

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
	leaching test			
Bosse, E; Den Auwer, C; Berthon, C; Guilbaud, P; Grigoriev, MS; Nikitenko, S; Le Naour, C; Cannes, C; Moisy, P	Solvation of UCl62- anionic complex by MeBu3N+, BuMe2IM+, and BuMeIm(+) cations	INORGANIC CHEMISTRY	2008, 47, 13, 5746-5755	4,657
Loyo, RLD; Nikitenko, SI; Scheinost, AC; Simonoff, M	Immobilization of selenite on Fe3O4 and Fe/Fe3C ultrasmall particles	ENVIRONMENTAL SCIENCE & TECHNOLOGY	2008, 42, 7, 2451-2456	4,630
Marestin, C; Gebel, G; Diat, O; Mercier, R	Sulfonated Polyimides	ADVANCES IN POLYMER SCIENCE	2008, 216, 185-258	4,600
Dahirel, V; Jardat, M; Dufreche, JF; Turq, P	Ion-mediated interactions between charged and neutral nanoparticles	PHYSICAL CHEMISTRY CHEMICAL PHYSICS	2008, 10, 33, 5147-5155	4,116
Basset, C; Dedieu, A; Guerin, P; Quemeneur, E; Meyer, D; Vidaud, C	Specific capture of uranyl protein targets by metal affinity chromatography	JOURNAL OF CHROMATOGRAPHY A	2008, 1185, 2, 233-240	4,101
Kreuer, KD; Schuster, M; Obliers, B; Diat, O; Traub, U; Fuchs, A; Klock, U; Paddison, SJ; Maier, J	Short-side-chain proton conducting perfluorosulfonic acid ionomers: Why they perform better in PEM fuel cells	JOURNAL OF POWER SOURCES	2008, 178, 2, 499-509	3,792
Gebel, G; Diat, O; Escribano, S; Mosdale, R	Water profile determination in a running PEMFC by small-angle neutron scattering	JOURNAL OF POWER SOURCES	2008, 179, 1, 132-139	3,792
Dufreche, JF; Jardat, M; Turq, P; Bagchi, B	Electrostatic relaxation and hydrodynamic interactions for self-diffusion of ions in electrolyte solutions	JOURNAL OF PHYSICAL CHEMISTRY B	2008, 112, 33, 10264-10271	3,471
Bauduin, P; Testard, F; Zemb, T	Solubilization in alkanes by alcohols as reverse hydrotropes or "Lipotropes"	JOURNAL OF PHYSICAL CHEMISTRY B	2008, 112, 39, 12354-12360	3,471
Page, MG; Zemb, T; Dubois, M; Colfen, H	Osmotic pressure and phase boundary determination of multiphase systems by analytical ultracentrifugation	CHEMPHYSCHEM	2008, 9, 6, 882-890	3,453
Lenoir, M; Grandjean, A; Linard, Y; Cochain, B; Neuville, DR	The influence of Si,B substitution and of the nature of network-modifying cations on the properties and structure of borosilicate glasses and melts	CHEMICAL GEOLOGY	2008, 256, 03-avr, Sp. Iss. SI 316-325	3,407
Sawicki, M; Lecercle, D; Grillon, G; Le Gall, B; Serandour, AL; Poncy, JL; Bailly, T; Burgada, R; Lecouvey, M; Challeix, V; Leydier, A; Pellet-Rostaing, S; Ansoborlo, E; Taran, F	Bisphosphonate sequestering agents. Synthesis and preliminary evaluation for in vitro and in vivo uranium(VI) chelation	EUROPEAN JOURNAL OF MEDICINAL CHEMISTRY	2008, 43, 12, 2768-2777	3,269
Leydier, A; Lecercle, D; Pellet-Rostaing, S; Favre-Reguillon, A; Taran, F; Lemaire, M	Sequestering agent for uranyl chelation: a new family of CAMS ligands	TETRAHEDRON	2008, 64, 28, 6662-6669	3,219

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Leydier, A; Lecercle, D; Pellet-Rostaing, S; Favre-Reguillon, A; Taran, F; Lemaire, M	Sequestering agents for uranyl chelation: new calixarene ligands	TETRAHEDRON	2008, 64, 49, 11319-11324	3,219
Metay, E; Duclos, MC; Pellet-Rostaing, S; Lemaire, M; Schulz, J; Kannappan, R; Bucher, C; Saint-Aman, E; Chaix, C	Synthesis and anion-binding properties of novel redox-active calixarene receptors	EUROPEAN JOURNAL OF ORGANIC CHEMISTRY	2008, 25, 4304-4312	3,096
Makowski, P; Weber, J; Thomas, A; Goettmann, F	A mesoporous poly(benzimidazole) network as a purely organic heterogeneous catalyst for the Knoevenagel condensation	CATALYSIS COMMUNICATIONS	2008, 10, 2, 243-247	3,000
Gracia, S; Schulz, J; Pellet-Rostaing, S; Lemaire, M	Synthesis of new pyrrolobenzazepines via Pictet-Spengler cyclization	SYNLETT	2008, 12, 1852-1856	2,718
Kaper, H; Antonietti, M; Goettmann, F	Metal-free activation of C-C multiple bonds through halide ion pairs: Diels-Alder reactions with subsequent aromatization	TETRAHEDRON LETTERS	2008, 49, 29-30, 4546-4549	2,660
David, E; Lejeune, J; Pellet-Rostaing, S; Schulz, R; Lemaire, M; Chauvin, J; Deronzier, A	Synthesis of fluorescent rhodamine dyes using an extension of the Heck reaction	TETRAHEDRON LETTERS	2008, 49, 11, 1860-1864	2,660
Clavier, N; Wallez, G; Dacheux, N; Bregiroux, D; Quarton, M; Beaunier, P	Synthesis, Raman and Rietveld analysis of thorium diphosphate	JOURNAL OF SOLID STATE CHEMISTRY	2008, 181, 12, 3352-3356	2,340
Gromadzki, D; Lokaj, J; Cernoch, P; Diat, O; Nallet, F; Stepanek, P	Morphology of polystyrene-block-poly(styrene-co-acrylonitrile) and polystyrene-block-poly(styrene-co-acrylonitrile-co-5-vinyltetrazole) diblock copolymers prepared by nitroxide-mediated radical polymerization and "click" chemistry	EUROPEAN POLYMER JOURNAL	2008, 44, 1, 189-199	2,310
Dahirel, V; Jardat, M; Dufreche, JF; Lucas, IT; Durand-Vidal, S; Turq, P	Coarse-graining in suspensions of charged nanoparticles	PURE AND APPLIED CHEMISTRY	2008, 80, 6, 1229-1238	2,289
Zamoum, F; Benlaharche, T; David, N; Podor, R; Vilasi, M	Kinetics of high temperature oxidation of (Nb,Co,Cr)(7)Si-6 and (Nb,Co,Cr)(8)Si-7 silicide compounds	INTERMETALLICS	2008, 16, 4, 498-507	2,231
Dubois, M; Carriere, D; Iyer, R; Arunagirinathan, MA; Bellare, J; Verbavatz, JM; Zemb, T	From dispersed nanodiscs to thin films of layered organic material via reversible swelling	COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS	2008, 319, 01-mars, Sp. Iss. SI, 90-97	1,988
Tchakalova, V; Testard, F; Wong, K; Parker, A; Benczedi, D; Zemb, T	Solubilization and interfacial curvature in microemulsions I. Interfacial expansion and co-extraction of oil	COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS	2008, 331, 01-févr, Sp. Iss. SI, 31-39	1,988
Tchakalova, V; Testard, F; Wong, K; Parker, A; Benczedi, D; Zemb, T	Solubilization and interfacial curvature in microemulsions II. Surfactant efficiency and PIT	COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS	2008, 331, 01-févr, Sp. Iss. SI, 40-47	1,988

