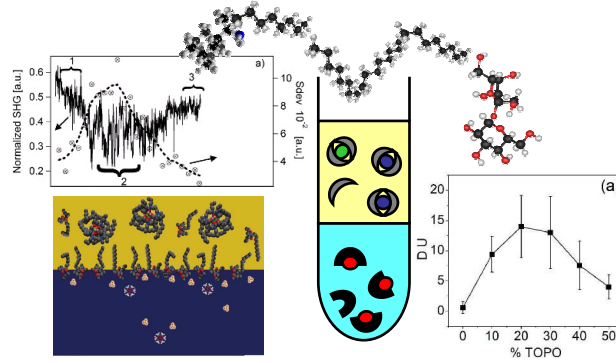




UMR 5257 CEA-CNRS-UM2-ENSCM

**INSTITUT DE CHIMIE SEPARATIVE
DE MARCOULE
ICSM**





Comprendre la séparation

Optimiser la séparation

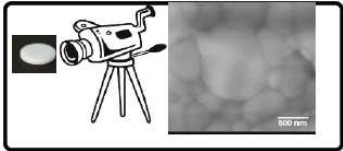


Sonoluminescence de l'uranyle

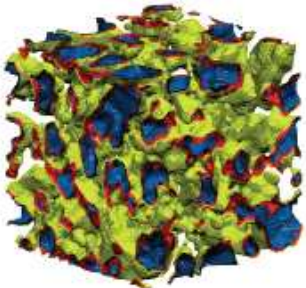
Chimie verte

Anticiper le cycle de vie des matériaux

Méthodes et théorie



Frittage "in situ" 1400°C



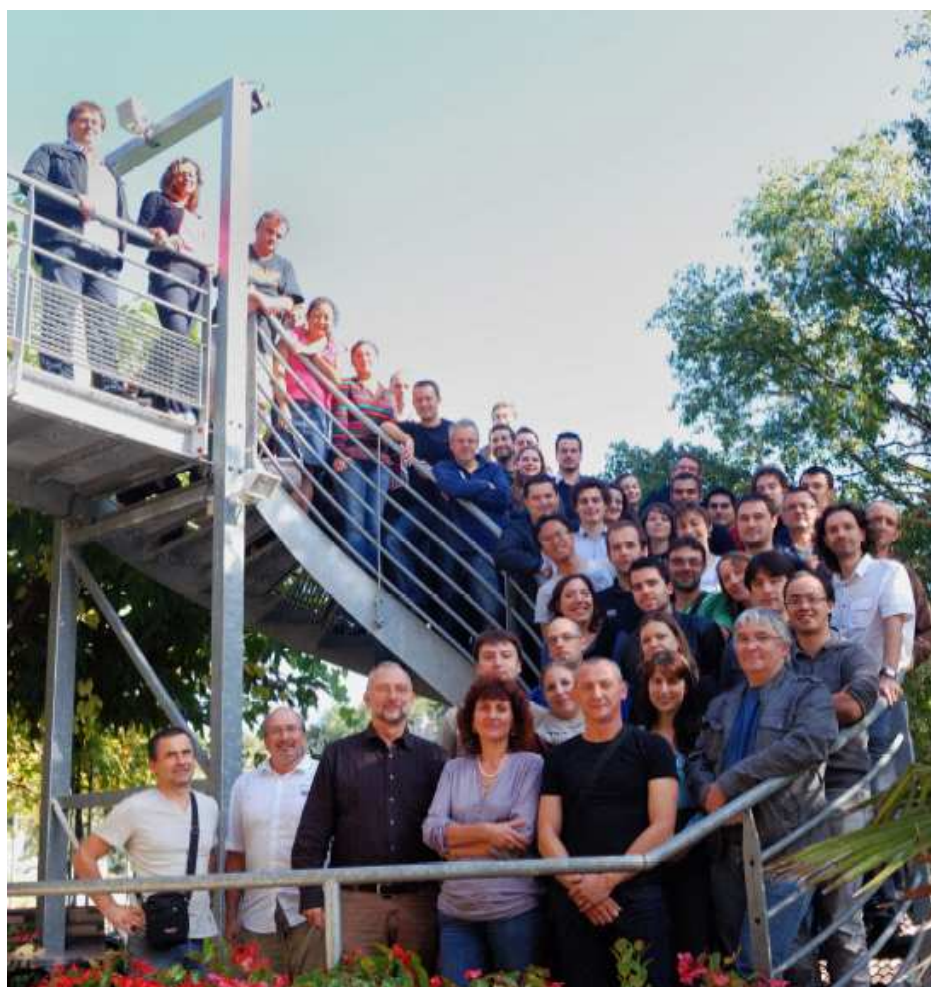
Modèle de microémulsion pauvre en eau





Institut de Chimie Séparative de Marcoule

SCIENTIFIC REPORT 2009 - 2012 Part 2



Permanent staff at ICSM as in October 2012



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CHIMIE Montpellier

Institut de Chimie



1 – Chemistry and Physical-chemistry of the Actinides

L'équipe est constituée de :

- Responsable équipe CEA/DEN (2007) Dr. D. Meyer
- Chercheur CEA/DSM (2009-2012) Dr C. Genre
- Chercheur CNRS (2009) Dr. D. Bourgeois
- Enseignant-Chercheur UM2 (2009) Dr J. Maynadié

Post-doctorants : Dr. Damien Hudry (2008-2010) Dr. G. Chatelain (2010-2012)

Dr. MC Dul (2010-)

Doctorants : Thomas Demars (2009-2012) Remy Poirot (2011)
Violaine Goudy (2012) Kevin Ruffray (2012)



Le cadre général de la recherche prévue au LCPA 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 prévues 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 la séparation des actinides ou l'évolution de matériaux et de composés 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 prévus au 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 essentiellement de type matériau moléculaire.

Dans l'état actuel, le LCPA dispose d'un accès à des boîtes à gants standards dans l'INB ATALANTE qui ne répondent d'un point de vue technique que très partiellement pour études envisagées, il est nécessaire pour mener à bien les projets originels du LCPA de disposer à minima d'une boîte à gants en atmosphère contrôlée permettant de s'affranchir des conditions d'oxydation et d'hydrolyse. Ce type d'installation est incontournable pour réaliser les études prévues au LCPA et d'une façon générale pour progresser dans la compréhension du comportement fondamental des espèces moléculaires des éléments transuraniens.

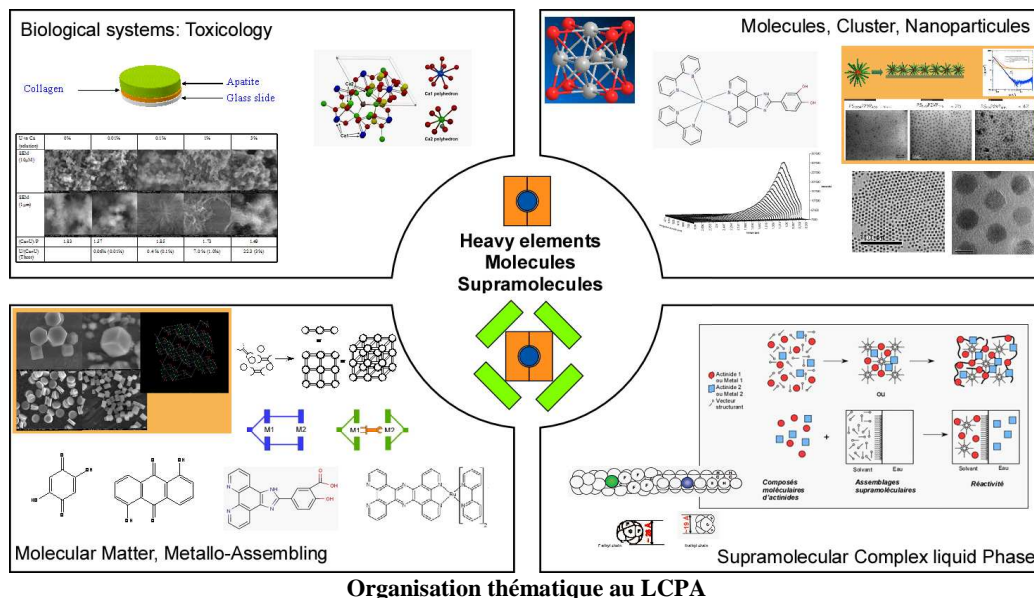
Ne disposant pas encore de ce type de boîte à gants, les actions de recherche du LCPA se sont centrées sur l'uranium et le thorium, ainsi que sur d'autres éléments tels que les lanthanides ou des métaux de transitions.

Les projets LCPA se sont donc portés sur la synthèse, caractérisation et étude de systèmes moléculaires à base de métaux (de transition d, 5f et U, Th) dans le cadre de l'élaboration de nouveaux matériaux ou solides moléculaires, de la structuration de phases organiques complexes et de la toxicologie nucléaire. Le LCPA collabore avec l'ITU dans le cadre de la synthèse et caractérisation de nanoparticules d'oxydes d'actinides.

Dans le cadre de la chimie moléculaire des éléments transuraniens et dans la mesure du possible, il est prévu de réaliser la synthèse de précurseurs de composés moléculaires du Np et du Pu dans les installations disponibles dans le cadre d'une thèse.

Les résultats des études menées antérieurement sur la conversion de composés moléculaires du silicium en carbure, présentée dans le rapport précédent, sont prévus pour être valorisés dans le cadre de support de catalyseur et/ou de catalyseur.

Enfin, le LCPA a également développé une collaboration avec VEOLIA Propreté/SARPI dans le cadre de la valorisation de métaux à partir du recyclage de batterie de véhicule électrique.



Matériaux et composés moléculaires

Polymère de coordination à base de dihydroxybenzoquinone (DHBQ)

Une première série de composés de type Ln_2L_3 à base d'Eu, de Nd et de Gd avec $L=DHBQ$ a été synthétisée par autoassemblage en solution homogène 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 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 composés Am-Gd ont été synthétisés et des mesures de magnétisme ont été réalisées en collaboration avec ITU.

Un des résultats remarquables pour ces composés est qu'il a été possible de contrôler la morphologie du grain élémentaire à l'échelle micrométrique et de garder cette morphologie lors de la conversion vers un matériau de type oxyde. Il a été possible d'obtenir des cylindres, disques, cubes, hexagones ainsi que des octaèdres tronqués.

Des essais complémentaires ont montré qu'il était possible d'intégrer des métaux d et de faire des composés mixtes avec des lanthanides avec le développement de nouvelles approches de synthèses en milieu anhydre. D'autres ligands tel que la naphazarine, ont également été étudiés.

Plusieurs collaborations sont à l'étude, une avec CEA/DRT pour une application dans le domaine des matériaux d'électrodes et une autre pour une application en catalyse.

Photosystème Ru-4f,5f

Un projet à base de systèmes mixtes contenant un photosensibilisateur à base de Ru et un métal f lié entre eux par un ligand de type polyaromatique sont en cours d'étude. Dans un premier temps des ligands et des molécules mono et bimétalliques ont été synthétisés et caractérisés (spectroscopie, temps de vie,...). Ces systèmes seront dans un deuxième temps intégrés dans un solide moléculaire type polymère de coordination. L'objectif est de comprendre le transfert intramoléculaire d'un

photoélectron dans un système comprenant un élément f, de développer un système permettant une séparation des charges pour une mise en œuvre dans un système catalytique (réduction substrat ou de l'eau). Cette étude est en collaboration avec le Laboratoire de Chimie des Processus Biologique du Collège de France, spécialisé dans les systèmes de photosynthèse artificielle.

Phase organique complexes (Chimie Séparative)

Ces études se placent dans le contexte de la détermination des forces fondamentales qui régissent la stabilité d'une phase organique contenant des ions métalliques, un système moléculaire extractant et un solvant. Dans le cadre de la compréhension du rôle des interactions faibles dans un processus de solubilisation d'éléments métalliques dans une phase organique complexe, le LCAP a développé deux approches :

Système fluorés vs hydrogénés

Cette étude s'intéresse plus spécifiquement au rôle des interactions de polarisation dans une phase solvant-extractant-métal par substitution d'une partie hydrogénée de l'extractant de type amphiphile, par une partie fluorée tout en gardant le volume moléculaire et la partie polaire constante. Afin de maîtriser la topologie moléculaire de l'extractant modifié, des études via différentes approches synthétiques ont été nécessaires pour accéder à des amphiphiles fluorés (diamides, phosphonates, phosphates, mono ou bi caténares,...). Enfin la solubilité de métaux de type lanthanides a été mesurée et des caractérisations des phases par diffusion (Rayons-X et neutrons) sont en cours.

Pd(II) vs Lanthanide(III)

Dans certains procédés étudiés dans le cadre du retraitement du combustible irradié, il a été observé une séparation entre des lanthanides légers et des lanthanides lourds en même temps qu'une co-extraction d'éléments tels que le Pd, le Mo ou le Zr par exemple. Une approche alternative à l'étude classique centrée sur les lanthanides consiste à déterminer pourquoi deux éléments ayant des propriétés chimiques très différentes tel que certains lanthanides et le Pd se comportent de façon similaire en extraction alors que des éléments ayant une chimie proche, les lanthanides légers et lourds, se comportent de façon différente toujours pour un même système extractant. Dans ce contexte le comportement du Pd lors d'une solubilisation, soit via une solution aqueuse ou via un système solide, a été étudié par rapport aux lanthanides.

Toxicologie Nucléaire : Uranium dans le tissu osseux

Afin de comprendre la façon dont l'uranium s'intègre dans le tissu osseux et dont il peut éventuellement s'en extraire, tout en se passant d'expérimentation animale, une approche mettant en œuvre des systèmes d'os synthétiques a été développée en collaboration avec le CEA/DSV, KIT-INE (Karlsruhe) et l'INSERM de Lyon. Différentes méthodes de synthèses ont été développées qui ont conduit à l'obtention de différents types de composés synthétiques. Ces composés ont été caractérisés et leur compatibilité avec la croissance de cellules type ostéoclaste et ostéoblaste a été validée. Cette approche permet ainsi d'obtenir un matériau biomimétique contenant une quantité d'uranium contrôlée et d'étudier le niveau chimique, biochimique et cellulaire du système biologique contenant de l'uranium dans un processus soit d'insertion, soit de décorporation d'uranium du tissu osseux.

Nanoparticules

Après une première collaboration entre l'ITU et l'ICSM qui a permis de mettre au point une approche combinée supramoléculaire et plasma pour l'obtention de couches de nanoparticules d'oxydes d'actinides sur substrats, la synthèse de nanocristaux d'oxydes d'actinides « libres » a été mise au point. Ces études réalisées au JRC-ITU sur U, Th et Np montrent une nette différence de réactivité et de morphologie entre le système U et le système Th. Les conditions d'obtentions de nanoparticules avec une morphologie donnée et une excellente distribution (taille et forme) ont été déterminées.

Carbure de Silicium

Les approches de synthèse de carbure de silicium via la conversion thermique de polysilanes obtenus par la condensation de silanes en phase supramoléculaire, développé au cours de la période précédente de sont à l'étude pour le revêtement en SiC de catalyseur de voiture.

Réactivité théorique des actinides

La réactivité de composés moléculaires a été étudiée théoriquement dans le cadre d'une collaboration avec l'Université de Toulouse et de Montpellier 2. Plus précisément, 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 a été déterminé. Ces premiers résultats devaient aboutir à l'étude de la réaction de condensation entre liaison actinide-chlore et actinide-alcoxyde (actinides = Pu et Np) et la condensation redox entre actinyle (V/VI) et actinide (III/IV) mais en raison de la complexité des calculs et de la limite actuelle des méthodes pour les configurations électroniques supérieures à 5f² cette action a été reportée.

From Coordination Polymer to Doped Rare-earth oxides

Thomas Demars, Jérôme Maynadié, Johann Ravaux, Renaud Podor, Caroline Genre, Daniel Meyer

Rare-earth mixed oxides are attractive compounds in a number of technological areas, such as catalysts for various organic reactions, thermal barrier coating materials or components in fuel cells. Doped ceria, for example, are of considerable interest as solid oxide fuel cell (SOFC) anodes and electrolytes, because of their high ionic conductivity. They are also choice components for molecular electronics. Other *f*-metal oxides, namely actinide oxides, are currently used as fuels in nuclear plants and are considered promising materials for new fuels in the fourth generation of nuclear power reactors.

We have developed a synthesis route towards *f*-elements oxides, based on thermal conversion of coordination polymers of controlled structure and morphology.¹ In a first step, mixed metal coordination polymers are prepared as solid solutions. Synthesis by auto-assembly of metal ions and ligand 2,5-dihydroxy-1,4-benzoquinone (DHBQ) lead to mixed coordination polymers. Two ways have been developed, an aqueous way and an anhydrous one, leading to species with different structure. In both ways, the proportions of the different metals in the CPs are equal to the proportions of the metal ions introduced in the starting synthesis mixture. Mixed Ln(III)/Ln(III), Ln(III)/Th(IV), Ln(III)/U(IV) and Th(IV)/U(IV) with controlled composition were easily obtained, and PXRD measurements proved they are indeed solid solutions.

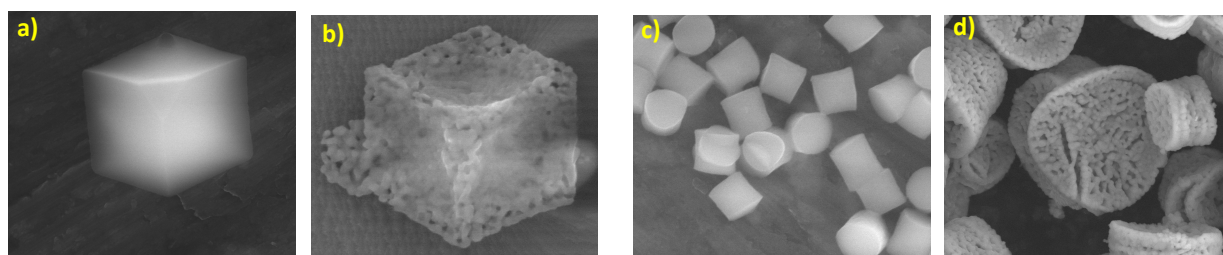


Figure 1: a) and b): a micrometric cube of the coordination polymer $Nd_2(DHBQ)_3 \cdot 24H_2O$: before and after 900°C heat treatment ; c) and d): a micrometric cylinder of the same compound before and after 900°C heat treatment. The morphology of the mesocrystal is retained upon calcination and conversion to Nd_2O_3 .

In a second step, the CPs are heated under air at 900°C and converted to mixed Ln/Ln, Ln/Th, Ln/U and Th/U oxides as solid solutions of controlled composition. We observed that the morphology of the starting PCs is retained upon heating (see Fig. 1), allowing synthesis of mixed oxides with easily tailorable morphology. It is thus possible, through a careful choice of ligands, to transfer control over the composition and morphology of coordination polymers to hard inorganic materials.

¹ T. Demars, M. Boltoeva, N. Vigier, J. Ravaux, J. Maynadié, C. Genre, D. Meyer, « **From coordination polymers to doped Rare-Earth oxide** » *Eur. J. Inorg. Chem.*, **2012**, 3875-3884

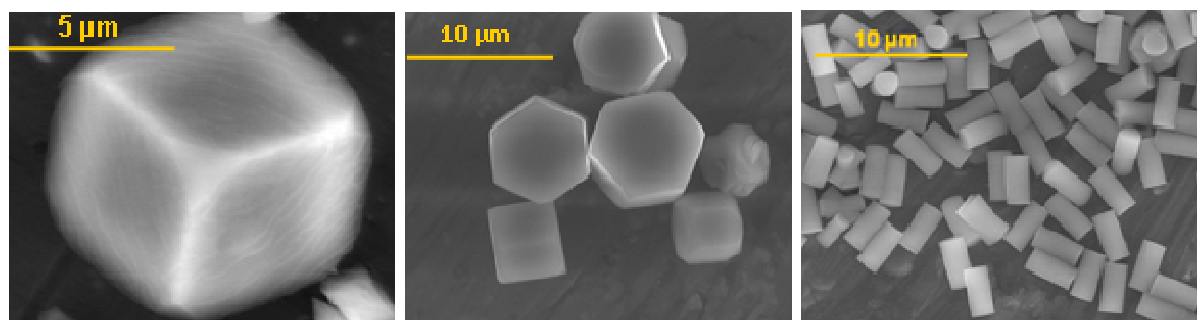
Rare-earth coordination Polymers with Controlled Morphology

*T. Demars, J. Ravaux, R. Podor, C. Genre, D. Meyer
T. Sievers, (MPI-Potsdam - Germany)*

Metal-organic coordination polymers (CPs) have been subjected to intense scrutiny due both to the diversity of their structures and to their huge potentiality as functional molecular materials for a variety of applications including gas storage, separation chemistry, catalysis, drug delivery, sensors, optical and magnetic devices among others (G. Férey, *Chem. Soc. Rev.*, **2008**, *37*, 191-214; b) S. Kitagawa *et al.*, *Angew. Chem. Int. Ed.*, **2004**, *43*, 2334-2375; c) O. m. Yaghi *et al.*, *Angew. Chem. Int. Ed.*, **2008**, *47*, 5136-5147). Coordination polymers properties can be highly dependent on crystal morphology (O. K. Farha, A. M. Spokoyny, K. L. Mulfort, S. Galli, J. T. Hupp, C. Mirkin, *Small*, **2009**, *5*, 1727-1731) and control of particle growth is therefore an important challenge for the design of functional CP-based materials. Thus far, attention has been primarily focused on macro-scale crystalline samples of CPs typically obtained by solvothermal or self-assembly methods. A few reports have been devoted to the synthesis of micro- or nano-sized CPs crystals of controlled size and shape, but understanding the growth mechanism of these objects remains a challenge (A) N. Stock, S. Biswas, *Chem. Rev.*, **2012**, *112*, 933-969 ; b) A. Carné, C. Carbonell, I. Inhar, D. Maspoch, *Chem. Soc. Rev.*, **2011**, *40*, 291-305 ; c) A. Uemura, S. Diring, S. Furukawa, H. Uehara, T. Tsuruoka, S. Kitagawa, *J. Am. Chem. Soc.*, **2011**, *133*, 15506-15513).