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Khedim, H; Podor, R; Rapin, C; Vilasi, M	Redox-Control Solubility of Chromium Oxide in Soda-Silicate Melts	JOURNAL OF THE AMERICAN CERAMIC SOCIETY	2008, 91, 11, 3571-3579	1,944
Picot, V; Deschanels, X; Peuget, S; Glorieux, B; Seydoux-Guillaume, AM; Wirth, R	Ion beam radiation effects in monazite	JOURNAL OF NUCLEAR MATERIALS	2008, 381, 3, 290-296	1,933
Tamain, C; Garrido, F; Thome, L; Dacheux, N; Ozgumus, A	Structural behavior of beta-thorium phosphate diphosphate (beta-TPD) irradiated with ion beams	JOURNAL OF NUCLEAR MATERIALS	2008, 373, 01-mars, 378-386	1,933
Ozgumus, A; Gilabert, E; Dacheux, N; Tamain, C; Lavielle, B	Study of radiogenic helium diffusion in the beta-thorium phosphate diphosphate ceramic	JOURNAL OF NUCLEAR MATERIALS	2008, 373, 01-mars, 112-118	1,933
Xie, LL; Favre-Reguillon, A; Pellet-Rostaing, S; Wang, XX; Fu, XZ; Estager, J; Vrinat, M; Lemaire, M	Selective Extraction and Identification of Neutral Nitrogen Compounds Contained in Straight-Run Diesel Feed Using Chloride Based Ionic Liquid	INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH	2008, 47, 22, 8801-8807	1,758
Lamarque, JF; Lamarque, C; Lassara, S; Medebielle, M; Molette, J; David, E; Pellet-Rostaing, S; Lemaire, M; Okada, E; Shibata, D; Pilet, G	Copper catalyzed 1,3-dipolar cycloaddition reaction of azides with N-(2-trifluoroacetylaryl)propargylamines A mild entry to novel 1,4-disubstituted-[1,2,3]-triazole derivatives	JOURNAL OF FLUORINE CHEMISTRY	2008, 129, 9, Sp. Iss. SI 788-798	1,730
Maitre, A; Beyssen, D; Podor, R	Modelling of the grain growth and the densification of SnO2-based ceramics	CERAMICS INTERNATIONAL	2008, 34, 1, 27-35	1,686
Testard, F; Bauduin, P; Martinet, L; Abecassis, B; Berthon, L; Madic, C; Zemb, T	Self-assembling properties of malonamide extractants used in separation processes	RADIOCHIMICA ACTA	2008, 96, 04-mai, 265-272	1,459
Mathieu, R; Khedim, H; Libourel, G; Podor, R; Tissandier, L; Deloule, E; Faure, F; Rapin, C; Vilasi, M	Control of alkali-metal oxide activity in molten silicates	JOURNAL OF NON-CRYSTALLINE SOLIDS	2008, 354, 45-46, 5079-5083	1,252
Abdelouhab, S; Podor, R; Rapin, C; Toplis, MJ; Berthod, P; Vilasi, M	Determination of Na2O activities in silicate melts by EMF measurements	JOURNAL OF NON-CRYSTALLINE SOLIDS	2008, 354, 26, 3001-3011	1,252
Grandjean, A; Malki, M; Montouillout, V; Debruycker, F; Massiot, D	Electrical conductivity and B-11 NMR studies of sodium borosilicate glasses	JOURNAL OF NON-CRYSTALLINE SOLIDS	2008, 354, 15-16, 1664-1670	1,252
Schuller, S; Pinet, O; Grandjean, A; Blisson, T	Phase separation and crystallization of borosilicate glass enriched in MoO3, P2O5, ZrO2, CaO	JOURNAL OF NON-CRYSTALLINE SOLIDS	2008, 354, 02-sept, 296-300	1,252
Lin, Y; Leydier, A; Metay, E; Favre-Reguillon, A; Bouchu, D; Pellet-Rostaing, S; Lemaire, M	Synthesis of original capping calixarenes with DTPA fragment	JOURNAL OF INCLUSION PHENOMENA AND MACROCYCLIC CHEMISTRY	2008, 61, 01-févr, 187-193	1,165
Alame, M; Meille, V; De Bellefon, C; Jahjah, M; Pellet-Rostaing, S; Berthod, M; Lemaire, M	Highly regioselective bromination of BINAP in [Hmim]PF6 ionic liquid	SYNTHETIC COMMUNICATIONS	2008, 38, 1, 141-147	0,961
Xie, LL; Chen, X; Wang, XX; Fu, XZ; Favre-Reguillon, A; Pellet-Rostaing, S; Lemaire, M	Removal of N-compounds from diesel fuel by using chloridized imidazole based ionic liquids	CHINESE JOURNAL OF INORGANIC CHEMISTRY	2008, 24, 6, 919-925	0,606