We were able to synthesize well-defined homogenous mesocrystals of the metal-organic framework $[\text{Nd}_2(\text{DHBQ})_3(\text{H}_2\text{O})_6] \cdot 18\text{H}_2\text{O}$ by direct precipitation. Mesocrystals with cylindrical, hexagonal, cubic and truncated octahedral shape and tunable size can be obtained easily and with good yields¹ (see pictures). Their morphology can be easily tailored through control of experimental conditions such as solvent, temperature, reactants concentration and reactants addition speed.

The mesocrystals are built from aggregated nano-scale crystalline particles, which assemble differently when the experimental conditions are modified.



Different shapes of coordination polymers obtained by kinetic controlled synthesis.

The study of these objects provides most valuable insight in the understanding of mesocrystals growth mechanisms. The influence of experimental parameters such as temperature, concentration, polarity of the solvent on the growth, nucleation and aggregation of these particles is under investigation.

¹ T. Demars, F. Bonnefond, T. Sievers, J. Ravaux, C. Genre, R. Podor, D. Meyer, "MOF Mesocrystals with tunable morphology" manuscript in preparation

Molecular Heavy Metal Matter: Photophysical properties

*V. Goudy, M. Autillo, J. Maynadié, C. Genre, D. Meyer
M. Fontecave (Collège de France)*

Main aims of this studies are

- development a new f-element (lanthanide or actinide) containing molecular matter (polymetallic coordination polymer)
- study of the photophysical properties, especially charge transfer and charge separation of the system in comparison with molecular species and with systems based on d-elements,
- potential application in RedOx catalyst

The first step of this work was to develop molecular bimetallic species containing a photosensitive element (Ru or Ir) and a f-element (Sm and U) to get the photophysical (spectra, lifetime,...) and electrochemical properties. Several systems containing Ru, Ru-Sm and Ru-U were synthetised and some basic characteristics (NMR, UV-Vis, voltammograms,...) were collected¹. These bimetallic species are built up in order to be used as potential basic blocks in high ordered matter. The organic bitopic ligand developed in this frame shows a delocalised electronic pi-system based on nitrogen containing aromatic rings (figure 1,2).

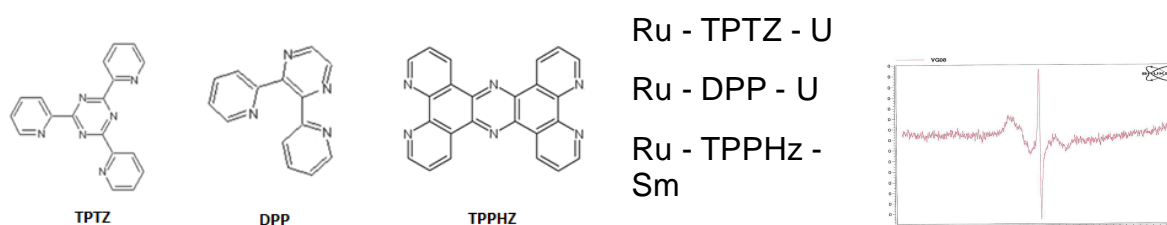


Figure 1: Bimetallic molecular photosystems containing f-elements, EPR Spectra of $Ru(bpy)_2(tptz)-U$

A second step will be the transposition in a 2D or 3D molecular hybrid network of the molecular build unit previously developed (figure 2).

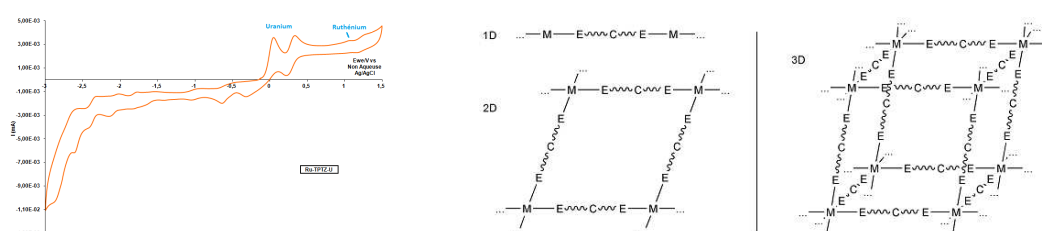


Figure 2: Voltammogram of $Ru(bpy)_2(tptz)-U$ and schematic view of a n dimensional molecular network: E-C-E is the organic unit, M the metallic element

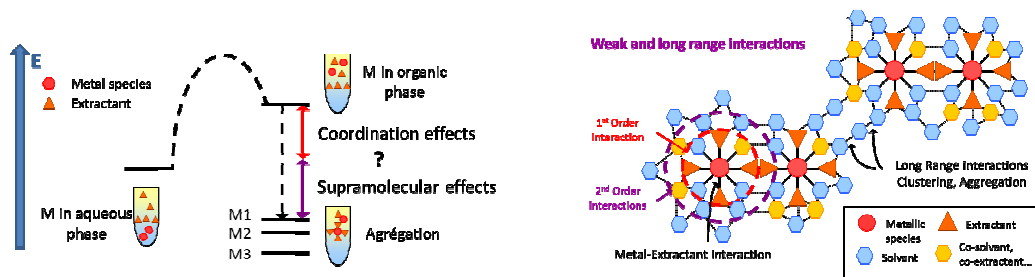
The comparison of the photophysical properties and the electrochemical behavior between the molecules and the molecular network will highlight the cooperative effect when going from single ordered system to a high ordered system. The comparison with the large work done on d-elements will also point the f-element specific behavior in intramolecular photon driven electronic-transfer between a “photoactivator” and a lanthanide or an actinide.

¹ Goudy V. « Synthèse et caractérisation de composés moléculaires pour la photochimie et les transferts de charge »- Stage Master II CSMP 2012 et Autillo M. « Activation intramolécule photo-induite de complexes de métaux f par un photo-sensibilisateur » - Stage Master II CSMP 2012.

Fluorinated vs hydrogenated molecules: organic phase model systems

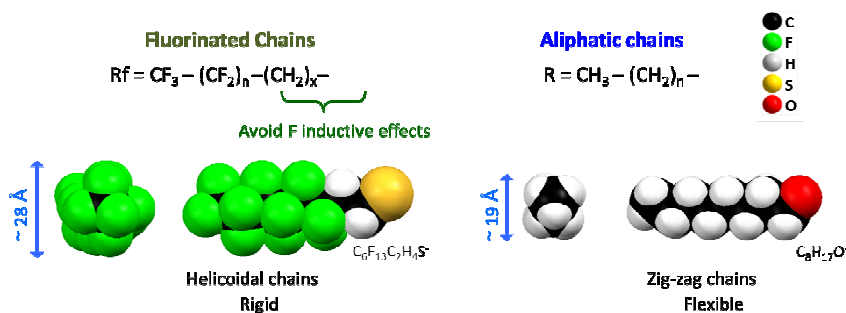
M.C. Dul, D. Bourgeois, S. Dourdain, S. Pellet-Rostaing, D. Meyer

Better understanding of how a metal ion usually not soluble in an organic phase can be maintained into by using an extractant is one of the main challenges in the liqui-liquid separation field.



Thermodynamic consideration in a liquid-liquid system and the related interactions

One part of this challenge is to elucidate the role of the interactions which can take place at the molecular level, especially the relations between first order interactions (such as chemical bonding or electrostatic interactions) and low energy second order interaction (H bonding, polarisation, dipole...). In this study we focused our interest on the importance of Van der Waals forces in the solubilisation of metal species in organic media using a comparative study between fluorinated and hydrogenated amphiphilic extractants. A key point is to keep the molecular volume and the polar part of the extractant as much as possible unchanged. This is of prime importance in order to minimize the impact of any other interactions, especially the volumic entropic term and the coordination interactions of the polar part with the metal center. To reach this aim, we have first developed the synthesis and purification of several fluorinated extractants (diamide, phosphate, phosphonate...). The short term objective is to study the difference in organization in the organic phase when a fluorinated extractant is used in place of hydrogenated analog and correlate this structural hints with the extraction behaviour (amount of extracted metal and specificity of the behaviour).



Fluorinated vs hydrogenated molecular systems

Thus we are comparing the supramolecular behaviour of diamide-dichloromethane-lanthanide phases as model system, from the extraction, solubility and structural points of view.

First results show that the extraction behavior is very different: the hydrogenated system extracts the lanthanides whereas the fluorinated system does not. The related structural studies (NMR, DOSY, SAXS, SANS) are still in progress to better understand this difference of behavior that probably comes from long range interactions.

Liquid/Liquid Extraction of Palladium with diamides

R. Poirot, D. Bourgeois, D. Meyer

Extraction and separation of multivalent cations is a subject of particular relevance for the retreatment of nuclear wastes. In this frame, the EXAM process was designed at the CEA to enable selective recovery of americium from a PUREX raffinate. During this process, Am(+III) is separated from Cm(+III), light lanthanides (at the +III oxidation state as well) follow the Am, and heavy lanthanides stay in the aqueous layer with Cm. Palladium follows americium during the whole process, although its physico-chemical behaviour is anticipated to be completely different: Pd(+II) is a cation softer than Ln(+III), and with a higher charge density. As a metal of particular interest, palladium has already been the subject of several L/L extraction study, but mostly devoted to hydrochloride media. We thus decided to explore the behaviour of palladium in presence of diamide-type extractants of interest (DMDOHEMA, TODGA, see Fig. 1), and in nitric media.

L/L extraction of Pd with the sole DMDOHEMA malonamide was fully characterised. Comparison with lanthanides reveals similar trends (Fig. 1), but the quantitative influence of parameters differs between +II and +III cations (number of diamide ligands, number of co-extracted nitrate counter-ions, influence of H^+ concentration).

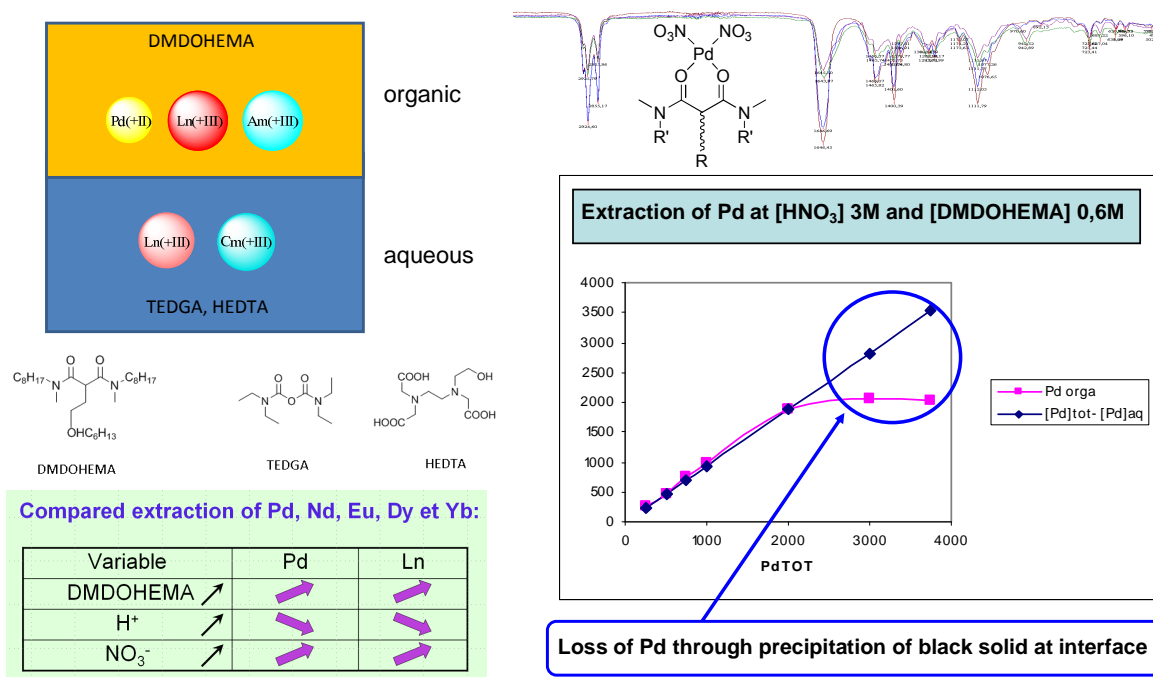


Figure 1: General behaviour of Pd during L/L extraction with DMDOHEMA from HNO_3 solutions

Interestingly, diverse precipitation phenomena were highlighted during these studies: formation of Pd black, PdO and Pd rich phases (third phase) were evidenced. On-going studies include the complexation behaviour of Pd with diamides (XRD, IR, NMR), the supramolecular state of the organic layer (SAXS, DLS), the characterization of RedOx processes during extraction, the theoretical speciation of aqueous layer (JChess modelling with thermodynamic databases), and the experimental detection of Pd colloids at low acidities (SAXS, DLS).

Uranyl interaction with bone mimics

*D. Bourgeois, G. Chatelain, D. Meyer
C. Vidaud (CEA-DSV Marcoule), G. Boivin (INSERM Lyon),
M. Denecke (KIT Karlsruhe), K. Dardenne (KIT Karlsruhe), J. Rothe (KIT Karlsruhe)*

Whatever its entry route into the body, the uranyl cation (UO_2^{2+}) is sent through the blood to its target organs: kidneys, for rapid elimination, and skeleton, for long term sequestration. The accumulation of uranyl in bones leads to an increased bone resorption and/or and inhibition of bone formation. To limit this accumulation, and favour excretion as a soluble form, several molecules with decorporating properties were evaluated. But today none of these presents a real efficiency, and the conception of new molecules deserves a prior understanding of chemical, biochemical and cellular mechanisms which lead to the accumulation of UO_2^{2+} into the skeleton.¹

Bone is a mineralized composite tissue with 5–10% water, 50–70% apatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], and 20–40% organic compounds composed mainly of collagen I protein (90%). Throughout the lifetime, bone tissue is continuously remodeled by cycles of events occurring at the same sites, alternating resorption and mineralization, mediated by osteoclasts and osteoblasts respectively. We recently set-up a method to synthesize biomimetic collagen-apatite hybrid materials, into which we can introduce uranium at various levels (Fig. 1). These samples are then used as bone cell culture support, and analysed and compared with biological samples using various techniques (XRD, IR, Raman, SEM, XANES, EXAFS, SLRT).

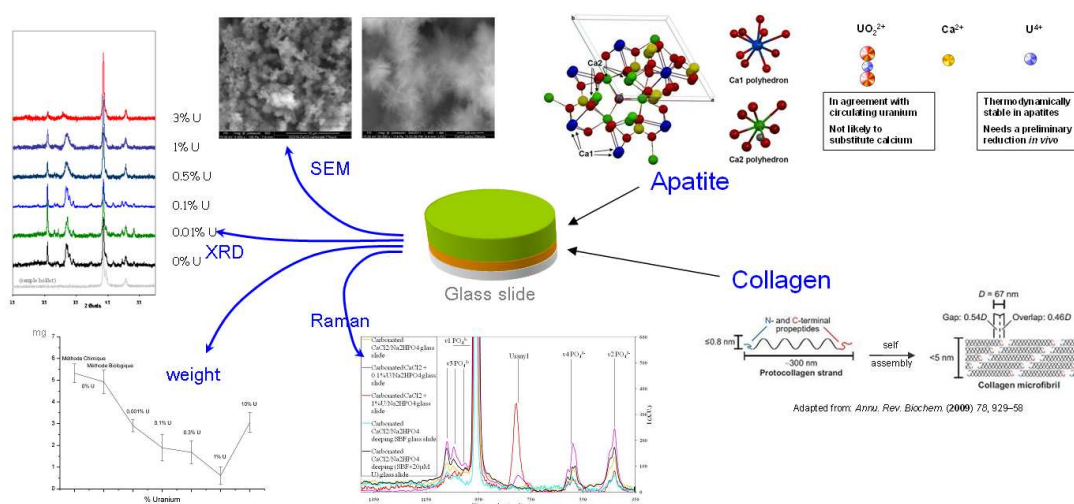


Figure 1: Biomimetic collagen-apatite hybrids prepared and some analytical results accounting for the influence of uranium on these systems

The interaction between uranium and the bone matrix is very complex. At the sole chemical level, several species can be obtained, and the presence of carbonate ions in the medium adds another complexity level. We have already established that low levels of uranium lead to a decrease in the mineralization efficiency, and also to a less crystalline material. Speciation studies at the molecular level are ongoing to establish the nature of the uranium species sorbed at the apatite surface. And further studies will be devoted to the factors governing the chemical equilibria between uranium(VI) and these biomimetic matrixes.

1 C. Vidaud, D. Bourgeois, D. Meyer, "Bone as target organ for metals: The case of f-elements" Chem. Res. Toxicol., 2012, 25, 1161-1175.

UO₂ and ThO₂ Nanocrystals

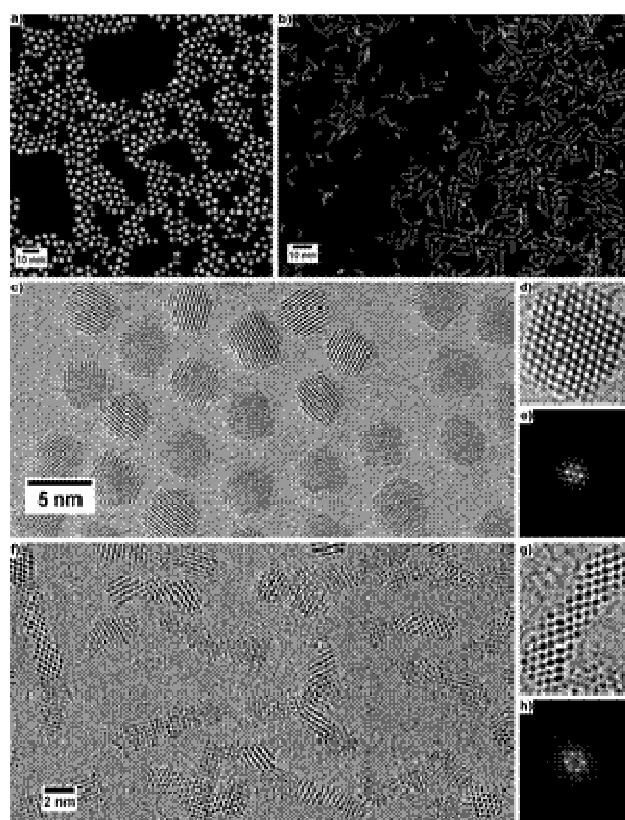
*D. Hudry (JRC-ITU Karlsruhe Germany)
J. Maynadié, D. Meyer*

These studies are done in the frame of the fundamental behaviour of 5f species and are focused on the controlled synthesis of nanocrystals of actinide dioxides. The chemical and physical properties of the nanometric matter will then be compared with the micrometric one.

A first series of studies were done on the synthesis of nanoparticles on a surface by a combined supramolecular (diblock polymer) and physical (H and O plasma) approach. The objective in this new part is to obtain “free” nanoparticles which can be easily handled after synthesis. The challenge is first to obtain the synthetic conditions to get crystalline nanoparticles with a narrow size distribution and second to avoid any agglomeration of the nanoparticles.

The approach developed consisted in the use of ternary (oleic acid, oleic amine, benzilic ether) and quaternary (oleic acid, oleic amine, benzilic ether, phosphine oxide) molecular systems with different actinides precursors (nitrate, acetate, acetonacetonate)¹.

Major studies were done on uranium and thorium as well as mixed uranium-thorium, neptunium and plutonium are under way.



The main results show that it is now possible to get several kind of nanoparticles. With uranium, these nanoparticles are usually spherical with a diameter of around 6 nm with more or less defined edges and with thorium, the particles are usually rod like with a 1 nm by 6 nm size. For both systems the nanoparticles are crystalline and the structure is in agreement with the crystallographic AnO₂ structure. With uranium, the particles can be obtained using U(IV) or U(VI) showing that in this case we have probably a RedOx mechanism combined with a condensation. For the thorium particles, the mechanism can be roughly compared with a non hydrolytic sol-gel condensation process. These points needs to be cleared.

HAADF-STEM (a,b), TEM (c,f) and HR TEM (d, g) of uranium oxide (a,c,d) and thorium oxide (b,f,g).

1, Damien Hudry, et al., "Non-aqueous Synthesis of Isotropic and Anisotropic Actinide Oxide Nanocrystals" Chemistry - A European Journal, 18(27), 2012 pp 8283-8287

Comparative Theoretical Study on Actinide Complexes Reactivity

A. Yahia, D. Meyer

L. Maron (Université de Toulouse), O. Eisenstein (Université de Montpellier 2)

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 $\text{Cp}_2\text{M}(\text{CH}_3)_2$ and pyridine N-oxide with $\text{M}=\text{Zr, Th}$ and U leading to oxo complexes. These reactions were experimentally observed by J. Kiplinger with $\text{Cp}_2\text{An}(\text{CH}_3)_2$ complexes ($\text{An} = \text{U}$ and Th). The expected mechanism is an oxygen transfer from the N-oxide moiety to the metal but the C-H activation route can also be considered. A first series of calculations 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 for the higher stabilisation of the Zr complex than the Th and U homologues leading to a less reactivity for the Zr species.

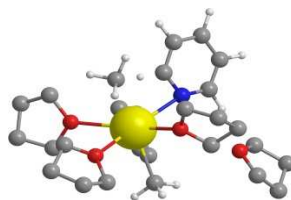


Fig. 2: Transition state of C-H activation

The C-H activation study on lanthanide complexes 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 ones.

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- Castro L, Yahia A and Maron L. "Are 5f Electrons Really Active in Organoactinide Reactivity? Some Insights from DFT Studies" *ChemPhysChem*, 11(5) 2010, 990-99

2 – Ions at Interfaces

L'équipe est constituée au 1er décembre 2012 de :
 1 chercheur CEA responsable d'équipe (Dr. O. Diat),
 1 chercheur CEA (Dr. P. Bauduin),
 1 enseignant-chercheur ENSCM (Dr. L. Girard),

Post-doctorants :

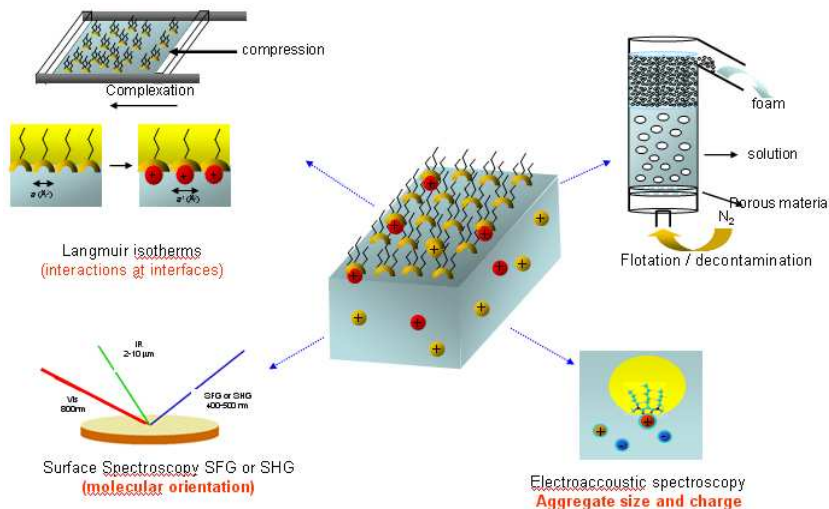
- Gaëlle Martin-Gassin (DEN et CNRS, 2010-2012) : dynamique d'interfaces liquide/liquide.
- Laurence de Viguerie (DEN-ANR CATASURF, 2011-2012) : film of POM-based surfactant
- Johnatan Lai (DEN-ANR CATASURF, 2011-2013) : micro-emulsion of POM-based surfactant
- Sievers Torsten (LEA, 2011-12) : Extraction liquide/solide.

Thésards :

- Cyril Micheau (DEN, 10/2010) : Flotation ionique comme procédé d'extraction.
- Damien Brusselle (UM2, 10/2010) : Auto-assemblage d'amphiphiles de type dicarbolles.
- Pierre-Marie Gassin (DEN, 10/2010) : transfert d'espèces au travers d'interfaces liquide/liquide.



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, le vieillissement de ces matériaux sous différents stress chimiques ou radiatifs qui sont examinés dans les laboratoires de l'ICSM, le groupe des "ions aux interfaces actives" (3 chercheurs dont un enseignant chercheur 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 fluides d'échange et les conséquences de cette répartition sur la réactivité 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 kinetics of ion separation. The figure shows the principles of the experimental techniques used to investigate ion distribution and mobility at fluid interfaces.

Le génie chimique lié à cette activité de séparation des ions en solution 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 leur environnement 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 chimie de la spécificité de chaque effet.

Dans ce rapport, un premier exemple concerne donc l'étude d'interface liquide/liquide par une technique d'optique non linéaire afin de pouvoir appréhender ce qui se passe dans le nanomètre autour de l'interface pendant un processus de transfert d'espèce. Une ANR blanche « ILLA » vient d'être acceptée autour de ce sujet permettant de réunir autour de l'ICSM d'autres équipes d'expérimentateurs (LASIM/UCB/LYON + DEN/DRCP) et de théoriciens (MSM/Univ Strasbourg + DEN/DRCP). Un second exemple (thèse CEA) choisi concerne le transfert d'une molécule tensioactive qui se partitionne à l'équilibre entre une phase aqueuse et une phase huile. C'est un sujet modèle pour essayer de comprendre la cinétique du transfert entre deux milieux non miscibles en prenant en compte une cinétique de sorbtion à l'interface. Un troisième exemple (thèse universitaire) concerne l'auto-assemblage de molécules amphiphiles (dicarbollide) de formes particulières (sans queue ni tête) étant sélective du Cs et Sr en extraction liquide/liquide pour le nucléaire en formant des espèces neutres (paires d'ions) dans des milieux de polarité moyenne. Le quatrième exemple choisi concerne un procédé de séparation alternatif à la séparation liquide/liquide : il s'agit de la flottation ionique. Ce sujet est abordé aussi dans le cadre d'une thèse en partenariat avec le DEN/DTCD avec la compréhension de l'équilibre effet moussant et effet de complexation ou d'interaction ionique aux interfaces liquide/air. Une étude sur la distribution des ions proches d'une interface solide en utilisant une technique de résonance en mode réflexion est toujours à l'ordre du jour et est maintenu au rythme des acceptations de propositions d'expériences sur grands instruments. Enfin un sujet de chimie verte sur l'emploi de liquides ioniques comme solvants compatibles avec l'auto-assemblage et l'extraction ionique est décrit dans une dernière partie.

Dynamics at interfaces

*G. Gassin, P.M. Gassin, O. Diat, S. Pellet-Rostaing, G. Arrachart
L. Couston¹, P.F. Brevet², E. Benichou*

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 shown in our previous work 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 bench. 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.

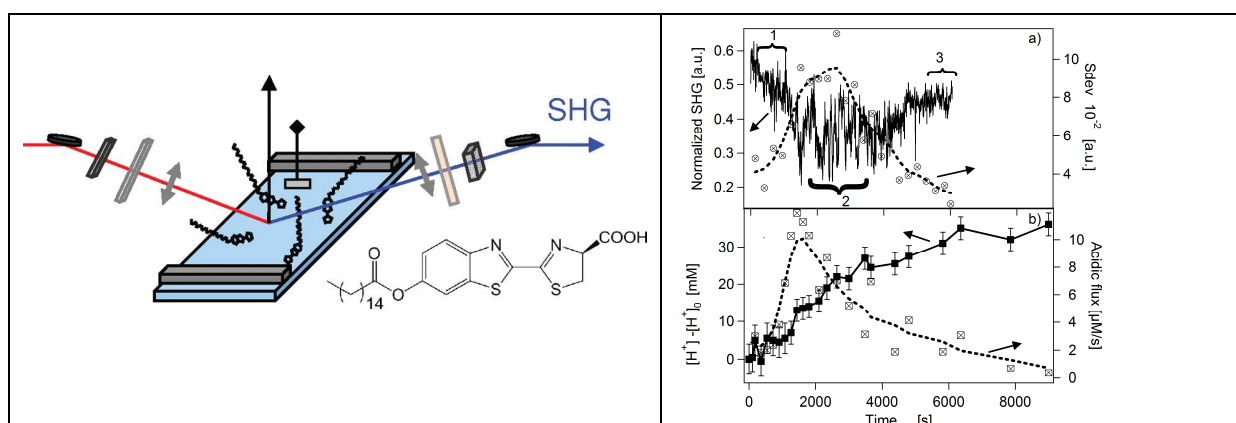


Fig.1: left: Schematic view of an L/L interface covered by synthetic luciferin molecule and probed by non linear optics[3]. Right: fluctuating SHG signal as a function of time from LL interface and during an extraction process of acidic molecules with monoamides (DEHiBA).

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¹ DRCP/LAMM

² LASIM, UCB Lyon

Surfactant transfer across a liquid/liquid interface probed with dynamics interfacial tension measurements

P-M Gassin, D. Meyer, J-F Dufreche, O. Diat

Mass transfer of solute across a liquid/liquid interface has great interests in many industrial processes such as liquid/liquid extraction. Beyond the volume and interfacial thermodynamic aspects, the kinetics of species transfer at interfaces is a key point to understand these transfer efficiencies. Among several approaches using model systems, we studied the transfer of non ionic surfactants across a water/oil interface by analyzing the L/L interfacial tension. This was performed by using the pendant drop technique, which permits to monitor the interfacial population evolution. Typical interfacial tension time variation are given in figure below (right-hand side) when a fresh droplet of surfactant in an oil phase is formed in a cell of water (left-hand side).

Interfacial tension exhibits a steep initial decrease, because of the surfactant adsorption at the interface, passes through a minimum and then increases because of the surfactant desorption and transfer in the other phase.

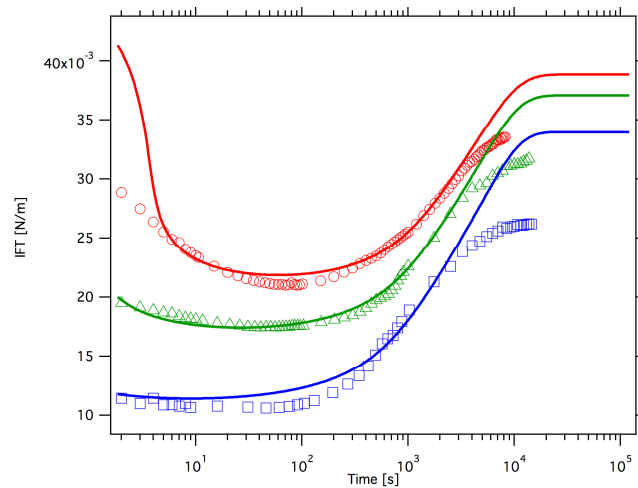
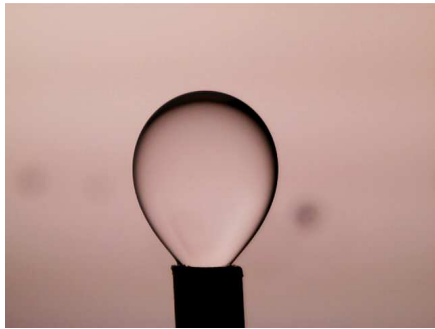


Fig.: left - Pendant droplet technique which permits to visualize the droplet shape and then to extract the averaged interfacial tension between both immiscible liquids. Right - Interfacial tension evolution for a fresh droplet of surfactant at various concentrations in dodecane (initially $c_0=2 \times 10^{-4}$ mol/L (blue square), 7.5×10^{-5} mol/L (green triangle) and 3.375×10^{-5} mol/L (red circle) in a water cell.

Those studies have shown, in the case of the Triton-X100 surfactant, that the interfacial tension evolution depends strongly on the phase where the surfactant is initially present: the transfer dynamic is found to be faster when the surfactant switches from dodecane to water compared to the reverse pathway from water to dodecane¹. To go further in the interpretation, a mixed model that coupled diffusion in the bulk phases with kinetics adsorption/desorption rate has been developed to describe interfacial tension evolution².

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A Theta-Shaped Amphiphilic Cobaltabisdicarbollide Anion

D. Brusselle, P. Bauduin, O. Diat, Th. Zemb, S.¹Prevost, P.²Farras and F.²Teixidor

We know the surfactant molecules constituted with a polar head, ionic or non ionic, and with one or more aliphatic chains; we understand their self-aggregation properties in an aqueous or organic phase or at the interface between non-miscible fluids; Organised in various complex structures characterized by multiple symmetries and at the origin of various applications, the field of the surfactant research still keep us some surprises owing to the weak forces in competition.

In this study, the concern is about a new class of amphiphilic molecules from the family of carborane: the bis-dicarbollide [Chevrot, Thesis 2008]. The cobalt bis-dicarbollide or COSAN [M.F.Hawthorne, 1965] is an anionic cluster of bore and carbon, highly stable from a chemical and thermal point of view with a cobalt cation at the centre of this molecule. This entity is hydrophobic through its two poles with a delocalised charge in its equatorial plan that can be counterbalanced by an acidic proton. Numerous and important applications has been developed like the radionuclide co-extraction, organic polymer synthesis or in medicine for radiotherapy or its inhibition action on the HIV protease [Plešek 1995; Galetta 2006; Cigler, 2005].

For all these reasons, we have started a complete fundamental study of this molecule in water because of its surprising property of self-assembly. From SANS (HZB, Berlin and SAXS(lab) experiments, absorption spectroscopy and TEM characterization we have evidenced a formation of large vesicles at very low concentration ($<5 \cdot 10^{-4}$ mol/l) and by increasing the concentration, the COSAN looks like a surfactant with a surface activity until to observe a transition towards small micelles provided by a strong Coulombic interaction [Bauduin 2011]. The chemistry of substitution on the carbon or on the bore is rich due to the geometric distribution and the availability of the B-H coordinant site at the surface of the cage [Teixidor, 2009]. Exchanging 2 or 4 Hydrogen by I or Cl respectively a gel with a highly ordered lamellar structure can be observed using SWAXS techniques and understood taken into account strong lateral interaction within COSAN monolayers.

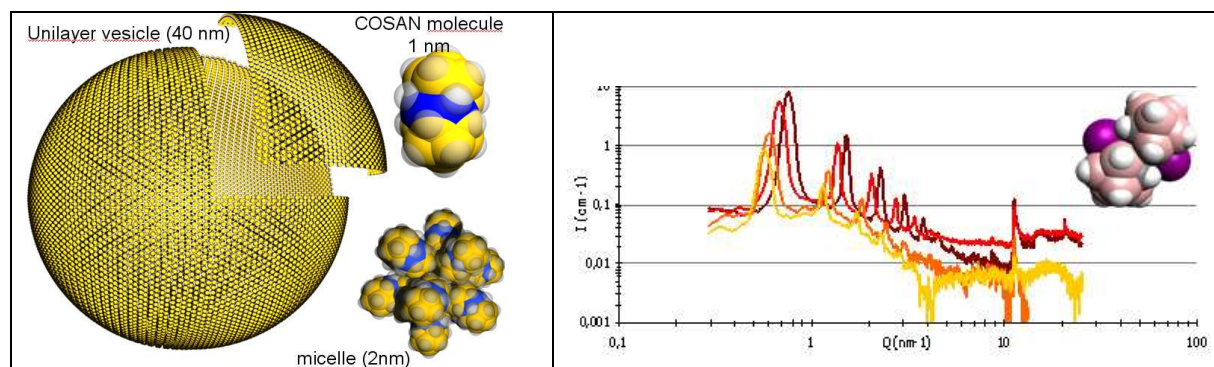


Fig: left- schematic view of self-assembling of COSAN molecules either in unilamellar vesicle at very low concentration or in small micelle at higher concentration, a transition that can be understood in term of lateral interaction energy. Right – SAXS spectra of Iodo-cosan gel at low temperature showing a lamellar structure with a periodicity of about 10nm.

Reference

P. Bauduin, S. Prevost, P. Farràs, F. Teixidor, O. Diat and T. Zemb, "A Theta-Shaped Amphiphilic Cobaltabisdicarbollide Anion: Transition From Monolayer Vesicles to Micelles" *Angew. Chem. Int. Ed.*, 50(23), 2011, pp 5298

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² ICMAB CSIC, Campus de la UAB, 08193 Bellaterra, Spain

Carboxylate based surfactant for Ion flotation

C. Micheau, P. Bauduin, O. Diat, S. Faure¹

The process called *ion flotation* allows to concentrate ions or other charged entities from aqueous solution within a foam that can be produced at the top of the solution. Foam is created by introducing gas bubbles in the solution that contains surfactant molecules at very low concentration (\leq CMC). The supplementary properties of such amphiphilic species is to be able to complex cations. Afterwards the drainage of the foam leads to concentrate the metal ions and the surfactant. The skimming of the foam enables ultimately to extract metal ions from the native solution. Moreover ion separation can be achieved by using selective complexing surfactants. To obtain an efficient ion extraction, the surfactant needs to combine good foaming and complexing properties. *Ion flotation* covers two main application fields: recovery of valuable material and water decontamination. Compared to solvent extraction, used for example in the nuclear fuel recycling, *ion flotation* shows the main advantage of using gas instead of an organic solvent.

In the present (PhD) study, the investigated surfactant is composed of an alkyl chain, ethoxy groups keeping efficient the foaming property, even after complexation, and a carboxylic acid function which acts as a complexing part when it is under its charged carboxylate form.

Ion flotation of multivalent cations was investigated as a function of pH and ionic strength. Titration, UV-vis spectroscopy, ICP, Zeta potential, small angle neutron scattering, conductimetry are numerous and complementary techniques used to determined and understand the interaction of the cations with the foam structure and more accurately with the polar head of the surfactant. This can be compared when amphiphiles are self-assembled into micelles. The extraction yield obtained by chemical analysis was discussed in terms of the surfactant and cation speciations.

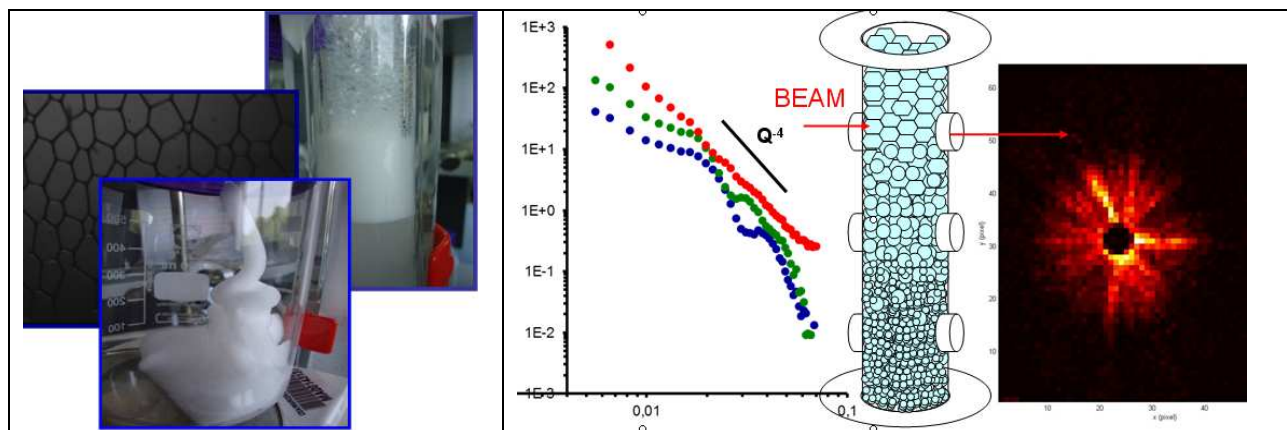


Fig : left – pictures of flotation column + zoom on the foam structure. Right: exemple of SANS curves from foam structure at different height within the column (drainage effect).