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Zemb, T	Meeting with Thomas Zemb, director of the ICSM	ACTUALITE CHIMIQUE	2008, , 322, 8-10	0,143
Diop, I; David, N; Fiorani, JM; Podor, R; Vilasi, M	Corrosion of T91 steel in LBE : contribution to the study of the Pb-Bi-O-Fe-Hg system - thermodynamic description of PbO-Fe2O3	HIGH TEMPERATURE CORROSION AND PROTECTION OF MATERIALS 7, PTS 1 AND 2	2008, 595-598, , 473-481	
Lebel, F; Rapin, C; Mareche, JF; Podor, R; Chaucherie, X; Guernion, PY; Brossard, JM	Development of a laboratory-scale pilot for studying corrosion on MSWI heat exchangers	HIGH TEMPERATURE CORROSION AND PROTECTION OF MATERIALS 7, PTS 1 AND 2	2008, 595-598, , 271-280	
Rapin, C; Podor, R; Gassert, J; Vilasi, M	Impedance spectroscopy applied to metal corrosion study in silicate melts	HIGH TEMPERATURE CORROSION AND PROTECTION OF MATERIALS 7, PTS 1 AND 2	2008, 595-598, , 1119-1126	
Khedim, H; Abdelouhab, S; Podor, R; Rapin, C; Vilasi, M	Relationship between chromia solubility and superalloy corrosion in silicate melts - A first attempt	HIGH TEMPERATURE CORROSION AND PROTECTION OF MATERIALS 7, PTS 1 AND 2	2008, 595-598, , 621-627	
2007				
Goettmann, F; Thomas, A; Antonietti, M	Metal-free activation CO2 by mesoporous graphitic carbon nitride	ANGEWANDTE CHEMIE-INTERNATIONAL EDITION	2007, 46, 15, 2717-2720	11,829
Dejugnat, C; Kohler, K; Dubois, M; Sukhorukov, GB; Mohwald, H; Zemb, T; Guttmann, P	Membrane densification of heated polyelectrolyte multilayer capsules characterized by soft X-ray microscopy	ADVANCED MATERIALS	2007, 19, 10, 1331-+	8,379
Hao, JC; Zemb, T	Self-assembled structures and chemical reactions in room-temperature ionic liquids	CURRENT OPINION IN COLLOID & INTERFACE SCIENCE	2007, 12, 3, 129-137	5,488
Zemb, T; Blume, A	Self-assembly weak long-range interactions at work	CURRENT OPINION IN COLLOID & INTERFACE SCIENCE	2007, 12, 3, 99-100	5,488
Goettmann, F; Sanchez, C	How does confinement affect the catalytic activity of mesoporous materials?	JOURNAL OF MATERIALS CHEMISTRY	2007, 17, 1, 24-30	4,795
Vilain, C; Goettmann, F; Moores, A; Le Floch, P; Sanchez, C	Study of metal nanoparticles stabilised by mixed ligand shell: a striking blue shift of the surface-plasmon band evidencing the formation of Janus nanoparticles	JOURNAL OF MATERIALS CHEMISTRY	2007, 17, 33, 3509-3514	4,795
Dacheux, N; Grandjean, S; Rousselle, J; Clavier, N	Hydrothermal method of preparation of actinide(IV) phosphate hydrogen phosphate hydrates and study of their conversion into actinide(IV) phosphate diphosphate solid solutions	INORGANIC CHEMISTRY	2007, 46, 24, 10390-10399	4,657
Bregiroux, D; Terra, O; Audubert, F; Dacheux, N; Serin, V; Podor, R; Bernache-Assollant, D	Solid-state synthesis of monazite-type compounds containing tetravalent elements	INORGANIC CHEMISTRY	2007, 46, 24, 10372-10382	4,657
Rubatat, L; Diat, O	Stretching effect on Nafion fibrillar nanostructure	MACROMOLECULES	2007, 40, 26, 9455-9462	4,539

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Truffier-Boutry, D; De Geyer, A; Guetaz, L; Diat, O; Gebel, G	Structural study of zirconium phosphate-nafion hybrid membranes for high-temperature proton exchange membrane fuel cell applications	MACROMOLECULES	2007, 40, 23, 8259-8264	4,539
Aroti, A; Leontidis, E; Dubois, M; Zemb, T	Effects of monovalent anions of the Hofmeister series on DPPC lipid Bilayers part I: Swelling and in-plane equations of state	BIOPHYSICAL JOURNAL	2007, 93, 5, 1580-1590	4,39
Leontidis, E; Aroti, A; Belloni, L; Dubois, M; Zemb, T	Effects of monovalent anions of the Hofmeister series on DPPC lipid Bilayers part II: Modeling the perpendicular and lateral equation-of-state	BIOPHYSICAL JOURNAL	2007, 93, 5, 1591-1607	4,39
Bauduin, P; Testard, F; Berthon, L; Zemb, T	Relation between the hydrophile/hydrophobe ratio of malonamide extractants and the stability of the organic phase: investigation at high extractant concentrations	PHYSICAL CHEMISTRY CHEMICAL PHYSICS	2007, 9, 28, 3776-3785	4,116
Fratini, E; Page, MG; Giorgi, R; Colfen, H; Baglioni, P; Deme, B; Zemb, T	Competitive surface adsorption of solvent molecules and compactness of agglomeration in calcium hydroxide nanoparticles	LANGMUIR	2007, 23, 5, 2330-2338	3,898
Abecassis, B; Testard, F; Arleth, L; Hansen, S; Grillo, I; Zemb, T	Electrostastic control of spontaneous curvature in catanionic reverse micelles	LANGMUIR	2007, 23, 20, 9983-9989	3,898
Maurer, E; Belloni, L; Zemb, T; Carriere, D	Ion exchange in catanionic mixtures: From ion pair amphiphiles to surfactant mixtures	LANGMUIR	2007, 23, 12, 6554-6560	3,898
Renoncourt, A; Vlachy, N; Bauduin, P; Drechsler, M; Touraud, D; Verbavatz, JM; Dubois, M; Kunz, W; Ninham, BW	Specific alkali cation effects in the transition from micelles to vesicles through salt addition	LANGMUIR	2007, 23, 5, 2376-2381	3,898
Pineri, M; Gebel, G; Davies, RJ; Diat, O	Water sorption-desorption in Nafion (R) membranes at low temperature, probed by micro X-ray diffraction	JOURNAL OF POWER SOURCES	2007, 172, 2, 587-596	3,792
Grandjean, A; Malki, M; Simonnet, C; Manara, D; Penelon, B	Correlation between electrical conductivity, viscosity, and structure in borosilicate glass-forming melts	PHYSICAL REVIEW B	2007, 75, 5	3,475
Delorme, N; Bardeau, JF; Carriere, D; Dubois, M; Gourbil, A; Mohwald, H; Zemb, T; Fery, A	Experimental evidence of the electrostatic contribution to the bending rigidity of charged membranes	JOURNAL OF PHYSICAL CHEMISTRY B	2007, 111, 10, 2503-2505	3,471
Kohler, K; Dejugnat, C; Dubois, M; Zemb, T; Sukhorukov, GB; Guttmann, P; Mohwald, H	Soft X-ray Microscopy to characterize polyelectrolyte assemblies	JOURNAL OF PHYSICAL CHEMISTRY B	2007, 111, 29, 8388-8393	3,471

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Alame, M; Jahjah, M; Pellet-Rostaing, S; Lemaire, M; Meille, V; de Bellefon, C	2,2 '-bis-[bis(4-substituted-phenyl)phosphinol-1,1 '-binaphthyl derivatives in Rh(I)-catalyzed hydrogenation of acetamidoacrylic acid derivatives: Electronic effects	JOURNAL OF MOLECULAR CATALYSIS A-CHEMICAL	2007, 271, 01-févr, 18-24	3,135
Aubry, S; Pellet-Rostaing, S; Lemaire, M	Oxidative nucleophilic Substitution(SNOX) of the benzylic position as a tunable synthesis of tetrahydroisoquinoline natural alkaloid analogues	EUROPEAN JOURNAL OF ORGANIC CHEMISTRY	2007, 31, 5212-5225	3,096
Dahirel, V; Jardat, M; Dufreche, JF; Turq, P	New coarse-graining procedure for the dynamics of charged spherical nanoparticles in solution	JOURNAL OF CHEMICAL PHYSICS	2007, 126, 11	3,093
Dahirel, V; Jardat, M; Dufreche, JF; Turq, P	Toward the description of electrostatic interactions between globular proteins: Potential of mean force in the primitive model	JOURNAL OF CHEMICAL PHYSICS	2007, 127, 9	3,093
Rotenberg, B; Marry, V; Dufreche, JF; Giffaut, E; Turq, P	A multiscale approach to ion diffusion in clays: Building a two-state diffusion-reaction scheme from microscopic dynamics	JOURNAL OF COLLOID AND INTERFACE SCIENCE	2007, 309, 2, 289-295	3,019
Goettmann, F; Fischer, A; Antonietti, M; Thomas, A	Mesoporous graphitic carbon nitride as a versatile, metal-free catalyst for the cyclisation of functional nitriles and alkynes	NEW JOURNAL OF CHEMISTRY	2007, 31, 8, 1455-1460	3,006
Larpent, C; Prevost, S; Berthon, L; Zemb, T; Testard, F	Nonionic metal-chelating surfactants mediated solvent-free thermo-induced separation of uranyl	NEW JOURNAL OF CHEMISTRY	2007, 31, 8, 1424-1428	3,006
Cortial, G; Goettmann, F; Mercier, F; Le Floch, P; Sanchez, C	Bioinspired enantioselective catalysis: Racemic or achiral metal complexes grafted on mesoporous material functionalized with chiral molecules	CATALYSIS COMMUNICATIONS	2007, 8, 3, 215-219	3,000
Nikitenko, SI; Le Naour, C; Moisy, P	Comparative study of sonochemical reactors with different geometry using thermal and chemical probes	ULTRASONICS SONOCHEMISTRY	2007, 14, 3, 330-336	2,993
Chabert, JFD; Marquez, B; Neville, L; Joucla, L; Broussous, S; Bouhours, P; David, E; Pellet-Rostaing, S; Marquet, B; Moreau, N; Lemaire, M	Synthesis and evaluation of new arylbenzo[b]thiophene and diarylthiophene derivatives as inhibitors of the NorA multidrug transporter of Staphylococcus aureus	BIOORGANIC & MEDICINAL CHEMISTRY	2007, 15, 13, 4482-4497	2,822
Aubry, S; Pellet-Rostaing, S; Chabert, JFD; Ducki, S; Lemaire, M	Synthesis and inhibition of cancer cell proliferation of (1,3 ')-bis-tetrahydroisoquinolines	BIOORGANIC & MEDICINAL CHEMISTRY LETTERS	2007, 17, 9, 2598-2602	2,822

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
	and piperazine systems			
Lin, Y; Favre-Reguillon, A; Pellet-Rostaing, S; Lemaire, M	Synthesis of pyridine-based polyaminocarboxylic ligands bearing a thioalkyl anchor	TETRAHEDRON LETTERS	2007, 48, 19, 3463-3466	2,660
Aubry, S; Razatindrabe, CR; Bourdon, B; Pellet-Rostaing, S; Lemaire, M	Synthetic studies towards (+/-)-phthalascidin 650: synthesis of a fully functionalized N-protected-alpha-amino-aldehyde	TETRAHEDRON LETTERS	2007, 48, 52, 9163-9166	2,660
Jahjah, M; Jahjah, R; Pellet-Rostaing, S; Lemaire, M	Asymmetric hydrogenation of aromatic ketones with new P-chirogenic monophosphine ligands	TETRAHEDRON-ASYMMETRY	2007, 18, 10, 1224-1232	2,625
Quintard, A; Darbost, U; Vocanson, F; Pellet-Rostaing, S; Lemaire, M	Synthesis of new calix[4]arene based chiral ligands bearing beta-amino alcohol groups and their application in asymmetric transfer hydrogenation	TETRAHEDRON-ASYMMETRY	2007, 18, 16, 1926-1933	2,625
Dahirel, V; Jardat, M; Dufreche, JF; Turq, P	How the excluded volume architecture influences ion-mediated forces between proteins	PHYSICAL REVIEW E	2007, 76, 4	2,400
Podor, R; David, N; Rapin, C; Vilasi, M; Berthod, P	Mechanisms of corrosion layer formation during zirconium immersion in a (Fe)-bearing glass melt	CORROSION SCIENCE	2007, 49, 8, 3226-3240	2,316
Xu, F; Diat, O; Gebel, G; Morin, A	Determination of transverse water concentration profile through MEA in a fuel cell using neutron scattering	JOURNAL OF THE ELECTROCHEMICAL SOCIETY	2007, 154, 12, B1389-B1398	2,241
Abdelouhab, S; Rapin, C; Podor, R; Berthod, P; Vilasi, M	Electrochemical study of chromium corrosion in Na2O-xSiO(2) melts	JOURNAL OF THE ELECTROCHEMICAL SOCIETY	2007, 154, 9, C500-C507	2,241
Nikitenko, SI; Hennig, C; Grigoriev, MS; Le Naour, C; Cannes, C; Trubert, D; Bosse, E; Berthon, C; Moisy, P	Structural and spectroscopic studies of the complex [BuMeIm](2)[UCl6] in the solid state and in hydrophobic room temperature ionic liquid [BuMeIm][Tf2N]	POLYHEDRON	2007, 26, 13, 3136-3142	2,207
Cornet, SM; Maya, I; Sarsfield, MJ; Kaltsoyannis, N; Haller, J; Den Auwer, C; Meyer, D	Actinyl chemistry across the U, Np and Pu series	JOURNAL OF ALLOYS AND COMPOUNDS	2007, 444, 453-456	2,135
Zemb, T; Carriere, D; Glinel, K; Hartman, M; Meister, A; Vautrin, C; Delorme, N; Fery, A; Dubois, M	Catanionic bilayers as micro-crystals with in-plane ordered alternated charges	COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS	2007, 303, 01-févr, 37-45	1,988
Mohwald, H; Zemb, T	Complex Fluids - from 2D to 3D - Preface	COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS	2007, 303, 01-févr, 1-2	1,988
Colfen, H; Page, MG; Dubois, M; Zemb, T	Mineralization in complex fluids	COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS	2007, 303, 01-févr, 46-54	1,988