Reference

C. Micheau, S. Faure, P. Bauduin, O. Diat, Eufoam proceeding in preparation

¹ DTCD/LCFI

Probing ion distribution at solid/liquid interface with x-ray standing waves

Luc Girard, Sambhunath Bera¹, Jean Daillant¹, Florent Malloggi¹, Dmitri V. Novikov²

The interaction between electrolytes and charged surface play a key role in many physico-chemical and biological processes. In spite of the importance of the electrical double layer (EDL) and its study for more than 150 years, the knowledge of the ion distribution close to solid-liquid interface is very poor. It has been limited by the lack of techniques for probing this distribution with an accuracy of a few Å. In this study, we have employed x-ray standing waves (XSW) technique to measure the EDL structure including the location of ions as well as the ion distribution along the normal direction. For generating long-period XSW, we used dynamical Bragg diffraction above a Si/Mo multilayer using x-ray beam from a synchrotron. Batterman first demonstrated that the standing wave inside the multilayer has a period equal to the one of the multilayer and a phase depending on the incidence angle. As XSW extend above the multilayer surface, this interference effect can be used to locate the position of an adsorbed atomic layer on the surface as well as the ion distributed in the EDL. This information is obtained by measuring the modulation of the atom fluorescence as the XSW antinodes shift inward by one-half of a spacing period during an angle scan through the Bragg reflection. This technique was previously applied to different samples such as Zn ion layer embedded in a Langmuir-Blodgett multilayer above a gold mirror surface, Zn²⁺ distribution profile in an electrolyte solution in contact with a phospholipid charged surface above a Si/W multilayer or Sr²⁺, Zn²⁺ and Y³⁺ adsorbed to the rutile-water interface. We have investigated solution of 10⁻⁴ and 10⁻⁵M of mono and trivalent cations CeCl₃/GdCl₃, KCl/CsCl, LaCl₃/EuCl₃ and LaCl₃/GdCl₃, above Si/Mo multilayer substrates with 30Å period. The XSW measurement was performed at the BW1 beamline (DESY synchrotron, Hamburg, Germany) and ID10B beamline (ESRF, France) with an incident beam of 8 keV with a microfluidic cell. The reflectivity of the first order Bragg reflection and the fluorescence yields were simultaneously recorded. The ions fluorescence angular dependence as well as the ion distribution in the diffuse Gouy-Chapman layer were determined from the analysis of the fluorescence data using a homemade program[1] with a few Å accuracy.

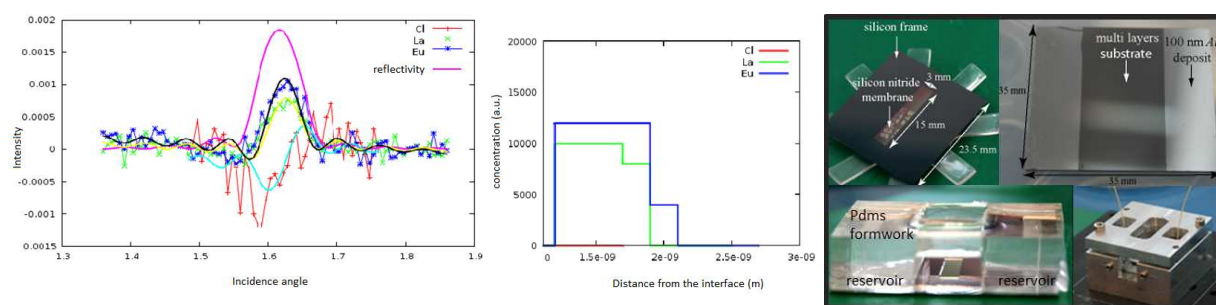


Fig.1 : Left: Intensity of fluorescence and reflectivity from a LaCl₃/EuCl₃ solution in contact with a silicon molybdenum multilayer. Middle: Concentration of the ions above the solid surface (compared to the bulk). Right: The microfluidic cell used for the experiments.

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¹ CEA Saclay, IRAMIS

² HASYLAB DESY

Ionic liquids as an advanced solvent compatible with self-assembly and cooperative extraction processes

Thomas Zemb, Pierre Bauduin

*Julian Eastoe (University of Bristol) and Jingcheng Hao (University of Shandong, China),
Agnès Harrar, Oliver Zech and Werner Kunz,*

For efficient hydrometallurgic processes, amount of water co-extracted with the ions needs to be controlled. Traditionally, « low » temperature molten salts are considered for the temperatures above electrochemical separation at high temperature for pyrometallurgy and concentrated solutions of ionic extractants in room temperature processes. Since the discovery of the existence of self-assembly, i.e. thermodynamic stability and spontaneous self-assembly of micelles¹, reverse micelles, microemulsions in low (i.e. -50 to 200 C) temperature ionic liquids, a large new window opens for hydrometallurgic processes²: it relies on new formulations of ionic liquids with a large temperature window, electrochemical window *and* low miscibility with water or apolar solvents.

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. The ultra-low interfacial tension measurements confirmed the formation of middle-phase microemulsions. 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.³

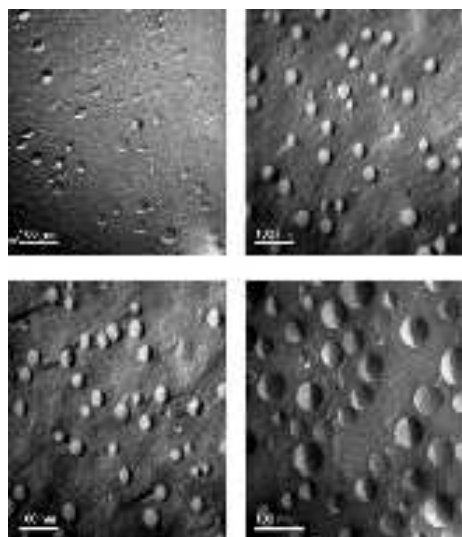


Fig.1: FF-TEM images of microemulsion samples of [bmim][BF₄]/TX-100/cyclohexane with the molar ratios (R) of IL/TX-100, 0.2 (top, left), 0.5 (top, right), 1.0 (below, left), and 1.5 (below, right), respectively. The weight fraction of TX-100 is 0.45.

¹ Werner Kunz and Thomas Zemb : (2012). "Using ionic liquids to formulate microemulsions: Current state of affairs." *Current Opinion in Colloid & Interface Science* 17(4): 205-211.

² Agnès Harrar, Oliver Zech, Pierre Bauduin, Olivier Diat, Thomas Zemb et Werner Kunz, "[emim] [etSO₄] as the Polar Phase in Low- Temperature-Stable Microemulsions." (2011) *Langmuir* 27(5): 1635-1642.

³ Liu, Liping; Pierre Bauduin, Thomas Zemb, Julian Eastoe, Jingcheng Hao, "Ionic liquid tunes microemulsion curvature" *Langmuir* (2009), 25(4), 2055-2059.

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

L'équipe est constituée actuellement de :

- 1 DR CNRS responsable d'équipe (Stéphane Pellet-Rostaing),
- 1 MDC UM2 (Guilhem Arrachart)
- 1 Ingénieur CEA/DSM (Sandrine Dourdain)
- 1 Technicienne CEA (Véronique Dubois)

Post-doctorants :

- Raphaël Turgis (DEN, 2010-2012) : extractants spécifiques de l'uranium.
- Stéphanie Gracia (DEN, 2011-2013) : analogues du h4tpaen pour la séparation Am/Cm.
- Fanny Mary (DEN, 2012-2013) : Ligands sélectifs des terres rares en milieu phosphorique.
- Raphaël Turgis (LABEX Chemisyst, 2013-2015) : Recyclage des métaux stratégiques en IL.

Thésards :

- Simon Chapron (DEN, 10/2011) : analogues du TEDGA dans le procédé EXAm.
- Olivia Pécheur (DEN/DSM, 10/2011) : mécanismes synergiques d'extraction de l'uranium.
- Marie Guillot (CIFRE FCBA, 02/2012) : traitement de la biomasse en eau sous-critique.
- Romain Besnard (DSM, 10/2012) : synthèse one-pot de matériaux extractants hybrides.
- Moussa Touré (DEN, 10/2012) : pertraction pour le recyclage de métaux stratégique.
- Donatien Gomez-Rodriguez (Carnot/Labex, collaboration ICSM/ICGM/IEM 10/2012) : membranes organiques fonctionnalisées pour le recyclage des terres rares en phase aqueuse.



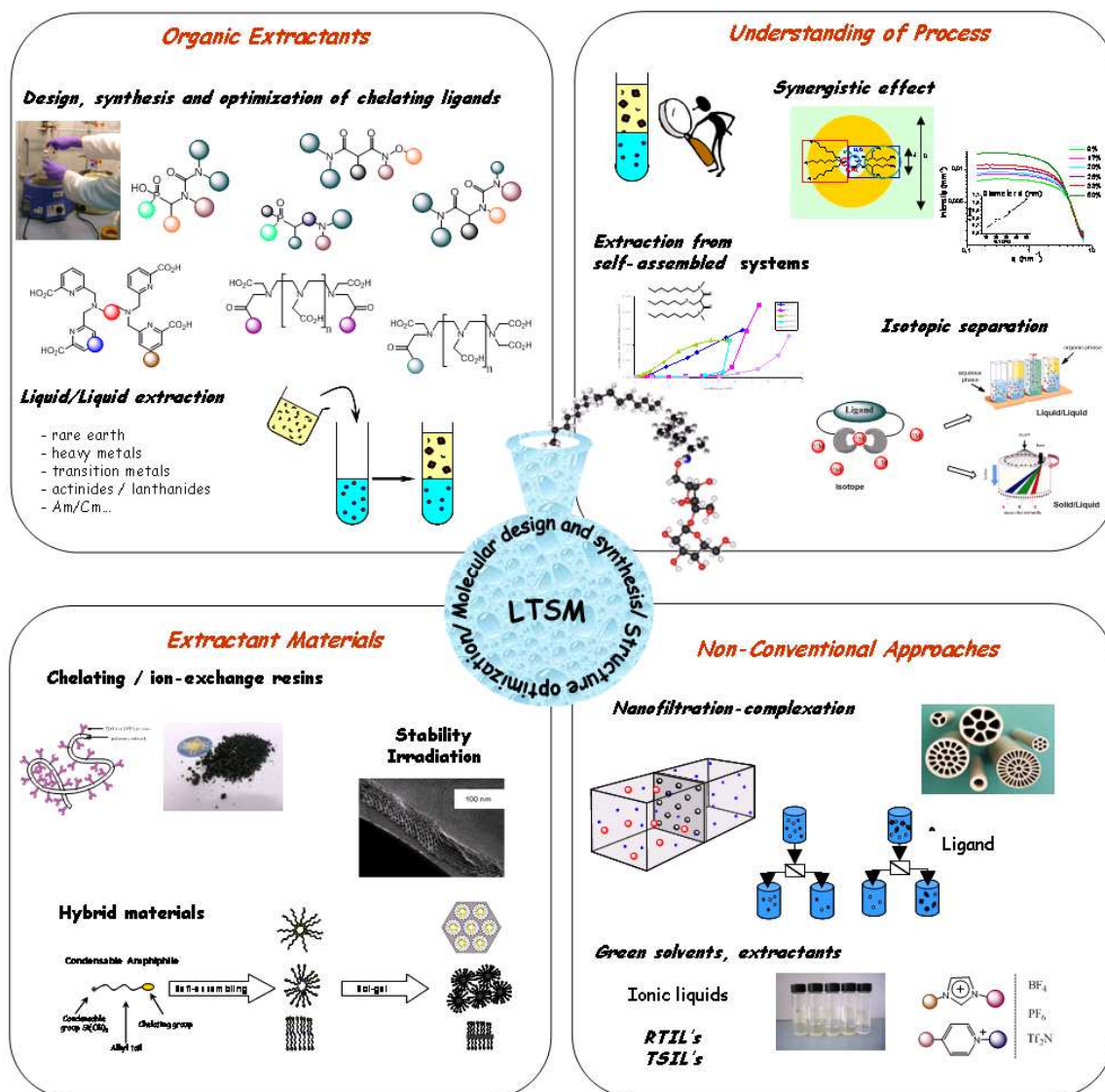
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Initiées depuis la création de l'institut, les différentes thématiques que développe l'équipe « Tri Ionique par des Systèmes Moléculaires Auto-assemblés » (LTSM) s'appuient au départ sur les compétences et le savoir-faire des chercheurs qui composaient l'équipe à sa création (Thomas Zemb et Christophe Déjугnat CR CNRS ayant muté au 01/2010), aidés d'une technicienne CEA (Mme Dubois, arrivé en 2009).

L'arrivée du Dr Stéphane Pellet-Rostaing (DR CNRS, mutation au 01/2009) comme nouveau responsable d'équipe, la nomination de Guilhem Arrachart au poste de Maître de Conférence UM2 et plus récemment de Sandrine Dourdain comme Ingénieur CEA/DSM affectés au LTSM ont permis à l'équipe d'initier concrètement des travaux de recherche dans le domaine de la synthèse de ligands et matériaux spécifiques pour la séparation d'ions, mis en œuvre dans des procédés d'extraction classiques (liquide/liquide, solide/liquide) ou non conventionnels (membranes, liquides ioniques) 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, microémulsions, 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 l'élaboration et la synthèse d'extractant spécifiques originaux ainsi que par l'étude des mécanismes associés qui gouvernent la sélectivité, notamment par des phénomènes coopératifs supramoléculaires, est au cœur des missions du groupe LTSM. La possibilité d'exalter la complexation par auto-association des complexants sous forme de micelles, fibrilles ou cristaux liquides, doit être explorée, pouvant conduire à des procédés en rupture de tri ionique 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 des métaux stratégiques.

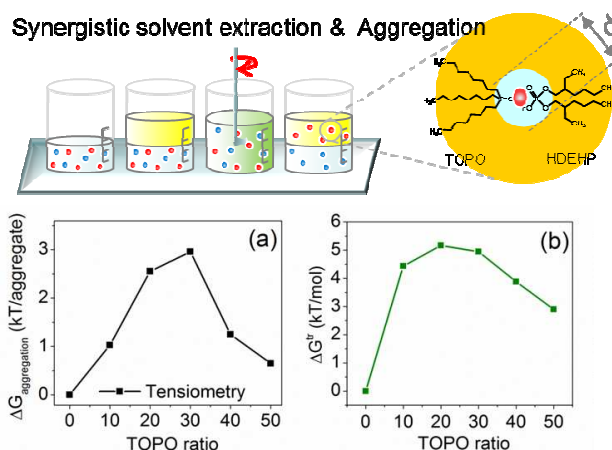


Synergism by co-assembly in liquid-liquid extraction of uranium from phosphoric ores

*S. Dourdain, I. Hofmeister, J-F. Dufrêche, R. Turgis, S. Pellet-Rostaing, T. Zemb
O. Pecheur, A. Leydier (CEA DRCP)
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Exploitation of phosphate rocks, 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 di (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 molecules, and by providing information on the 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]^{2,3}. 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. Small angle X ray scattering data showed that there is no peculiarity in the aggregates microstructure at the maximum of synergism. The Critical Aggregation Concentration (CAC) was therefore determined experimentally to derive the free energy of aggregation necessary to form mixed aggregates containing extracted ions in their polar core. It was found that the aggregation energy is comparable to the transfer free energy difference between target and non-target ions, as deduced from the synergistic selectivity peak (Figure a and b), showing that the synergistic extraction of uranium is related to an easier aggregation of the two extractant molecules.⁴

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 processing, - secondary resources, Springer Berlin, 2003.

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

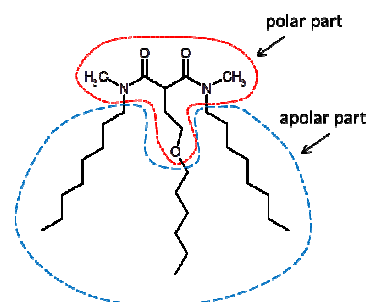
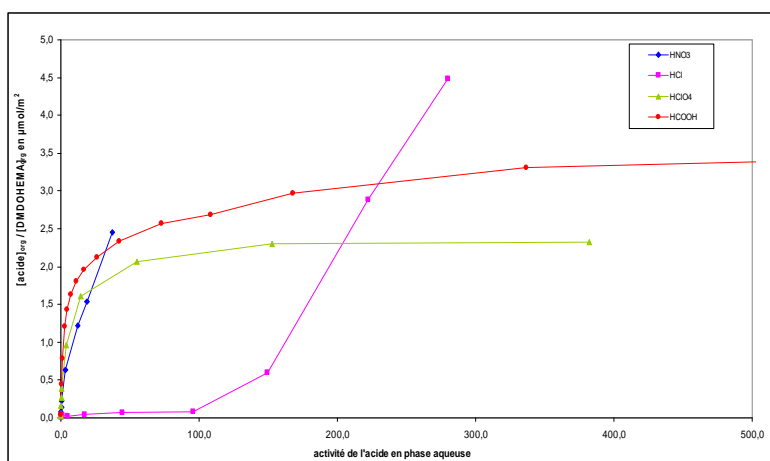
4 S. Dourdain, I. Hofmeister, O. Pecheur, J-F. Dufrêche, R. Turgis, A. Leydier, J. Jestin, F. Testard, S. Pellet-Rostaing, T. Zemb, "Synergism by Coassembly at the Origin of Ion Selectivity in Liquid-Liquid Extraction" *Langmuir*, 2012, 28, 11319.

Extraction of acids and water by a malonamide in an alkane: effect of the anion on extraction and aggregation properties

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L. Berthon (CEA DRCP)*

Chemical analysis of phases in equilibrium in a Winsor-II regime, i.e. when an acidic solution is in contact with an oil phase containing solvent, an amphiphile with complexing properties, water and extracted ions, allows to determine extraction isotherms of ions as well as amount of co-extracted water. By comparing absorption isotherms of acids of N,N'-dimethyl-N,N'-dioctyl-2-(2(hexyloxy)ethyl)-malonamide (DMDOHEMA) chosen as a typical oil-soluble extractant, all other things being equal, a strong effect of the anion position in the Hofmeister series can be evidenced.

The size and shape of the aggregate depends only slightly on the chaotropic/cosmotropic nature of the anion. Interactions between polar cores as well as amount of co-extracted water vary in large proportions. This is related to different modes of extraction of acids, either as ion pairs or by protonation of the extractant, which implies a larger free energy of transfer.



It was also shown that the free energy of formation of reverse micelles in the solvent phase strongly depends on the presence of polar solutes. Free energies per molecule vary typically from 0 to 2 kT/molecule (5 kJ), depending on the kosmotropic/chaotropic nature of the anion extracted as well as on the quantity of co-extracted water. Variations of the reverse aggregation free energy introduced by acids and other co-extractant as deduced from the critical aggregation concentrations cannot be neglected while modelling extraction. With typical aggregation numbers of 4-6, the free energy of formation of one reverse aggregate varies by up to 20 kJ, four times the typical difference in free energy of one single cation transfer between a “target” and a non-target ion in practical extraction and stripping industrial processes.

C. Déjugnat, L. Berthon, V. Dubois, Y. Meridiano, S. Dourdain, S. Pellet-Rostaing, T. Zemb, “**Extraction of acids and water by a malonamide in an alkane: effect of the anion**”, to be submitted in Langmuir.

C. Déjugnat, S. Dourdain, V. Dubois, L. Berthon, S. Pellet-Rostaing, J.-F. Dufrêche, T. Zemb, “**Reverse aggregates nucleation induced by acids in liquid-liquid extraction processes**”, to be submitted in Langmuir.

Weak adsorption of salts and oil-water solubility balance of peptides: Is the concept of molecular intrinsic hydrophilicity self-consistent?

T. Zemb, J-F. Dufrêche
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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 hydrophobic due 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 Charles Tanford as a concept based on observed free energy of transfer and hence relative solubility in the form of monomers.

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.

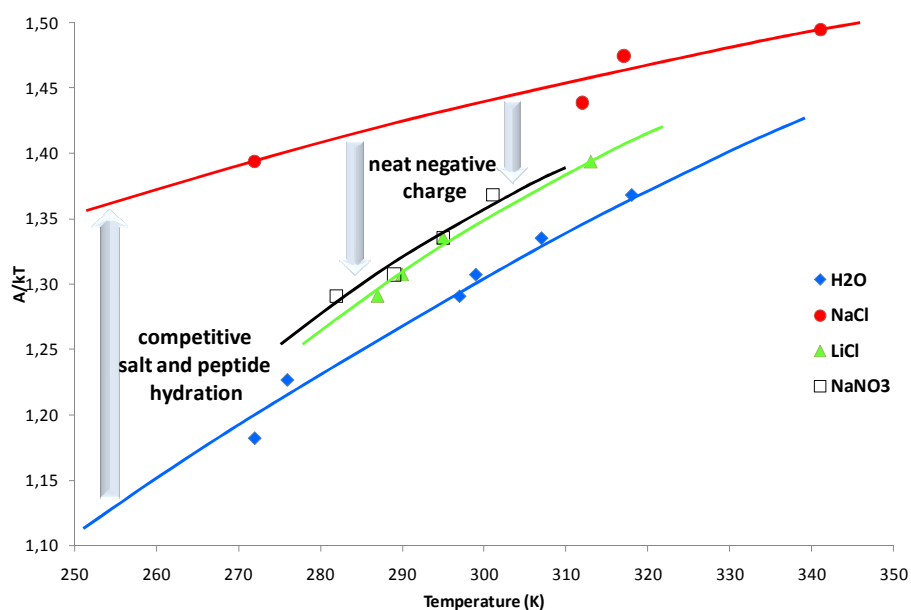


Figure 1: Figure: The apparent Hamaker A/kT constant driving towards coacervation decreases with temperature; due to weak adsorption of salt. The “neutral” salt is always salting-in, while specific ion adsorption-desorption induces partial quenching of the attraction due to electrostatic repulsion: Hydrophilicity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

¹ C. Déjugnat, J-F. Dufrêche, T. Zemb "Ion-specific weak adsorption of salts and water/octanol transfer free energy of a model amphiphilic hexapeptide." *Phys. Chem. Chem. Phys.*, 2011, 13(15): 6883-6893.