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Aroti, A; Leontidis, E; Dubois, M; Zemb, T; Brezesinski, G	Monolayers, bilayers and micelles of zwitterionic lipids as model systems for the study of specific anion effects	COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS	2007, 303, 01-févr, 144-158	1,988
Carriere, D; Page, M; Dubois, M; Zemb, T; Colfen, H; Meister, A; Belloni, L; Schonhoff, M; Mohwald, H	Osmotic pressure in colloid science: clay dispersions, catanionics, polyelectrolyte complexes and polyelectrolyte multilayers	COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS	2007, 303, 01-févr, 137-143	1,988
de Kerdaniel, ED; Clavier, N; Dacheux, N; Terra, O; Podor, R	Actinide solubility-controlling phases during the dissolution of phosphate ceramics	JOURNAL OF NUCLEAR MATERIALS	2007, 362, 02-mars, 451-458	1,933
Peuget, S; Broudic, V; Jegou, C; Frugier, P; Roudil, D; Deschanels, X; Rabiller, H; Noel, PY	Effect of alpha radiation on the leaching behaviour of nuclear glass	JOURNAL OF NUCLEAR MATERIALS	2007, 362, 02-mars, 474-479	1,933
Roudil, D; Jegou, C; Broudic, V; Muzeau, B; Peuget, S; Deschanels, X	Gap and grain boundaries inventories from pressurized water reactor spent fuels	JOURNAL OF NUCLEAR MATERIALS	2007, 362, 02-mars, 411-415	1,933
Wiss, T; Deschanels, X; Hiernaut, JP; Roudil, D; Peuget, S; Rondinella, VV	Helium release from plutonium and curium-doped zirconolite	JOURNAL OF NUCLEAR MATERIALS	2007, 362, 02-mars, 431-437	1,933
Tamain, C; Dacheux, N; Garrido, F; Thome, L	Irradiation effects on thorium phosphate diphosphate: Chemical durability and thermodynamic study	JOURNAL OF NUCLEAR MATERIALS	2007, 362, 02-mars, 459-465	1,933
Terra, O; Audubert, F; Dacheux, N; Guy, C; Podor, R	Synthesis and characterization of uranium-bearing britholites	JOURNAL OF NUCLEAR MATERIALS	2007, 366, 01-févr, 70-86	1,933
Favre-Reguillon, A; Fiaty, K; Laurent, P; Poriel, L; Pellet-Rostaing, S; Lemaire, M	Solid/liquid extraction of zirconium and hafnium in hydrochloric acid aqueous solution with anion exchange resin-kinetic study and equilibrium analyses	INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH	2007, 46, 4, 1286-1291	1,758
Dacheux, N; Clavier, N; Wallez, G; Quarton, M	Crystal structures of Th(OH)PO4, U(OH)PO4 and Th2O(PO4)(2). Condensation mechanism of M-IV(OH)PO4 (M = Th, U) into M2O(PO4)(2)	SOLID STATE SCIENCES	2007, 9, 7, Sp. Iss. SI 619-627	1,675
Leroy, M; Henge-Napoli, MH; Zemb, T	Complex fluids, divided solids and their interfaces: Open scientific questions addressed at the Institute of Separation Chemistry of Marcoule for a sustainable nuclear energy	COMPTES RENDUS CHIMIE	2007, 10, 10-nov, 1042-1049	1,580
Meyer, DJM; Bourg, S; Conocar, O; Broudic, JC; Moreau, JJE; Man, MWC	Extraction of plutonium and americium using silica hybrid materials	COMPTES RENDUS CHIMIE	2007, 10, 10-nov, 1001-1009	1,580
Nikitenko, SI; Berthon, C; Moisy, P	Instability of actinide(IV) hexachloro complexes in room-temperature ionic liquid [BuMeIm]PF6 due to hydrolysis of the hexafluorophosphate anion	COMPTES RENDUS CHIMIE	2007, 10, 10-nov, 1122-1127	1,580

Auteurs	Titre	Journal	Année, Vol, num, pages	IF (2009)
Rotenberg, B; Marry, V; Dufreche, JF; Malikova, N; Giffaut, E; Turq, P	Modelling water and ion diffusion in clays: A multiscale approach	COMPTES RENDUS CHIMIE	2007, 10, 10-nov, 1108-1116	1,580
Favre-Reguillon, A; Sorin, A; Pellet-Rostaing, S; Bernier, G; Lemaire, M	Nanofiltration assisted by complexation: A promising process for the separation of trivalent long-lived minor actinides from lanthanides	COMPTES RENDUS CHIMIE	2007, 10, 10-nov, 994-1000	1,580
Rahal, R; Daniele, S; Pellet-Rostaing, S; Lemaire, M	New hybrid TiO2 nano-structured materials for lanthanides separation	CHEMISTRY LETTERS	2007, 36, 11, 1364-1365	1,460
Jegou, C; Muzeau, B; Broudic, V; Roudil, D; Deschanels, X	Spent fuel UO2 matrix alteration in aqueous media under oxidizing conditions	RADIOCHIMICA ACTA	2007, 95, 9, 513-522	1,459
Manara, D; Grandjean, A; Pinet, O; Dussossoy, JL; Neuville, DR	Sulfur behavior in silicate glasses and melts: Implications for sulfate incorporation in nuclear waste glasses as a function of alkali cation and V2O5 content	JOURNAL OF NON-CRYSTALLINE SOLIDS	2007, 353, 1, 12-23	1,252
Lokaj, J; Polikova, L; Holler, P; Starovoytova, L; Stepanek, P; Diat, O	Synthesis of diblock copolymers comprising poly(2-vinylpyridine-co-acrylonitrile) and polystyrene blocks by nitroxide-mediated radical polymerization	JOURNAL OF APPLIED POLYMER SCIENCE	2007, 105, 3, 1616-1622	1,203
Berthon, L; Martinet, L; Testard, F; Madic, C; Zemb, T	Solvent penetration and sterical stabilization of reverse aggregates based on the DIAMEX process extracting molecules: Consequences for the third phase formation	SOLVENT EXTRACTION AND ION EXCHANGE	2007, 25, 5, 545-576	1,163
Deschanels, X; Peuget, S; Cachia, JN; Charpentier, T	Plutonium solubility and self-irradiation effects in borosilicate glass	PROGRESS IN NUCLEAR ENERGY	2007, 49, 8, 623-634	0,677
Tamain, C; Ozgumus, A; Dacheux, N; Garrido, F; Thome, L; Corbel, C; Mendes, E	Consequences of external irradiation on the chemical durability of the beta-thorium phosphate-diphosphate during leaching tests	JOURNAL OF RADIOANALYTICAL AND NUCLEAR CHEMISTRY	2007, 273, 3, 597-601	0,631
Clavier, N; Dacheux, N; Wallez, G; Quarton, M	Hydrothermal methods as a new way of actinide phosphate preparation	Scientific Basis for Nuclear Waste Management XXX	2007, 985, 169-174	
de Kerdaniel, ED; Clavier, N; Dacheux, N; Podor, R	Kinetic and thermodynamic study of the chemistry of neoformed phases during the dissolution of phosphate based ceramics	Scientific Basis for Nuclear Waste Management XXX	2007, 985, 341-346	

Appendix B

Liste des brevets

Liste des brevets

N° de dépôt	Année de dépôt	Titre du brevet	Déposants	Inventeur
	2010	Utilisation d'hydroxydes fondus pour la thermolyse de dérivé ligno-cellulosique	CEA	F. Goettmann, Ph. Makowski, A. Grandjean, D. Da Silva Perez, M. Petit Conil, A. Varet
dépôt n°10/51132	2010	Utilisation de lignigne comme substituant du sucre et des adjuvants lors de la calcination de solutions de radionucléides	CEA	V. Labe, F. Goettmann, C. Carrignon, A. Grandjean, A. Ledoux
dépôt n°10/52216	2010	Nouvelle iodopatite, son procédé de préparation et ses utilisations	CEA	D. Laurencin, A. Grandjean, L. Campayo
FR2888576	2010	Procédé de confinement d'une matière par vitrification	CEA	O. Pinet, T. Blisson, A. Grandjean, S. Schuller

Appendix C

Résumé du projet de LABEX proposé par le Pole de Chimie Balard du Languedoc-Roussillon

CHIMIE DES SYSTEMES - CHEMISYST- DU PÔLE DE CHIMIE BALARD DU LANGUEDOC-ROUSSILLON

Chimie des systèmes -CHEMISYST- du pôle de chimie Balard du Languedoc-Roussillon

Le projet CheMISyst du Pôle Balard bénéficie d'une puissante dynamique initiée depuis plusieurs années :

- Tout d'abord, la volonté des chimistes de Montpellier et de sa région de travailler au sein d'une structure fédérative commune, le pôle de chimie Balard, dont la mission est d'harmoniser l'offre de formation et la valorisation entre les établissements partenaires, ainsi que la politique de recherche des Instituts dans le cadre de la fédération de recherche CNRS FR 3105 Balard. Cet ensemble rassemble plus de 400 chercheurs et enseignants-chercheurs permanents sur les sites de Montpellier, Marcoule et Alès, travaillant au sein de vingt-six équipes identifiées, dont les projets ont été notés "A+" pour onze d'entre elles et "A" pour douze autres par l'AERES (évaluation 2010).
- Ensuite, la décision récente, dans le cadre du plan campus, de créer sur Montpellier pour la chimie un lieu unique de recherche (trois Instituts), d'enseignement (nouvelle implantation de l'ENSCM) et de transfert et valorisation (un centre de recherche et innovation pour les « jeunes pousses » et un hôtel d'entreprises). En association avec le site de Marcoule et l'Ecole des Mines d'Alès, l'objectif est de créer un centre universitaire de taille critique à l'échelle européenne, sur le modèle de Lund ou Potsdam.

Trois domaines d'expertise sont actuellement bien identifiés sur le Pôle Balard. Deux domaines historiques sont d'une part celui des matériaux fonctionnels (matériaux pour la catalyse, matériaux membranaires, matériaux pour l'énergie, polymères, matériaux hybrides organiques-inorganiques, matériaux pour la santé) et celui de la synthèse et de l'assemblage des biomolécules (incluant des approches innovantes sur la conception de nouveaux médicaments, la vectorisation, le ciblage ou la toxicologie prédictive). Le troisième domaine provient des compétences uniques en Europe du CEA dans les procédés de séparation (ICSM), sur lesquelles reposent non seulement les procédés d'un nucléaire de plus en plus renouvelable, mais aussi le recyclage stratégique des terres rares et autres métaux. L'objectif du présent projet est de renforcer la synergie des équipes des différents Instituts autour d'une ambition scientifique commune s'inscrivant dans la durée et de créer un corpus d'expertises et de compétences identifiable à l'échelle internationale, tant sur le plan académique que de l'innovation industrielle.