Instabilities in liquid/liquid extraction: a colloidal approach

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W. Kunz (Regensburg), C. Larpent (Université de Versailles), B. Demé (ILL-Grenoble)

The interaction potential between reverse aggregates responsible 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 instability 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 Hamaker constant depends probably on the polarisability of the core containing extracted ion pairs as well as co-extracted acid. A review of all available papers including some predictive modelling in phase behaviour has been written¹. >Q

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 these two approaches as well as simple analytic expression in case of non-ionics is proposed². 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 dilution³. 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 liquid-liquid extraction.⁴

¹ F. Testard, T. Zemb, P. Bauduin, L. Berthon, "Third-phase formation in liquid/liquid extraction: a colloidal approach" *Ion Exchange and Solvent Extraction* 2010, 19, 381.

² W. Kunz, F. Testard, T. Zemb, "Correspondence between Curvature, Packing Parameter, and Hydrophilic-Lipophilic Deviation Scales around the Phase-Inversion Temperature" *Langmuir* 2009, 25(1), 112.

³ T. Zemb, "Flexibility, persistence length and bicontinuous microstructures in microemulsions" *C. R. Chim.*, 2009, 12(1-2), 218.

⁴ F. Testard, L. Berthon, T. Zemb, "Liquid-liquid extraction: An adsorption isotherm at divided interface?" *C. R.Chim.*, 2007, 10(10-11), 1034.

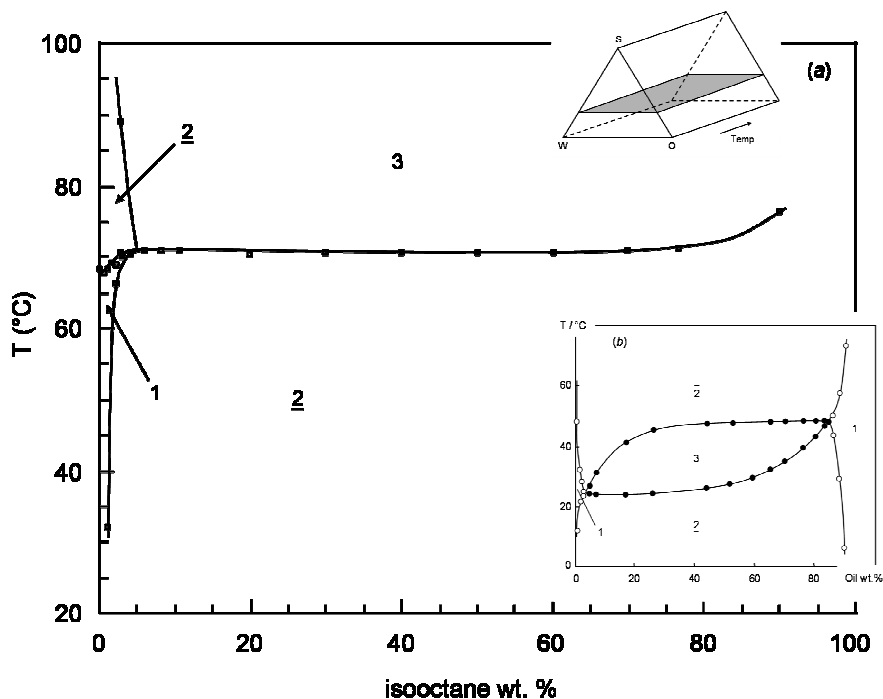


Fig.1: Constant surfactant cut in the ternary phase prism: oil-water-surfactant at different balances of water and oil content. Low water-content reverse aggregates are possible without co-surfactant, however with a limited domain available for extraction. Phase sequence and extension demonstrates that this type of microemulsions belong to the class of rigid surfactant film, with a bending constant larger than kT ⁵

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.

⁵S. Nave, F. Testard, H. Coulombeau, K. Baczko, C. Larpent, T. Zemb, "Ternary phase diagrams of a thermoreversible chelating nonionic surfactant" *Phys. Chem. Chem. Phys.*, 2009, 11(15), 2700.

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

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A. Favre-Réguillon, M. Lemaire (Université Claude Bernard Lyon 1)

First separation of Ln(III) using inorganic nanofiltration membrane has been achieved. Ln(III) ions are strongly repelled by the $\text{ZrO}_2/\text{TiO}_2$ 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 $[\text{EuDTPA}]^{2-}$ complex is formed at lower pH than $[\text{LaDTPA}]^{2-}$ and so these two elements can be separated. With an equimolar mixture of Eu^{3+} and La^{3+} , a $\text{La}^{3+}/\text{Eu}^{3+}$ 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 $\text{La}^{3+}/\text{Eu}^{3+}$ separation factor has been also evaluated with a TiO_2 nanofiltration membrane and results are comparable.

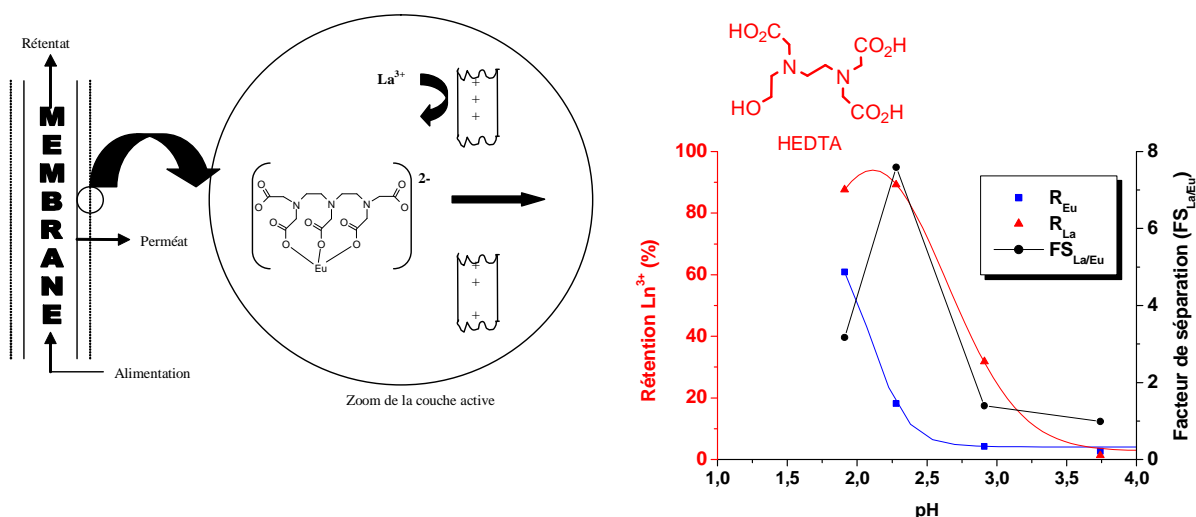


Fig. 1: Principle of ion separation with an inorganic nanofiltration membrane by complexation with the organic ligand DTPA and rejection of Eu^{3+} and La^{3+} by the membrane with HEDTA ligand versus pH. $[\text{La}^{3+}] = [\text{Eu}^{3+}] = 2.5 \times 10^{-4} \text{ molL}^{-1}$; $[\text{HEDTA}] =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

Using organic membranes, the rejection of Ln(III) increases as the charge of the complex increases²³ 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, "Separation of lanthanides (III) by inorganic nanofiltration membranes using a water soluble complexing agent" *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. Sbai, A. Szymczyk, P. Fivet, M. Lemaire, *J. Membr. Sci.* 2005, 267, 41.

Actinides (III) / Lanthanides (III) separation by nanofiltration assisted by complexation and liquid/liquid extraction

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G. Bernier, C. Hill (CEA DRCP)*

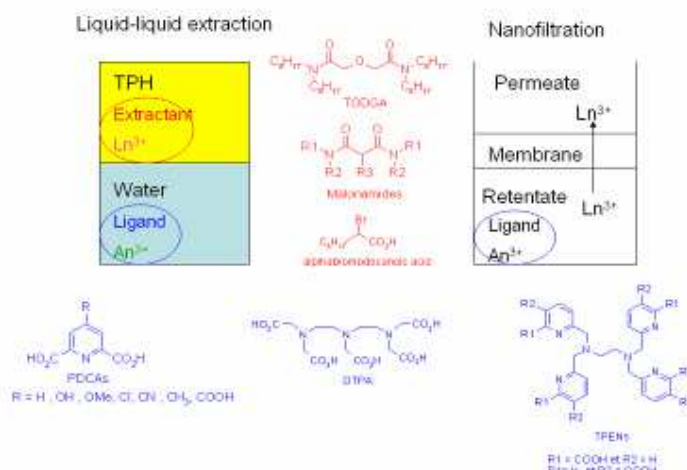
M. Lemaire, A. Favre-Réguillon (Université Claude Bernard Lyon 1)

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 work was 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 then 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 was that ligands have to be hydrophilic.

The first part of this work was focused on the synthesis of these ligands by introducing hydrophilic functions such as carboxylic acids, amides, urea, alcohols, etc.

The second part of the project was to test these new ligands on nanofiltration membrane in order to separate lanthanides first. These tests have been carried out in Lyon in non-radioactive media in order to get the good conditions. Both organic and inorganic membrane have been tested in order to compare their separation capacity. Organic membrane¹ are able to separate americium (III) from lanthanides(III) but they can not resist to high radioactivity. For this reason we choose to replace them by ceramic nanofiltration membranes more suitable for these conditions.

The third part was 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 C₁₂ alkyl chains) or dodecane. Hydrophilic ligands will extract selectively americium (III) in the aqueous phase. Very promising results, FS Am/Eu = 300-700 and FS Am/Cm = 3-4, have been obtained in liquid/liquid extraction with water soluble ethylenediamine derivative.² In order to improve the solubility and selectivity of such ligands a recent study has been initiated³ focused on the synthesis of new ligands and their characterization in regards to the actinides (III) / lanthanides (III) separation.



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

¹ A. Sorin "Séparation actinides(III) / lanthanides(III) par nanofiltration assistée par complexation" - 2006, thèse de l'Université Lyon1.

² X. Heres, F. Burdet, J. Borrini, M.-T. Duchesne, M. Mazzanti, G. Bernier, S. Pellet-Rostaing, A. Favre-Reguillon, M. Lemaire, "Process for separating americium from other metallic elements present in an acidic aqueous or organic phase and applications thereof" 2010, WO201269573 - FR2968014.

³ S. Gracia (DEN, 2011-2013) : "Analogues du h4tpaen pour la séparation Am/Cm" collaboration M. Mirguiditchian, C. Marie (CEA/DRCP/LEPS).

Liquid-liquid cation extraction without solvent

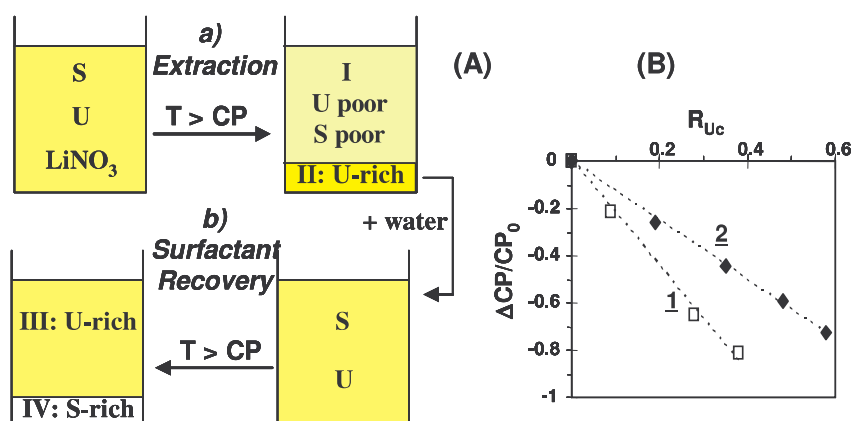
T. Zemb,

F. Testard, S. Prévost, S. Nave (LIONS-Saclay),

K. Baczkó, C. Coulombeau, C. Larpent (Université de Versailles)

Chantal Larpent and co-workers have shown ten years ago that efficient solvent-free extraction can be obtained with complexing molecules of a general class of tri-block molecules composed of one hydrophobic chain, one complexing group with "recognition" functionality as well as a temperature sensitive non ionic head. This type of molecule presents a cloud point two phase region where liquid-gas phase separation occurs¹. The concentrated phase made of anisometric micelles allows efficient extraction-desextraction without solvent. Surprisingly, process works best when complexing group is in between the temperature sensitive head and the apolar chains².

Extremely efficient selectivities for uranium of this type of molecule have been evidenced. A drawback hindering up to now applications in the domain of nuclear interest is the variation of the cloud point with external constraints, such as the variable amounts of radiolized complexing surfactant. However, a large domain of stable reverse micelles, with and without ions has been detected in the phase diagram structures³.



(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 C. Larpent, S. Prévost, L. Berthon, T. Zemb, F. Testard, "Nonionic metal-chelating surfactants mediated solvent-free thermo-induced separation of uranyl" *New J. Chem.*, **2007**, 31(8), 1424.

² S. Prévost, H. Coulombeau, K. Baczkó, L. Berthon, N. Zorz, H. Desvaux, F. Testard, T. Zemb, C. Larpent, "Thermo-responsive metal-chelating surfactants: properties and use in cloud point extraction of uranyl nitrate" *Tenside Surfact. Det.*, **2009**, 46(2), 100.

³ S. Nave, F. Testard, H. Coulombeau, K. Baczkó, C. Larpent, T. Zemb, "Ternary phase diagrams of a thermoreversible chelating non-ionic surfactant" *Phys. Chem. Chem. Phys.*, **2009**, 11(15), 2700.

The supra-molecular mechanisms at the origin of ion extraction processes in hydrometallurgy

*T. Zemb, S. Dourdain, V. Dubois, S. Pellet-Rostaing
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We study liquid-liquid extraction at supramolecular and colloidal scale, considering the pseudo-ternary phase diagram of water-extractant with all ionic species as perturbations. Combined SAXS/SANS and osmometry allows to determine microstructures 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 pairs¹.

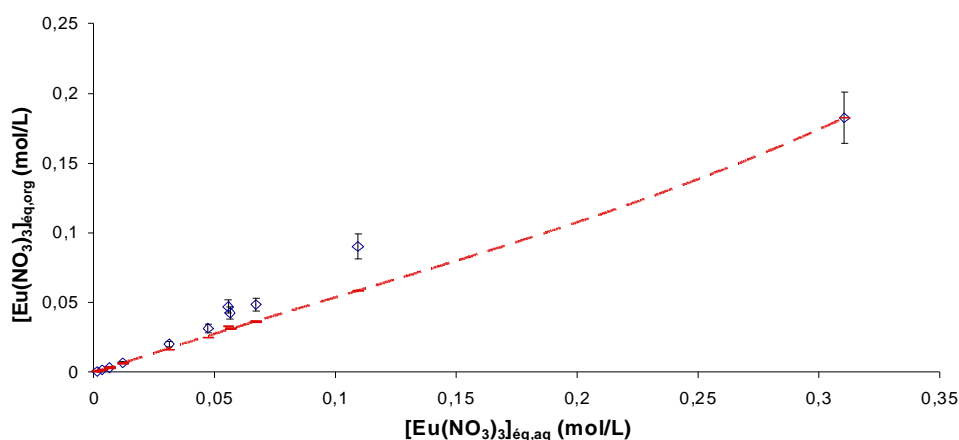


Figure 1: Simultaneous determination of ion per extractant in the organic phase and cation molarity in the aqueous phase. This type of plot allows to determine free energy of transfer from water to solvent phase and relate this to the volume and curvature of the reverse aggregate, the colloidal aggregate 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 columns¹. 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

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.³

¹ L. Berthon, F. Testard, L. Martinet, T. Zemb, C. Madic, "Influence of the extracted solute on the aggregation of malonamide extractant in organic phases: Consequences for phase stability" *C. R. Chim.*, 2010, 13(10), 1326.

² L. Berthon, F. Testard, L. Martinet, P. Bauduin, T. Zemb, C. Madic, "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.

³ Y. Meridiano, L. Berthon, X. Crozes, C. Sorel, P. Dannus, M. R. Antonio, R. Chiarizia, T. Zemb, "Aggregation in Organic Solutions of Malonamides: Consequences for Water Extraction" *Solvent Extraction and Ion Exchange* 2009, 27(5-6), 607.

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.⁴

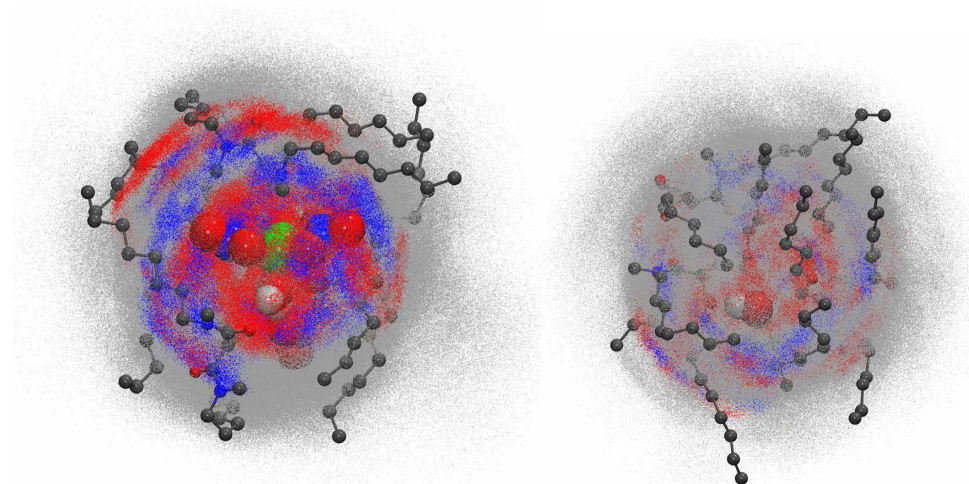


Figure 2: molecular model of a loose un-organized w/o aggregate (right) and a more organized reverse aggregate (left), when a more compact micellar core of polar materials (ions, water and complexing oxygen atoms) can be distinguished: Neutron scattering and X-ray scattering in so-called "wide angle" region of Small angle scattering distinguish these two states, who differ by a Born energy of the order of a few kT , i.e. the order of magnitude in driving force used in industrial liquid-liquid extraction. The grey shaded area is the region of presence of CH_2 , the red region the one of oxygen atoms and the blue one reflects the presence of water molecules.

⁴ L. Berthon, Y. Meridiano, S. Lagrave, X. Crozes, C. Sorel, N. Zorz, F. Testard, T. Zemb, "Aggregation of organic extractant phases: consequences on extraction properties" Solvent Extraction: Fundamentals to Industrial Applications, Proceedings of ISEC 2008 International Solvent Extraction Conference, Tucson, AZ, United States, Sept. 15-19, 2008, 2 1017.

Self-assembly of amphiphilic peptides for ion separation

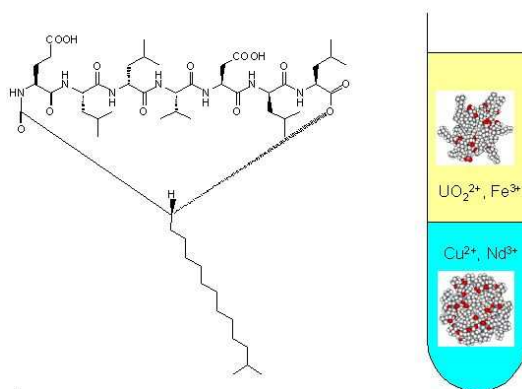
O. Diat, T. Zemb

C. Déjugnat (ICSM – IMRCP Université Toulouse 3)

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 amphiphilic 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 (lipopeptides) 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 iron¹.



Surfactine molecule that allows metal selective extraction in biphasic system.

¹ C. Déjugnat, O. Diat, T. Zemb "Surfacting Self-Assembles into Direct and Reverse Aggregates in Equilibrium and Performs selective Metal Cation Extraction.", *ChemPhysChem*, 2011 12(11): 2138-2144

Sequestering agents for uranyl decorporation

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Y. Lin, A. Favre-Reguillon, M. Lemaire (Université Claude Bernard Lyon 1)

D. Lecerclé, F. Taran (CEA Saclay)

At each step of the fuel cycle: extraction, concentration, purification, enrichment or recycling, workers can be subjected to uranium contamination. Accidental internal contamination by inhalation or through skin lesions is the major risk for workers, whether acute and/or repeated.