Résumé du projet de recherche

Alors que classiquement la chimie essaie de décrire la matière dans sa complexité comme un assemblage d'unités constitutives susceptibles d'être étudiées séparément, la science moderne voit apparaître le concept de "système", défini comme l'organisation d'espèces en interaction les unes avec les autres, formant un ensemble « intégré » dont les propriétés ne sauraient être interprétées à partir de celles de chaque constituant. Dans le futur, l'enjeu de la chimie serait moins de synthétiser des espèces nouvelles que de découvrir des combinaisons inédites d'espèces connues : nanocomposites, agrégats, clusters, colloïdes etc., porteurs de propriétés innovantes insoupçonnées. Cette approche est la clé de la chimie interfaciale qui vise à étudier des phénomènes complexes comme les interactions des ions et molécules adsorbés dans/sur des structures solides hôtes, et de relier les effets sur leur conformation, dynamique et réactivité avec les caractéristiques géométriques et électroniques de ces structures. Cette approche est également la clé vers la construction bottom-up de systèmes « intelligents » capables de répondre à des stimuli externes et / ou de manière sélective reconnaître, encapsuler, transporter ou transformer chimiquement des ions et des molécules dans les liquides, solides ou de gels. La chimie des "systèmes moléculaires et interfaciaux" est un thème transverse aux quatre Instituts de Balard, fondé sur la connaissance et la modélisation des interactions à longue distance, qui s'appuiera sur l'action CECAM à développer sur Montpellier. Cette approche "chimie des systèmes" offre à leurs projets de recherche respectifs un horizon de dépassement à moyen et long termes, avec une résonance dans la chimie du recyclage de la matière utilisée économiquement.

Projet de formation associée

L'offre de formation actuelle, qui couvre les différents domaines de la chimie et de ses interfaces avec les sciences de la vie, la physique et le génie des procédés, est déjà bien en phase avec les axes stratégiques du projet CheMISyst. Cette offre couvre également tous les niveaux en formation initiale et continue, du DUT au Doctorat, en passant par l'ingéniorat.

CheMISyst a vocation à promouvoir la création de formations innovantes et leur attractivité nationale et internationale, favorisant ainsi l'intégration des élèves diplômés sur le marché du travail.

La clé de voûte est la création de quatre chaires à vocation internationale. Ces chaires seront associées avec les trois axes stratégiques (matériaux à tâches spécifiques, séparation, décontamination et recyclage, et systèmes biomoléculaires spécifiques) et le thème transversal du projet, à savoir les interactions à longue portée. En collaboration avec les détenteurs des chaires, CheMISyst aura en charge l'organisation annuelle d'une école d'été internationale sur la chimie des systèmes, sur la base minimale de sept jours et trente-cinq participants et conçue comme une extension des thèmes de l'*European Practical Summer School of Separation Chemistry*, annuelle depuis 2007.

Cette évolution continue dans le contenu de l'offre de formation s'accompagnera par une amplification de son internationalisation, déjà bien réelle avec, en fer de lance, le master européen Erasmus Mundus EM3E coordonné par l'UM2, le master EMASCO-COSOM de la fédération Gay-Lussac piloté depuis Regensburg et le Master Chimie séparative, matériaux et procédés. Ce master, sélectif et généraliste qui couvre l'ensemble chimie séparative et énergie nucléaire est en cours d'internationalisation. De nouveaux projets de partenariats internationaux sont actuellement en construction, notamment avec la Chine (ENSCM).

Un autre axe important concerne l'amplification de la formation technologique via la constitution d'une plate-forme technologique mutualisant les moyens déjà existants sur les différents sites (UM2, ENSCM, CEA et EMA) et créant des outils complémentaires comme la plate-forme technologique dédiée aux masters (UM2).

Projet de valorisation et de diffusion des résultats

Une originalité du projet est l'intégration/immersion d'entreprises sur les sites de recherche :

- Centre d'Innovation et de Transfert de Technologies Balard (campus Balard, Montpellier) : le CIT (2000 m²) sera dédié à l'hébergement des « jeunes pousses » (starts up) générées par les innovations développées dans les Instituts.
- Incubateur Galera (Montpellier) : cet incubateur de 140 m² de laboratoires et bureaux permet d'héberger ponctuellement des équipes-projets issues de PME.
- Hôtel d'entreprise Balard (CRDI, campus Balard, Montpellier) d'une superficie de 4000 m².
- Incubateur technologique InnoV'up à l'Ecole des Mines d'Alès (point 5.4).
- Réserve foncière du Parc Marcel Boiteux à Marcoule : un critère de succès à quatre ans du LABEX CheMISyst serait le démarrage effectif de démonstrateurs de recyclage de métaux, polymères bio-sourcés et résidus de fabrication sur ce site.

Le projet de valorisation s'appuiera également sur la SATT en cours de création. Les quatre partenaires industriels, membres fondateurs de la Fondation Balard (TOTAL, AREVA, SANOFI et UIC) participent à la vie du LABEX dans son fonctionnement, comme dans l'organisation de colloques de type "Solvay" destinés aux grands groupes et (séparément) aux PME. Dès les premiers mois de fonctionnement du laboratoire d'excellence, des partenariats à long terme seront proposés aux grands groupes, comme Rhodia pour le recyclage des métaux stratégiques, ainsi que des contrats d'externalisation de la R/D au sein des équipes du LABEX et ayant accès aux infrastructures dans le cas des PME pour la mise au point de nouvelles membranes. L'interface avec les PME sont les pôles de compétitivité TRIMATEC et EUROBIOMED.

Gouvernance du LABEX CheMISyst

- Les Universités de Montpellier 1 et 2, le CNRS, le CEA et l'Ecole Nationale Supérieure de Chimie de Montpellier (ENSCM) ont uni leurs compétences dans le Pôle chimie Balard, créé le 19 décembre 2007 par convention constitutive entre l'Etat, la Région et les membres fondateurs (http://www.enscm.fr/polechimie-balard/polechimie-balard.htm). Ce pôle dispose d'une structure opérationnelle de pilotage qui englobe quatre Instituts de Recherche regroupés au sein d'une Fédération de Recherche CNRS 3105. Il s'appuie également sur deux Chaires, une Chaire UNESCO (« Sciences des Membranes Appliquées à l'Environnement ») d'une part, une Chaire Européenne de chimie nouvelle pour un développement durable ChemSUD ; il est partie prenante de trois pôles de compétitivité (DERBI, EUROBIOMED et TRIMATEC) et contribue au développement d'un Institut Carnot (« Chimie, Environnement, Développement Durable»).
- Le Labex Chemisyst est un projet de site qui s'inscrit, d'une part, dans les trois missions fondamentales du Pôle Chimie Balard -Recherche, Formation et Valorisation- et d'autre part, dans les trois axes stratégiques de développement du Pôle : Energie, matériaux et vecteurs –

Valorisation des ressources naturelles et procédés de la chimie durable - Biologie et Santé - enfin, dans les politiques des Etablissements et Organismes, membres fondateurs du Pôle.

- Le Labex représente une opération transversale pluriannuelle de Balard (2011-2020). De façon naturelle, le Labex Chemisyst sera géré sous un « mode projet » par la gouvernance du Pôle au travers de :
    - sa direction scientifique, sous forme d'un Directoire (Directeurs d'unités mixtes constituant Balard, Fédération de recherche CNRS, Ecole doctorale et recherches et Directeurs des structures contractuelles non pérennes associées) qui assurera le suivi du projet,
    - son Collège scientifique, formé de scientifiques extérieurs, principalement étrangers, choisis pour leur expertise scientifique reconnue internationalement. Ce conseil sera en charge d'éclairer la Direction et son Comité de Pilotage Stratégique sur la pertinence des grandes orientations scientifiques adoptées dans le cadre de la politique incitative du LabEx.
    - son Comité de Pilotage Stratégique, composé des représentants des membres fondateurs UM1 et UM2, l'ENSCM, CNRS et CEA, de l'Etat et de la Région. Ce comité de piloatge stratégique accompagnera la direction pour la définition d'une politique incitative du site se traduisant par la mise en place de programmes portant sur les crédits du LabEx mais aussi sur les crédits attribués par la Fondation de Coopération Scientifique de site associé au projet IDEX déposé par les Universités du site de Montpellier. La Fondation universitaire Balard est en charge notamment des partenariats industriels.

Intégration du projet de laboratoire d'excellence dans la stratégie nationale et de l'établissement.

Le projet de LABEX Chemisyst se place au point triple des alliances nationales ANCRE, dans la chimie pour l'énergie nucléaire comme pour l'électro-mobilité, AVISAN dans la partie toxicologie et pharmacologie, ainsi qu'ALLENVI pour les divers projets qui ont pour point commun l'économie d'atomes dans la synthèse et l'intensification des procédés de la chimie du développement durable. Dans ce dernier aspect, un chercheur du Pôle Balard (S. Pellet-Rostaing) co-pilote le GDR de "Synthèse et Procédés du développement durable" du CNRS (2010-2013). Le lien avec la société hors des cercles académiques se fera *via* un partenariat durable avec les musées, dont celui centré sur chimie, énergie et société au *Visiatome*, semblable au musée de la chimie de Ludwigshafen, et actuellement unique en France, ainsi que l'Institut Carnot Balard, la chaire ChemSud et des partenariats à monter avec le Pôle SHS de Montpellier sur les musées.

La synergie avec les autres pôles identifiés de l'Université de Montpellier Sud de France se fera à travers une Fondation de Coopération Scientifique chargée de la gouvernance de l'IdEx montpelliérain. Le LABEX CheMISyst se veut acteur des IRT (énergie, eau, micro-algues etc..) et aura vocation à servir d'expert et de partenaire dans les programmes associés.

Liste des membres du Conseil Scientifique de l'ICSM

au 26 novembre 2010

Nom Prénom	Adresse	Tel	Fax	Mail
BAGLIONI Piero Professeur	Department of Chemistry Via della Lastruccia University of Florence 50019 Sesto Fiorentino Italy	+39 055 457-3033	+39 055 457-3032	piero.baglioni@unifi.it
BOULLIS Bernard Directeur de Programme	DEN/DISN/Direction du Cycle et des Déchets Bât 121 - CEA Saclay F-91191 Gif-sur-Yvette	01 69 08 64 55	01 69 08 32 32	bernard.boullis@cea.fr
CABUIL Valérie Professeur	Cabinet du Haut-commissaire à l'Energie Atomique CEA/SACLAY – Bât. 447 F-91191 Gif sur Yvette	01 64 50 26 83	01 64 50 19 75	valerie.cabuil@cea.fr
GUINOT François Président de l'Académie des Technologies	Académie des Technologies 28, rue Saint Dominique F-75007 Paris	01 53 85 44 48	01 53 85 44 45	president@academie-technologies.fr
GARDERET Philippe Directeur Scientifique	AREVA-SA 33 rue La Fayette F-75442 Paris cedex 09	01 34 96 10 46 Secrétariat : 01 34 96 10 48	01 34 96 16 14	philippe.garderet@areva.com
LEMAIRE Marc Professeur	Université Claude Bernard - Campus Scientifique de la Doua - Laboratoire de Catalyse et de Synthèse Organique - Bât CPE 43, Boulevard du 11 Novembre 1918 F-69626 Villeurbanne Cedex	04 72 43 14 07	04 72 43 14 08	marc.lemaire@univ-lyon1.fr
LEROY Maurice Professeur Président du Conseil Scientifique ICSM	4 rue Henri Heine F-67100 Strasbourg	06 84 52 64 03		mjf.leroy@gmail.com m.leroy@unistra.fr
LIVENS Francis Professeur	School of Chemistry University of Manchester, Oxford Road UK, M13 9PL	+44 (0)161-275-4647		francis.livens@manchester.ac.uk
BAROIS Philippe	Centre de Recherches Paul Pascal 115, Av Albert Schweitzer 33600 PESSAC	05 56 84 56 69	05 56 84 56 00	barois@crpp-bordeaux.cnrs.fr
AUPIAIS Jean	CEA/DAM/DIF/DASE/SRCE Centre de Bruyères-le-Châtel (DAM/BIII) 91297 ARPAJON CEDEX	01 69 26 48 21		Jean.aupiais@cea.fr
AUGE Etienne	Institut national de physique nucléaire et de physique des particules – bat 200 – BP 34 UNIVERSITE DE PARIS 11 PARIS-SUD 91898 ORSAY CEDEX	01 64 46 83 00	01 69 86 98 63	eauge@admin.in2p3.fr auge@lal.in2p3.fr

Summary

Page

Group photography taken at the practical summer school "Separation chemistry",
during the electrochemistry session directed by Christian AMATORE
(ICSM Marcoule, August, 2009).

The common building for **ICSM** and **INSTN**, close to **VISIATOME** Museum near the Centre of Marcoule, with the **PHENIX** plant on the right of the image.