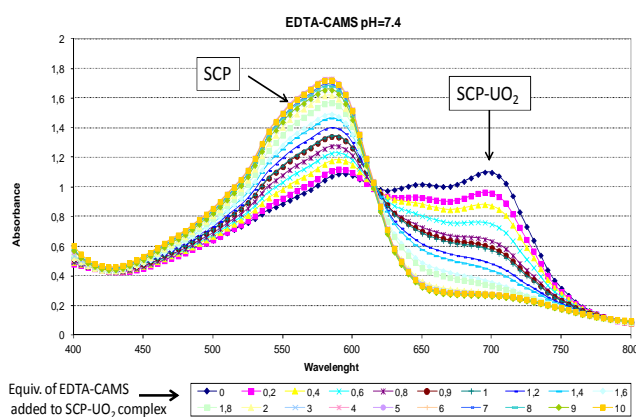
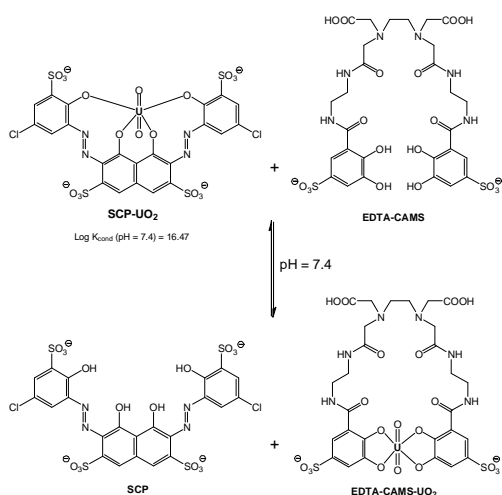
The hexavalent uranyl ion (UO_2^{2+} , U(VI)) was found to be the most stable form *in vivo* and is complexed in the blood by chelating agents such as proteins or carbonates. Inside the body, uranium creates risks both as a toxic heavy metal and as radioactive material in the case of chronic exposition.

After contamination it is rapidly transferred through the blood stream to deep organs, such as kidneys and bones that assimilate it strongly. To avoid these effects, heavy metals must be eliminated from the body by administrating non toxic chelating agents.

Most efficient uranophile chelating functions are oxygen-containing ligands like multidentate sulfocatecholamides (CAMS),¹ hydroxypyridones (HOPO),² carbamoylmethylphosphine oxide (CMPO),³ calixarene derivatives⁴ or bisphosphonate sequestering agents.⁵

Recently, we focused our attention on the preparation of new chelating agents based on EDTA and DTPA skeletons as potential sequestering agents for uranyl chelation.

In order to increase the affinity regarding uranyl ion, we designed and synthesized a series of modified water-soluble EDTA and DTPA using various substituted amines.⁶ A series of 16 ligands were synthesized and their binding abilities towards uranium were investigated using UV spectrophotometry (competitive uranium binding with sulfochlorophenol - SCP) in aqueous media under physiological pH (close to neutral) as well as under acidic and basic conditions. In regard to decorporation applications the best uranophile ligand was found to be the EDTA-CAMS, which exhibits significant association constants under the range of pH studied. Further investigation before a possible evaluation of their *in vivo* efficiency will be necessary.



¹ A. Leydier, D. Lecerclé, S. Pellet-Rostaing, A. Favre-Réguillon, F. Taran, M. Lemaire, *Tetrahedron* 2008, 64, 6662.

² A. Leydier, D. Lecerclé, S. Pellet-Rostaing, A. Favre-Réguillon, F. Taran, M. Lemaire, *Tetrahedron Lett.* 2011, 52, 3973.

³ F. Sansone, M. Galletta, E. Macerata, E. Trivellone, M. Giola, R. Ungaro, V. Böhmer, A. Casnati, M. Mariani, *Radiochim. Acta* 2008, 96, 235.

⁴ A. Leydier, D. Lecerclé, S. Pellet-Rostaing, A. Favre-Reguillon, F. Taran, M. Lemaire, *Tetrahedron* 2008, 64, 11319.

⁵ M. Sawicki, D. Lecerclé, G. Grillon, B. Le Gall, A.-L. Sérandour, J.-L. Poncy, T. Bailly, R. Burgada, M. Lecouvey, V. Challeix, A. Leydier, S. Pellet-Rostaing, E. Ansoborlo, F. Taran, *Eur. J. Med. Chem.* 2008, 43, 27683.

⁶ A. Leydier, Y. Lin, G. Arrachart, R. Turgis, D. Lecerclé, A. Favre-Réguillon, F. Taran, M. Lemaire, S. Pellet-Rostaing, "EDTA and DTPA modified ligands as sequestering agents for uranyl decorporation" *Tetrahedron* 2012, 68, 1163.

Development of a methodology for the synthesis of hybrid silica with high extractant capacity

R. Besnard, G. Arrachart, J. Cambedouzou, A. Grandjean, S. Pellet-Rostaing

The sol-gel process is a convenient method for the preparation of hybrid organic-inorganic materials which are widely used in many applications including solid-liquid extraction.

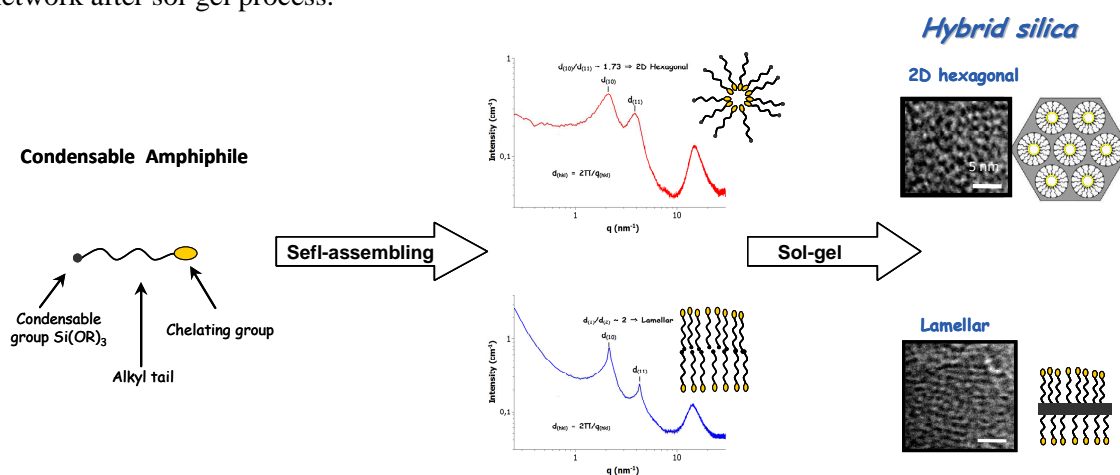
The ability to control the structure of the materials on the nanoscale is of great interest for the design and the improvement of material properties. In this field, utilization of surfactant as external structuring agent represents a way to form periodic mesoporous hybrid materials.

Incorporation of organic components within an inorganic silica framework is available from three pathways: Grafting, Co-condensation and Periodic Mesoporous Organosilicas (PMOs).

In the context of solid-phase extractants, the organically functionalized silica should have a high density of functional groups with a satisfying homogeneity and accessibility. These requirements are usually difficult obtained with conventional approaches. The aim of this work was to develop a suitable “all-in-one” approach using condensable surfactant precursor either for preparation of hybrid materials or functionalization of the channel walls of mesoporous silica. 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. Based on a recent feasibility study conducted in the laboratory¹, we focused our choice to simple groups such as carboxylate or IDA (iminodiacetic acid).

- a second polar head shaped on condensable $\text{Si}(\text{OR})_3$ functionalities in order to generate the silica network after sol-gel process.



The project aims at the study of phenomena that influence the self-associative properties of amphiphilic molecules in the controlled preparation of mesoporous materials and nanoparticles with specific chelating properties. The self-assembly is considered depending on the hydrophilic-hydrophobic balance of condensable surfactants, depending on the volumes of their polar heads / the nature of the hydrophilic chelating site, the nature of the solvents and the use of co-surfactant ...

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.²

With the support of LDD and LNER laboratories, the understanding of physico-chemical phenomena that govern the supramolecular organization of condensable surfactants and the properties of the resulting hybrid materials will be the focus of the project.³

¹ S. Sene, “Synthèse de systèmes chélatants de type acide iminodiacétique pour la préparation de précurseurs silylés” Stage Master I CSMP Montpellier 2010.

S. Sene, “Amphiphiles silylés pour la préparation de matériaux hybrides” Stage Master II CSMP Montpellier 2011.

² R. Besnard, “Etude des propriétés auto-associatives de tensioactifs bifonctionnels utilisés pour la synthèse one pot de silices extractantes” Stage Master II CSM Rennes 2012.

³ R. Besnard, “Développement d’une méthodologie de synthèse de silices hybrides à haute capacité extractante” Thèse CEA/DSM 2012-2015.

Catanionic aggregates with surface charge controlled by mole ratio of co-crystallizing amphiphiles

T. Zemb,

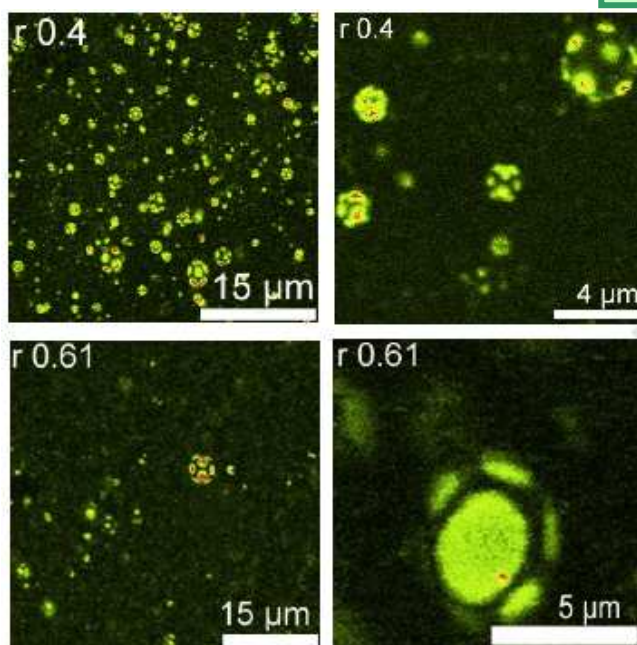
B. Abécassis, F. Testard (LIONS-Saclay)

Understand Separation

Green Chemistry

Self-assembly of anionic and cationic amphiphiles, i.e. catanionic colloids and polymers in *non-stoichiometric* ratios has been proven to be a general route to produce not only new materials, but only surface with surface charge depending on mole ratio, and not on pH of the aqueous solvent used. The 2D distribution of charges has been established for the first time by combined WAXS-WANS measurement of diffuse scattering of these 2D crystals¹. The analogy between anti-ferro-magnetism and charge distribution in the plane of contact with water has been demonstrated. In-plane segregation is coupled with chemical potential of monomers, as measured by cmc of the mixed system². The 2D crystals are very stiff³, and this has allowed to identify a new route for producing salt-resilient Pickering emulsions of tetradecane in water, stabilized by stacks of catanionic nanodiscs (figure)⁴.

Among various synthesis procedures for nanoparticles, the use of so-called “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 nano-reactor and the nanoparticles are obtained by mixing two microemulsions containing reacting precursors. Catanionic formulations of microemulsions involve surface networks of alternated positive and negative charges and produce the most rigid surfactant monolayer films known. Spherical gold nanoparticles are synthesized in worm-like catanionic reverse micelles. 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 involved⁵.



¹ D. Carriere, L. Belloni, M. Dubois, T. Zemb “**In-plane distribution in mixtures of cationic and anionic surfactants**” *Soft Matter* 2009 5(24), 4983-4990.

² Y. Michina, D. Carriere, T. Charpentier, R. Brito, E.F. Marques, J-P. Douliez, T. Zemb “**Absence of Lateral Phase Segregation in Fatty Acid-Based Catanionic Mixtures**” *J. Phys.Chem. B* 2010,114(5), 1932-1938.

³ Y. Michina, D. Carriere, C. Mariet, M. Moskura, P. Berthault, L. Belloni, T. Zemb “**Ripening of Catanionic Aggregates upon Dialysis**” *Langmuir* 2009, 25(2), 698-706.

⁴ N. Schelero, A. Stocco, H. Moehwald, T. Zemb “**Pickering emulsions stabilized by stacked catanionic micro-crystals controlled by charge regulation**” *Soft Matter* 2011, 7(22), 10694-10700.

⁵ B. Abecassis, F. Testard, T. Zemb, “**Gold nanoparticle synthesis in worm-like catanionic micelles: microstructure conservation and temperature induced recovery**” *Soft Matter* 2009, 5(5), 974-978.

4 - Sonochemistry in Complex Fluids

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Rachel Pflieger (CEA/DEN)

Tony Chave (CNRS)

Matthieu Viot (CEA/DEN depuis avril 2012)

Nathalie Navarro (thésarde, CEA/DEN/DRCP/AREVA – ICSM)

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Vincent Morosini (post doc CEA/DEN)



Domaines de recherches

- (i) Sonoluminescence dans les fluides complexes
- (ii) Cavitation à l'interface solide-liquide
- (iii) Synthèse sonochimique de nanocatalyseurs et sonocatalyse
- (iv) Sonochimie des actinides

Projets (partenaires)

- ANR-2010-BLAN-0810 NEQSON "Sonochimie en conditions hors équilibre" (ICG/CMOS, CEA/DEN)
- Dissolution sonochimique des oxydes d'actinides (CEA/DEN, AREVA)
- Dégradation sonochimique des composés organiques (CEA/DEN, AREVA)
- Sonochimie d'uranium (AREVA)
- Colloïdes de plutonium(IV) (NEEDS, CEA/DEN)
- Sonoluminescence dans les fluides complexes (LCME, Chambéry)

Study of the nonequilibrium plasma formed during ultrasonic cavitation in water

A.A. Ndiaye, R. Pflieger, B. Siboulet, J. Molina, J.-F. Dufre che, and S.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.

The sonoluminescence (SL) spectra of OH ($A^2\Sigma^+$) excited state produced during the sonolysis of water sparged with argon were measured and analyzed at various ultrasonic frequencies (20, 204, 362, 609, and 1057 kHz) in order to determine the intrabubble conditions created by multibubble cavitation.¹ The relative populations of the OH ($A^2\Sigma^+$) $v' = 1-4$ vibrational states as well as the vibronic temperatures (T_v , T_e) have been calculated after deconvolution of the SL spectra. The results of this study provide evidence for nonequilibrium plasma formation during sonolysis of water in the presence of argon. At low ultrasonic frequency (20 kHz), a weakly excited plasma with Brau vibrational distribution is formed ($T_e \sim 0.7$ eV and $T_v \sim 5000$ K). By contrast, at high frequency ultrasound, the plasma inside the collapsing bubbles exhibits Treanor behavior typical for strong vibrational excitation. The T_e and T_v values increase with ultrasonic frequency, reaching $T_e \sim 1$ eV and $T_v \sim 9800$ K at 1057 kHz.

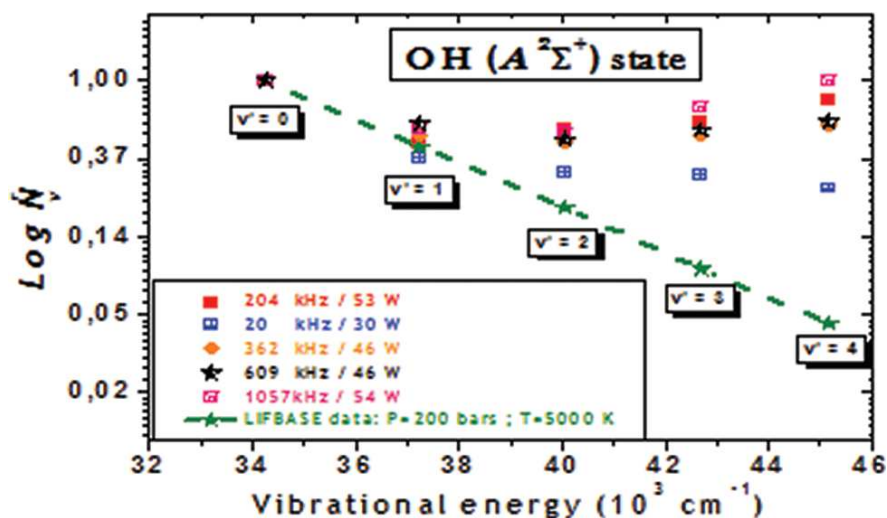


Figure 1: Relative vibrational population distribution of the OH($A^2\Sigma^+$) state as a function of vibrational energy for different ultrasonic frequencies.

¹ Ndiaye, Abdoul Aziz; Pflieger, Rachel; Siboulet, Bertrand; Molina, John; Dufre che, Jean-Francois; Nikitenko, Sergey I., "Nonequilibrium Vibrational Excitation of OH Radicals Generated During Multibubble Cavitation in Water" in Journal of Physical Chemistry A (2012), 116(20), 4860-4867

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

*J. Schneider, R. Pflieger, S. I. Nikitenko
D. Shchukin, H. 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 Young² and Liang³ who determined the experimental conditions necessary to observe line emission in SBSL.

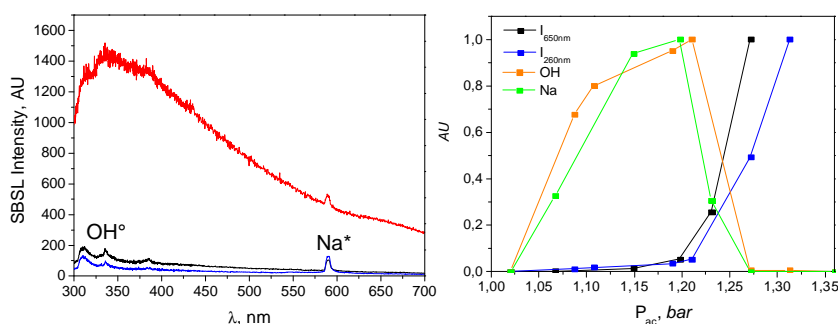


Fig.1: Left : Evolution of the SBSL spectra of 0.5M NaCl equilibrated with 70 mbar Ar with the acoustic pressure (blue: 1.13 bar, black: 1.20 bar, red: 1.25 bar). Right: Evolution with the acoustic pressure of the peak heights of OH[•] and Na*, and of the continuum (represented by SBSL intensities at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

This work⁴ 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 10⁴ 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 excited OH[•] radicals and Na are observed. The shape of the excited OH[•] 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[•] 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.

Excitation of chemical species in solutions by ultrasound

R. Pflieger, J. Ravaux, and S.I. Nikitenko.

N. Barré, P. Moisy, J. Schneider, D. Shchukin, H. Möhwald

*IPNO, Orsay BP1-9140 France, CEA/DEN/MAR/DRCP Marcoule BP 17171 France,
MPI-KG Potsdam Germany*

Power ultrasound has shown to be effective for in situ excitation of volatile and non-volatile species in solutions in many cases. The observed effects are generally attributed to acoustic cavitation which is the nucleation, growth, and rapid implosive collapse of vapor filled micro-bubbles during the ultrasonic irradiation of a liquid medium. However the mechanism(s) of excitation and the corresponding optimal experimental conditions remain largely unclear.

Bubble collapses in liquids produce chemically active species (excited species and radicals such as OH°) as well as sonoluminescence (SL, emission of light from the core of collapsing bubbles). Some species in solution may be excited directly by in situ produced photons (SL), others by collisions with hot species from the collapsing bubbles, others by the produced radicals (e.g. OH°). However, particular quenching conditions also exist under ultrasound, by sonolytical products and by collisions with hot species at the bubble interface. We showed that under proper conditions, the uranyl ion can be excited by SL and exhibits ultrabright sonoluminescence even in relatively diluted solutions.¹ Besides, we determined, in the framework of the LEA SONO (collaboration with MPI-Potsdam), the conditions in which luminol can be excited (sonochemiluminescence) by OH° radicals produced by a single cavitation bubble.²

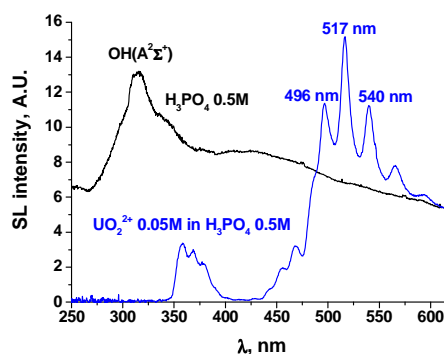


Figure 1: Photograph of 0.031M UO_2^{2+} sonoluminescence in $0.5\text{M H}_3\text{PO}_4$ at 203kHz under argon flow, $LP = 63\text{W}$, $T = 10^\circ\text{C}$, exposure time 30 sec, and sonoluminescence spectra of $0.5\text{M H}_3\text{PO}_4$ and 0.05M UO_2^{2+} in $0.5\text{M H}_3\text{PO}_4$ at 203kHz , $LP = 61\text{W}$, $T = 10^\circ\text{C}$, Ar.

1 Pflieger, Rachel; Cousin, Virginie; Barré, Nicole; Moisy, Philippe; and Nikitenko, Sergey I., "Sonoluminescence of Uranyl Ions in Aqueous Solutions" in Chemistry – a European Journal (2012), 18(2), 410-414

2 Brotchie, Adam; Schneider, Julia; Pflieger, Rachel; Shchukin, Dmitry; Moehwald, Helmuth, "Sonochemiluminescence from a Single Cavitation Bubble in Water", in Chemistry-a European Journal (2012), 18(36), 11201-11204

Mechanisms and applications of sonochemical reduction of noble metals

T. Chave, N.M. Navarro and S.I. Nikitenko

S. Nitsche (CiNAM, Marseille), A. Ayrat (IEM, Montpellier), P. Lacroix-Desmazes (ICG-Montpellier)

Noble metal nanoparticles have been widely studied especially for their unique size-dependent properties. Several metals have drawn the attention like gold, palladium or platinum which can be found in many applications such as catalytic converters or industrial processes. Platinum nanoparticles (NPs) can be prepared by Pt^{IV} or Pt^{II} reduction with a large array of synthesis routes in the presence of templates, stabilizers, or surfactants. However, surfactants or amphiphilic polymers adsorbed at the surface of NPs would modify their catalytic activity.

Initially focused on platinum, we reported the design of a synthetic route for monodispersed NPs in pure water without any templates or capping agents using ultrasonic irradiation at 20 kHz¹. This study provided new insights on the sonochemical reduction of Pt^{IV} at low ultrasonic frequency in pure water and under Ar/CO atmosphere but also in presence of formic acid under Ar. The obtained results confirmed that even in pure water the reduction of Pt ions can be triggered by in situ formed hydrogen but the reaction remains incomplete even after several hours due to the steady formation of oxidizing species under ultrasonic irradiation namely OH radicals and H₂O₂ accumulated in solution. Addition of only 10% of CO in the gas phase leads to an effective scavenging of OH^o radicals and also contributes to the direct reduction of Pt ions. Similar results can be obtained in presence of 3M HCOOH. Carbon monoxide or formic acid ability to reduce platinum ions at room temperature is enhanced due to the local heating in the liquid shell surrounding the bubble during its collapse. In these conditions the sonochemical reduction at room temperature could be observed within few hours and lead to the formation of metallic Pt particles within the range of few nanometers (Fig. 1a). This procedure can be applied in various media and is also compatible with a large array of experimental conditions. In fact the deposit of platinum nanoparticles was achieved on several supports such as metal oxides (TiO₂, CeO₂...) but also on thermal sensitive materials like polystyrene beads (Fig. 1b). Pt catalyst activity prepared under ultrasonic irradiation was assessed with oxalic acid degradation in nitric media and show similar to better activity compared to catalysts made by incipient wetness impregnation with hydrogen reduction in temperature. Finally, homogenous dispersion of Pt nanoparticles on different supports can be obtained by sonochemical synthesis under Ar/CO atmosphere in water and can be of great importance to avoid subsequent aggregation processes and possible loss of catalytic activity.

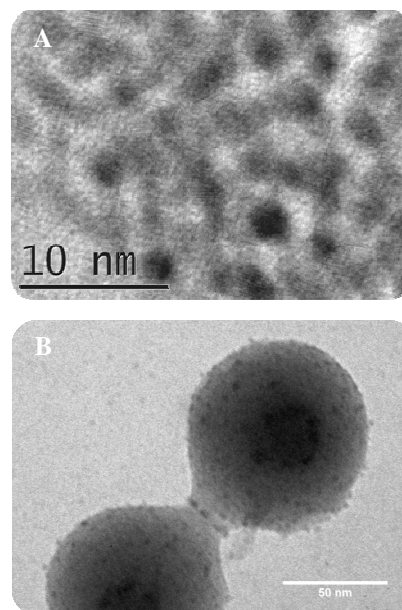


Figure 2 : TEM pictures of Pt NPs obtained in pure water under Ar/CO atmosphere and 20 kHz ultrasonic irradiation in homogenous media (A) and deposited on polystyrene particles (B: scale bar is 50 nm).

¹ Chave, Tony; Navarro, Nathalie M.; Nitsche, Serge; Nikitenko, Sergey I.; "Mechanism of Pt^{IV} Sonochemical Reduction in Formic Acid Media and Pure Water" in Chemistry - A European Journal (2012), 18, 3879-3885.

Catalytic dissolution of ceria under mild conditions

M. Virot, T. Chave, D. Horlait, N. Clavier, N. Dacheux, J. Ravaux, S. I. Nikitenko

The dissolution of ceria is studied through a catalytic reduction process involving platinum nanoparticles in mild conditions at near ambient temperature. The deposition of platinum nanoparticles is made by sonication (Ar, 18 W.cm⁻², 20 kHz), and further dissolution is studied as a function of different parameters such as stirring, sonication, dissolution media, and temperature. The dissolution is evaluated using UV-Vis spectrophotometry, ICP-AES, and SEM. The quantitative dissolution of ceria can be performed in HNO₃ - HCOOH - [N₂H₅][NO₃], [HNO₃] - [N₂H₅][NO₃] or H₂SO₄ - HCOOH mixtures at 40°C. Nevertheless, it is shown that the combined use of ultrasound with nitric media in the presence of platinum nanoparticles can lead to passivating phenomena resulting in a decrease of the dissolution rate.

Catalytic dissolution of CeO₂/Pt material offers a simple and non-expensive route to separate cerium and platinum potentially suitable for catalysts recycling. Furthermore, the observed phenomenon can have a significant impact on the chemical durability of ceria-based catalysts involved in catalytic and sonocatalytic wet air oxidation processes of organic pollutants in solutions. Finally, the dissolution of CeO₂ is often considered as a model system for the dissolution of refractory PuO₂ which is an important process in the manufacturing of nuclear materials.

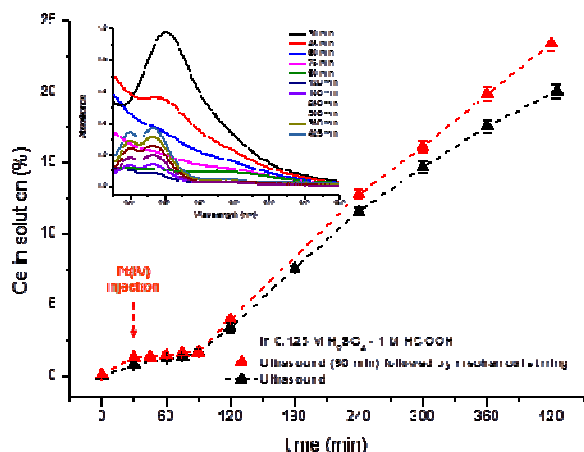


Fig. 1. Kinetics of CeO₂/Pt catalytic dissolution (40°C, Ar, SBET = 54 m²g⁻¹) under ultrasound or mechanical stirring (after reduction of Pt(IV) with ultrasound at 18 Wcm⁻²) in H₂SO₄ - HCOOH mixture. Insert shows the evolution of the UV-VIS spectra for the treated solution which corresponds to Pt(IV) reduction (~260 nm) and Ce(III) accumulation in solution (~255 nm).

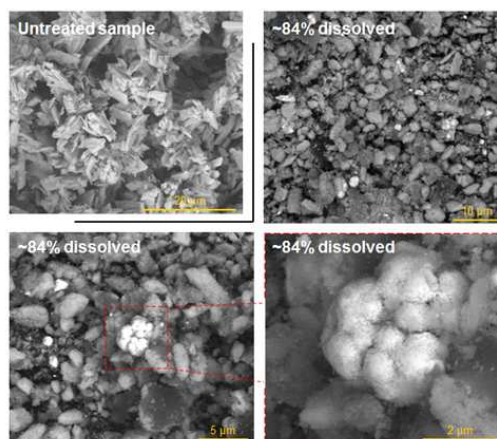


Fig. 2. SEM images of CeO₂ powder after catalytic dissolution at 40°C. Platinum is observed as bright white globular aggregates, checked with X-EDS.

M. Virot, T. Chave, D. Horlait, N. Clavier, N. Dacheux, J. Ravaux, S. I. Nikitenko; "Catalytic dissolution of ceria under mild conditions" In J. Mat. Chem. 2012, 22, 14734-14740.

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

*N. Navarro, T. Chave, S.I. Nikitenko
P. Pochon, I. Bisel (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[•] 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 H₂ and CO₂ in the gas phase as well as the trace amounts of oxalic acid and formaldehyde in the liquid phase, whereas CO and CH₄ 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-Tropsch hydrogenation of carbon monoxide.

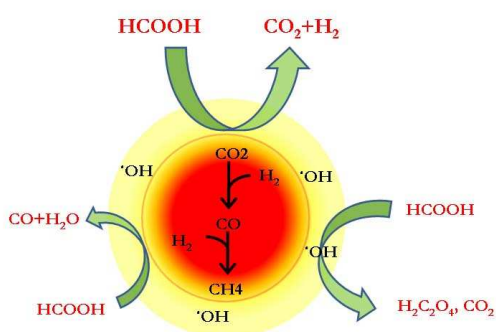


Fig. 1: Mechanism of HCOOH sonochemical degradation.

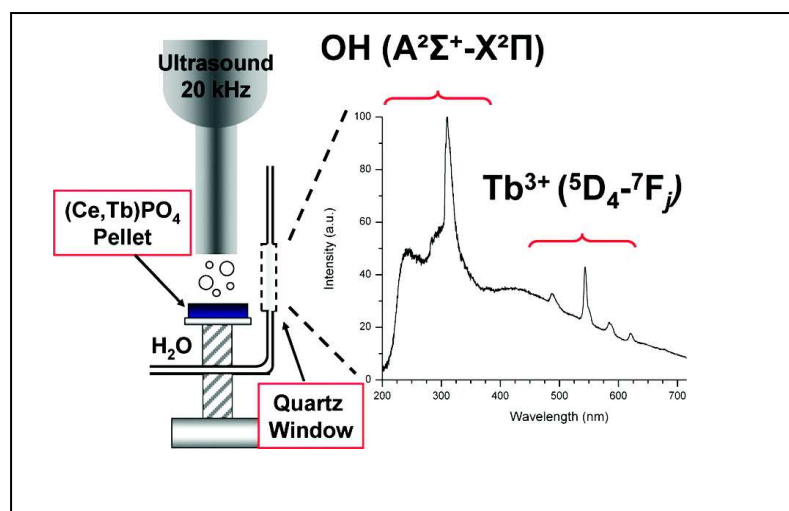
Sonochemically driven Fischer-Tropsch hydrogenation of CO causes formation of methane and formaldehyde as by-products of HCOOH degradation. Finally, we found the catalytic decomposition of sonochemically formed H₂O₂ on the surface of titanium particles originated from the cavitation erosion of the ultrasonic 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, 2011, 115, 2024-2029

Sonoluminescence of Tb(III) at the extended solid-liquid interface

M. Viot, R. Pflieger, J. Ravaux, and S.I. Nikitenko

For the first time, acoustic cavitation was used as a source of excitation for photoactive species contained in an extended solid phase. Spectroscopic measurements performed during the sonication of $(\text{Ce}_{0.9}\text{Tb}_{0.1})\text{PO}_4$ sintered pellets with 20 kHz power ultrasound in cooled water under argon showed the Tb(III) light emission resulting from ${}^5\text{D}_4\text{-}{}^7\text{F}_j$ f-f transitions. The emission spectra were measured as a function of the focus within the cavitation zone, as a function of the distance between the pellet and the ultrasonic horn, or using sonoluminescence quenchers (air or *tert*-butanol). Bubbling of air into the sonicated water presaturated with argon results in a dramatic decrease of SL including OH^* and Tb(III). Once argon is totally replaced with air, the SL is no more observable. Although SL disappears in the presence of air, acoustic cavitation at the surface is known to still occur. Hence, this experiment supports the idea that Tb(III) emission is induced by sonoluminescence. When compared with the sonication of the pellet in argon saturated water, the addition of 0.1 M *tert*-butanol decreases dramatically the SL intensity. In addition, OH^* emission, as well as Tb(III) lines, almost completely vanishes. By contrast, new particular features appear and stand at 431, 469, 515, and 550–563 nm. These lines are attributed to the transitions $\text{d}^3\Pi_g\text{-a}^3\Pi_u$ of the excited C_2^* molecules, also called Swan bands. The large and intense peak at 431 nm was assigned to a combination of $\Delta v = +2$ of the $\text{d}^3\Pi_g\text{-a}^3\Pi_u$ Swan transition and to the $\text{A}^2\Delta\text{-X}^2\Pi$ transition of CH. The formation of C_2^* species in the sonochemical reactions is attributed to the pyrolysis of organic molecules or to their reactions with OH^* radicals inside the cavitation bubbles. Even if the total SL is decreased, the presence of Swan bands emission in our system univocally indicates that acoustic cavitation still occur in the presence of *tert*-butanol. Since Tb(III) lines disappear while acoustic cavitation still operates, this experiment definitely confirms the sonophotoexcitation origin of Tb(III) emission.



Matthieu Viot, Rachel Pflieger, Johann Ravaux, Sergey I. Nikitenko, "Sonoluminescence of Tb(III) at the Extended Solid-Liquid Interface" *J. Phys. Chem. C* 2011, 115, 10752-10756.

5 – Nanomaterials for Energy and Recycling processes

L'équipe est constituée de :

- 1 chercheur CEA responsable d'équipe (Dr. A. Grandjean),
- 2 chercheurs CEA (Dr. X. Deschanel et Dr. J. Causse)
- 1 enseignant-chercheur ENSCM (Dr. G. Toquer)
- 1 IE de l'UM2 (C. Rey)
- 5 doctorants (C. Delchet, S. El Mourabit, A. Charlot, A. Gossard, M. Coulibaly)
- 2 doctorants en co-tutelle (A. Saravia (CAD/DEC), C. Lavaud (MAR/DTCD))
- 2 post-doctorants (M. Moloney et A. Tokarev)
- 1 apprenti ingénieur (A. Bex)



Les recherches développées par cette équipe ont été construites dans le cadre décrit à la création de l'ICSM, à partir de la grande diversité d'horizon, d'expérience et d'expertise de ses membres qui ont tous fait une mutation thématique en arrivant au LNAR. Ce relatif « foisonnement » nécessaire au début a permis de faire émerger des axes de recherche propres au laboratoire. Ainsi, au cours de la période 2010-2012, l'équipe a recentré ses thématiques de recherche pour une meilleure visibilité. Le nom de l'équipe a alors été modifié (LNER) pour tenir compte de cette évolution. Durant cette période, nous avons également recruté en CDI Cyrielle Rey (ingénieur d'étude, UM2), et Jérémy Causse (CEA/DEN) est arrivé en mutation en remplacement de Frédéric Goettmann parti au CEA Marcoule favorisant ainsi une forte collaboration avec le département de Traitement et Conditionnement des Déchets.

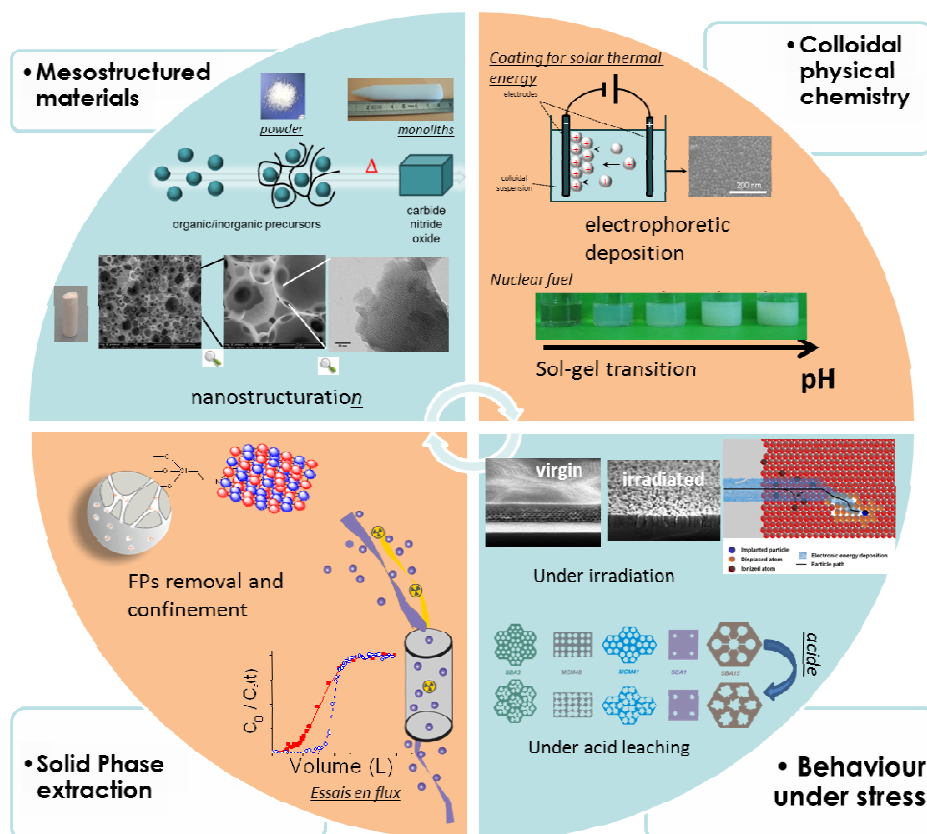
Durant cette période (2010-2012), l'équipe a accompagné la soutenance de 3 thèses: Bernard Smutek (« Organic reactions of alcohols under hydrothermal conditions », co-tutelle avec l'université de Regensburg), Aurélie Merceille (cotutelle avec CEA/DTCD, « Etude d'échangeurs d'ions minéraux pour la décontamination liquide en strontium »), et Carole Delchet (cotutelle avec UM2/ICGM/CMOS, « Matériaux hybrides pour l'extraction sélective du Césium »).

Le laboratoire développe plusieurs compétences scientifiques, techniques et d'enseignement pour répondre aux défis posés par la recherche sur les énergies dé-carbonées. Le fil conducteur de l'ensemble des thématiques de recherche du LNER est le développement de matériaux structurés à différentes échelles du point de vue de la compréhension des phénomènes mis en jeu lors des différentes étapes d'élaboration, complété par l'étude des propriétés d'intérêt de ces matériaux. Ainsi, le couple « maîtrise et compréhension de l'élaboration d'un matériau mésostructuré – propriétés physico-chimiques » définit l'ensemble des recherches développées au LNER, à la fois dans un objectif cognitif mais également dans un objectif applicatif, en lien avec les diverses collaborations industrielles (et/ou CEA) existantes ou à venir.

L'ensemble des études menées au sein de cette équipe concerne les composites présentant plusieurs structures, de nature (porosités, phase hybrides, oxydes, carbures..), de taille (nano, méso et/ou micro), et de forme (ordonnée ou amorphe) contrôlées et présentant une ou plusieurs fonctionnalité (chimie séparative, propriétés optiques renforcées, incorporation d'éléments actinides...). Par ce type de structure hiérarchique, les propriétés physiques (fissuration, tenue à l'irradiation, propriétés optiques), mais aussi chimiques (extraction, lixiviation) de ces matériaux présentent des performances hautement non linéaires par rapport à celles des matériaux massifs, rendant ainsi possible le modelage de ces propriétés en fonctions des applications souhaitées. Dans tous les cas, pour concevoir ces matériaux, nous nous efforçons d'utiliser les avancées de la chimie « douce » (sol-gel, colloïdale, émulsion, hydrothermale,...) afin d'obtenir des réactivités lentes et contrôlées permettant alors une caractérisation précise et parfois « in situ » des différentes étapes réactionnelles et donc une meilleure maîtrise du matériau final.

Les thématiques principales développées au LNER dans la période 2010-2012 sont résumées dans les pages suivantes et peuvent s'inscrire dans les 4 grands thèmes suivants:

- Le développement de différentes voies d'élaboration de matériaux nanostructurés : du précurseur (colloïde, solution, émulsion...) au matériau (poudre, couche mince ou massif) ;
- Physico-chimie des suspensions colloïdales : propriétés de la suspension et mécanismes mis en jeu lors de la mise en forme (électrophorèse, coating, transition sol-gel) ;
- Propriétés extractives des matériaux fonctionnalisés : du macroscopique (courbe de percée, procédé continu) au nanoscopique (à l'échelle de l'extractant « hybride - solide »).
- Etude de l'impact d'un stress physique (irradiation, compaction) ou chimique (milieu très acide ou très basique) sur la structure hiérarchique d'un matériau.



Mesoporous materials in the field of nuclear industry

J. Causse, F. Goettmann, X. Deschanel, C. Rey, G. Toquer, A. Grandjean

In a context of increasing global energy demand associated with high prices for classical fossil fuels and raising concerns about CO₂ emissions, nuclear power is attracting a renewed interest. Despite the recent accident in the Fukushima power plant, numerous countries maintain very ambitious nuclear programmes. The Generation IV international forum¹ (an initiative launched by the US Department of Energy in 2000 to coordinate and promote efforts to design the next generation of nuclear power plants) supports works to develop new power plant designs and innovative concepts in the nuclear fuel cycle. These new concepts aim at achieving higher levels of security and resource efficiency as well as a higher resistance towards nuclear proliferation. Because of this blossoming of new ideas, mesoporous materials, which are already widely found in applications such as catalysis, sensing and optics, are expected to make their way in the field of nuclear power production. Up to now, some (hybrid) mesoporous solids have already been investigated as solid ligands to remove actinides and fission product contaminants from liquid effluents, but also as model materials to investigate radiation defects, as possible nuclear waste disposal form and as functional materials to be placed in or close to new forms of nuclear waste matrices [1].

Our own group has been working on some of the above mentioned applications for the last four years and we are convinced that there are great potentialities for mesoporous solids in many nuclear fields:

(i) In separation chemistry for actinide extraction or for the development of selective sorbents and/or getters. Desirable improvements in this field are the enhancement of the chemical stability of both the mesopores [2] and the grafted functions (especially in very aggressive acid media) and the design [3-4] of tailored macrostructures for the materials (to be able to really employ these hybrid materials in daily processes or to make them fit to existing experimental set-ups);

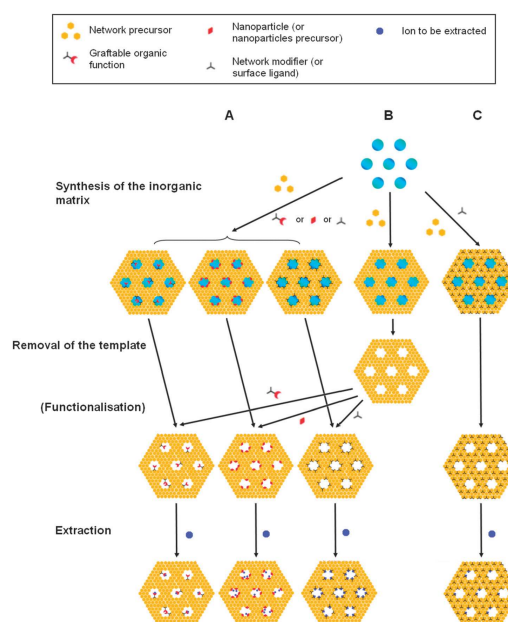
(ii) In waste management for the confinement of mobile or volatile radioactive species inside the porosity of such materials (using soft treatment to close the porosity). Here again, the development of suited macrostructures is required.

(iii) In the design of new fuel forms, which can accommodate gaseous fission product and sustain the important associated pressure increases;

(iv) In the study of irradiation defect using mesoporous solids as model materials. Here, the development of analytical techniques suited to characterize the materials after irradiation tests has to be undertaken (taking into account that for practical reasons the amount of tested material is often very low).

This team aimed at highlighting the great interest of the use of mesoporous solids in the field of nuclear

research, but also to evidence that there still is plenty of work to be done.



Schematic view of the three main ways to access functional mesoporous materials. Way A is the so-called one step way, where both the inorganic precursors and the functional groups are put together at the beginning of the synthesis. Way B is the multi step process in which the mesoporous inorganic matrix is preformed and a post functionalisation is done after wards. The third way (C) is less common and is a variation of the one pot approach. Here network modifier are added to the synthesis of the mesoporous matrix to yield an intrinsically functional material.

¹ Philippe Makowski, Xavier Deschanel, Agnès Grandjean, Daniel Meyer, Guillaume Toquer, Frédéric Goettmann, "Mesoporous materials in the field of nuclear industry", New Journal of Chemistry, 2012, 36, 531-541.

² S. El Mourabit, M. Guillot, G. Toquer, J. Cambedouzou, F. Goettmann and A. Grandjean, "Stability of mesoporous silica under acidic conditions", RSC Advances, 2012, 2 (99), 10916-10924.

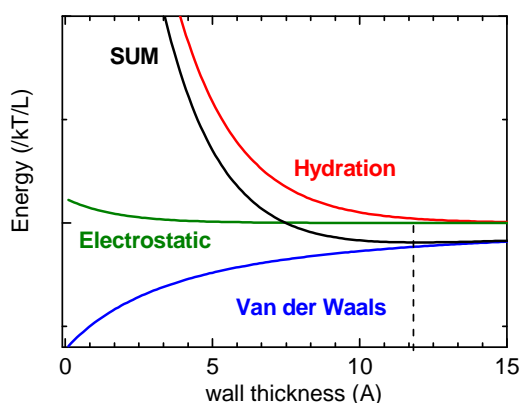
³ A. Grandjean, G. Toquer, Th. Zemb, "Wall thickness prediction in precipitated precursors of mesoporous materials", Journal of Physical Chemistry C, 115 (2011), 11525-11532.

⁴ G. Toquer, C. Delchet, M. Nemeč, A. Grandjean, "Effect of leaching concentration and time on the morphology of pores in porous glasses", Journal of non crystalline solids, 357 (2011) 1552-1557.

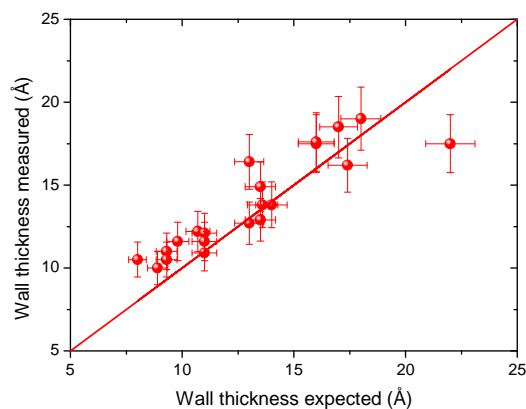
Molecular force balance allows the prediction of wall thickness of mesoporous materials

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 der 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, C, 115 (2011), 11525 - 11532.

Elaboration and partitioning chemistry properties of functionalized mesoporous materials

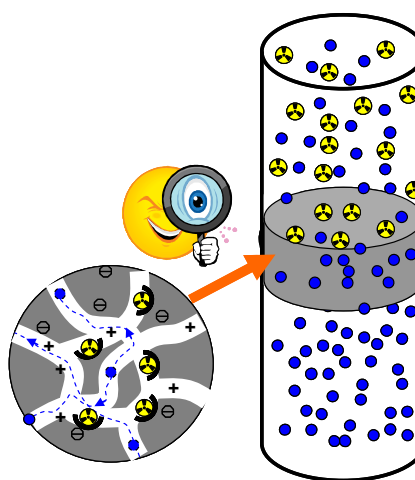
J. Causse, G. Toquer, C. Rey, H. Kaper, F. Goettmann, C. Delchet, S. El Mourabit, A. Merceille, A. Tokarev, M. Moloney, A. Grandjean

Mesoporous materials are promising materials for applications in the field of ion separation, environmental remediation, or even metallurgical purposes. Thus far, numerous hybrid mesoporous solids have been investigated as “solid ligands”, particularly for extracting heavy metal cations from waste fluxes. For example concerning the extraction of uranium (or rare earth metals) from new ores, less concentrated, feed stocks, we studied the use of mesoporous silica or carbon functionalised with specific ligand.

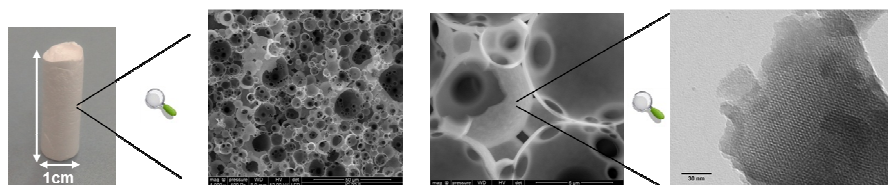
We have also proposed functionalised mesoporous materials for decontamination processes (ruthenium¹, or for cesium²⁻³). Indeed, numerous processes from nuclear facilities (fuel processing, power plants, laboratories, remediation or removal and others) generate important volumes of radioactive effluents which should be treated in order to minimize their impact on environment. Among those, radioactive cesium and strontium isotopes are ones of the most abundant fission products of uranium and have to be removed. Recently we have proposed a new approach to an efficient and selective extraction of Cs⁺ ions from pure water, or saline water enriched with ¹³⁷Cs⁺ by using porous silica- or glass-based nanocomposites containing Prussian blue type nanoparticles, Me²⁺/[Fe(CN)₆]³⁻ (Me = Co, Cu or Ni) covalently linked and homogeneously distributed into the matrix pores².

The kinetics of cesium sorption is faster and the sorption capacities per gram of metal hexacyanoferrate are higher in the case of the nanocomposites compared to the bulk Prussian blue analogues. This fact may be attributed to the high surface area of the Prussian blue nanoparticles in the case of nanocomposites. Moreover the nanocomposite materials also present a high selectivity to Cs⁺ comparable to the bulk materials even in the presence of high concentration of sodium in saline water. In case of strontium removal, sodium nonatitanate - a layered material that contains exchangeable sodium ions between layers- and Zeolite A - an aluminosilicate structure also with exchangeable sodium ions -are known to selectively trap strontium ions⁴⁻⁵. We have compared these two materials and shown that sodium nonatitanate has good decontamination properties for solutions with low calcium content and is only slightly affected by the presence of sodium. Conversely, zeolite is not affected by the presence of calcium, but its sorption properties decrease in solutions with a high sodium content. We have also proposed the used of novel material: a macroporous zeolite A monolith for efficient removal of Sr²⁺ ions from salty aqueous solutions in continuous flow process. This monolith shows high efficiency and selectivity for the in-flow treatment of radioactive water and possesses a decontamination capacity higher in comparison to batch processes⁶.

We have therefore shown the great potential of monolithic materials for applications in separation chemistry. Thus, we are developing recently multiscale porous monoliths from emulsion templates (as shown in the sketch below), with macro- and mesoporosity. This synthesis route is very interesting.



For instance, the sharp control of the shearing used in emulsification process allows to tune the size of macroporosity. Moreover, the understanding of the mechanisms involved in the synthesis allows us to consider the incorporation of selective extractants (organic or inorganic) within the porosity of these monoliths. The location of the active function depends on the chosen synthesis route. It could be either within the mesoporosity or the macroporosity. The latter is especially fitted for inorganic functionalization. This point is currently under study and is a prospect for this project.



Emulsion templated silica monoliths from various observation scales

- ¹ A. Tokarev, A. Grandjean, Y. Guari, J. Larionova, R. Pflieger, C. Guérin, *Journal of Nuclear Materials*, 400 (2010) 25-31.
- ² C. Delchet, A. Tokarev, X. Dumail, G. Toquer, Y. Barré, Y. Guari, Ch. Guérin, J. Larionova, A. Grandjean, **“Extraction of radioactive cesium using innovative functionalized porous materials”** *RSC Advances*, 2 (2012), 5707-5716.
- ³ A. Grandjean, J. Larionova, Y. Guari, Y. Barré, **« Matériau solide nanocomposite a base d'hexa et d'octacyanomattalates, son procédé de preparation et procédé de fixation de polluants minéraux le mettant en œuvre. »** FD11351. N° d'enregistrement FR 09/53379. Numéro de publication FR 2945756.
- ⁴ A. Merceille, E. Weinzaepfel, Y. Barre, A. Grandjean, **“Effect of the synthesis temperature of sodium nonatitanate on batch kinetics of strontium-ion adsorption from aqueous solution”**, *Adsorption*, (2011) 17, 967-975.
- ⁵ Aurélie Merceille, Evelyne Weinzaepfel, Yves Barré, Agnès Grandjean, (2011); **“The sorption behaviour of synthetic sodium nonatitanate and zeolite A for removing radioactive strontium from aqueous wastes”**, *Separation and Purification Technology*, 96 (2012), 81-88.
- ⁶ A. Sachse, A. Merceille, Y. Barré, A. Grandjean, F. Fajula and A. Galarneau, **“Macroporous LTA-monoliths for in-flow removal of radioactive strontium from aqueous effluents: Application to the case of Fukushima”** - *Microporous and Mesoporous Materials*, 164 (2012) 251-258.

Colloidal Physical chemistry

Application to nanoparticle electrophoretic deposition and nanostructured materials as simulating nuclear fuel

A. Charlot, X. Deschanel, A. Gossard, A. Grandjean, G. Toquer

This theme deals with controlled destabilization (under external or inherent forces) of initial stable colloidal dispersion towards the formation of nanostructured material associated with specific properties. In this way, two different main studies are currently in progress: The first one is focused on stable charged ceramic nanoparticle dispersion which is electrodeposited on substrate with tunable thickness. The final aim is to obtain a nanostructured film for controlled reflectance properties as a simulating selective optical material. The second one concerns the oxide mixtures (of nuclear interest) based on colloidal sol-gel transition. We focus more precisely on the kinetic condensation of colloidal oxide mixtures into gel to understand and predict their gel point. Afterwards, these systems will be transposed to nanocasting step by templating initial stable colloidal dispersion in order to obtain nanostructured hybrid materials as simulating nuclear fuel.

Nanoparticle electrophoretic deposition

Electrophoretic deposition (EPD) has been an attractive technique to obtain uniform films of high thickness (several microns) on large surface area substrates. In particular, it has been shown that EPD is an important tool for the fabrication of wide range of materials [1]. Nanoparticle electrophoretic deposition (NEPD) method is developed here to understand the mechanisms and the kinetic rate deposition of thin film (several nanometres) based on ceramic nanoparticles (SiO_2 , ZrO_2 , SiC , TiO_2 ...). The coating on the electrode surface is based on the migration of charged particles in a polar medium under an electric field (see figure a). This step implies necessary some physical-chemical conditions in order to reach both an efficient electrophoretic mobility (high Zeta potential) and a monodisperse system (studied by SAXS or DLS). Nanoparticles at the vicinity of the working electrode are expected to be sufficiently fixed due to attractive Van der Waals interactions. Further, nanoparticles coagulate and the rate of deposition which depends mainly of the nanoparticle concentration, deposition time and electric field magnitude, is studied *in situ* by quartz crystal microbalance. During NEPD, the electric field strength is the driven force promoting particle packing, affecting thereby the film density and the final thickness. Note that the drying process at post-deposition seems also to be a crucial step for the film adhesion behaviour. The composition of the films as well as the amount of the deposited material are analysed by X-film software from MEB measurements. Selective optical properties are analysed by coupling these latter with Fourier transform Vis-IR spectroscopy measurements.

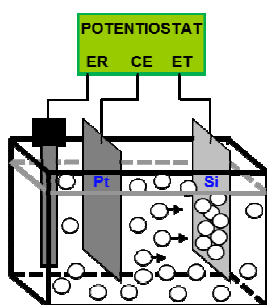


Figure a: three electrodes device for nanoelectrophoretic deposition

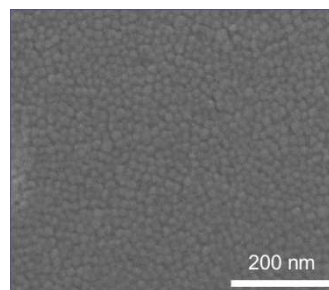


Figure b: SiO_2 nanoparticles electrodeposited on Pt substrate.

Nanostructured materials as simulating nuclear fuel

The technology process of nuclear fuel U-Pu (MOX type) or transmutation target is currently based on oxide powders converted into green pellets and then by sintering them in reductive area at high temperature (1700°C) into pellets. Initially, one way to obtain at the micrometric scale some mixed oxide is to grind together uranium oxide (UO₂) and plutonium oxide (PuO₂) powders before to press into pellets (dry mixing process). A second way at the molecular scale (co-precipitation process) consists of the conversion of uranyl nitrate and plutonium nitrate (in nitric acid) mixture by base and thermal treatment into a composite dioxide powder. The major drawback is the powder radioactive dust formation during all these processes. Consequently, through these processes, the transmutation target material or advanced nuclear fuel having high radioactive actinide elements such as ²³³U, ²⁴¹Am, ²⁴²⁻²⁴⁸Cm cannot be then considered. Thereby, an innovating way is to explore a powder free synthesis of oxide mixture based on colloidal sol-gel transition in order to obtain mesoporous hybrid materials. Several composite gels have already been investigated starting from colloidal zirconia [2] (Zr is simulating U) and recently colloidal thorium oxide (Th is simulating better U than Zr). More precisely, Zirconium hydrolysis occurs at low pH (≈3) followed by a rapid precipitation of oxy-hydroxide. A specific complexant as acetylacetonate is used in order to control the chemical surface of formed colloid and shift also the optimal pH for the condensation. By adjusting the physicochemical compounds, the kinetic of condensation and thus the sol-gel transition are well controlled. Note that Zr as inactive element has a structure able to integrate elements with III and IV oxidation degrees which permits to obtain sol composite as for example Zr-Ce (simulating Pu) or Zr-Nd (simulating Am). The gel point (main key parameter) of our systems is analyzed by rheology coupled with SAXS or DLS measurements. The upper step is to template these systems either by internal (impregnation of sol into a mesoporous material) or external (by using soft polymeric spheres as seen on figure d). After removal of the template, the final step is to fill the obtained mesoporous material (*e.g.* ZrO₂, ThO₂, UO₂) by colloidal sol actinide as Am, Cm to finally reach a nanostructured composite material as simulating nuclear fuel.



Figure c: sol-gel transition

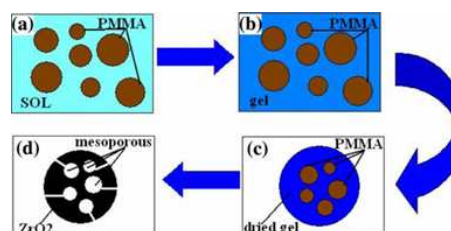


Figure d: soft templating from [3]

[1] Zhitomirsky I., *Advances in Colloid and Interface Science*, 279–317, 2002

[2] Lemonnier S., et al., *Dalton Transactions*, 2254-2262, 2010.

[3] Guorong D., et al., *Nanoscale Research Letters*, 118-122, 2008.

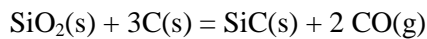
Soft chemistry routes for the synthesis of carbides

X. Deschanel, D. Héroult*, G. Arrachart, A. Saravia, O. Fiquet**, S. Szenknect
*Centrale Marseille, Aix Marseille Université, CNRS, iSm2 UMR 7313, 13397, Marseille, France
**CEA-Cadarache, DEC/SPUA/LCU, 13108 St-Paul Lez Durance

Soft chemistry routes are used for the production of carbide powders¹⁻². In a first, two approaches (colloidal and molecular routes) were compared in terms of temperature synthesis, microstructural characteristics, for the synthesis of silicon carbide. In a second step, these methods have been implemented for the synthesis of other carbides such as zirconium, titanium and uranium carbides.

Synthesis of carbide powders

Two different routes are used for the production of silicon carbide powders. The first, called the “colloidal route”, is inspired by methods used by H-P Martin³ and consists of the carboreduction of colloidal silica (nanometric or micrometric powders) by sugar. The second route, called the “molecular route”, uses a molecular chemistry approach, based on the immobilization of sugar derivatives in silica. Both synthesis routes use the same carbon source (carbohydrate) to achieve the carbothermal reduction of the silica depicted by the following equation:



In both cases, □-SiC powders with a high yield of submicrometric particles were successfully synthesized in the temperature range between 1300 and 1550 °C (Fig. 1 and 2).

The colloidal route was successfully applied to the synthesis of zirconium and uranium carbide. This last point is done in collaboration with a laboratory of CEA Cadarache (DEC/SPUA/LCU).

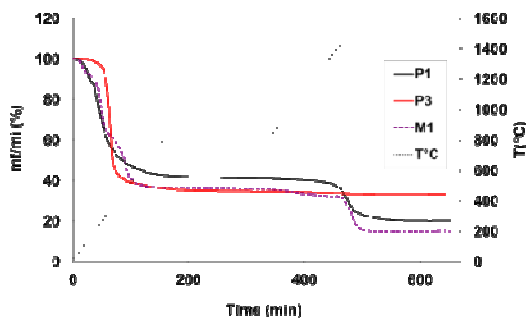


Figure.1: TGA curves (in argon) of precursors P1 (fumed silica + sucrose C/Si=3.6), P3 (fumed silica + mannitol C/Si=3.6), M1 (molecular route, C/Si=8)

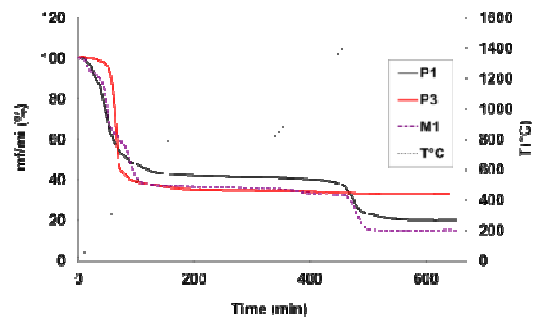


Figure 2: SiO₂ nanoparticles electrodeposited on Pt substrate

Characterization of the carbides

The powders obtained by the two routes exhibited a mesoporous structure. The structure of these materials was composed of grains of carbides embedded in a matrix of carbon (Fig. 3). Their characteristics depend on the amount of residual carbon, and the mesoporosity is located within the carbon matrix surrounding the carbide grains (Fig. 4). The largest surface area, 722 m²/g, was measured for a sample synthesized via the molecular route. A mechanism related to the release of the CO gas produced during the carbothermal reduction was invoked to explain the evolution of the surface area versus the volume fraction of residual carbon.

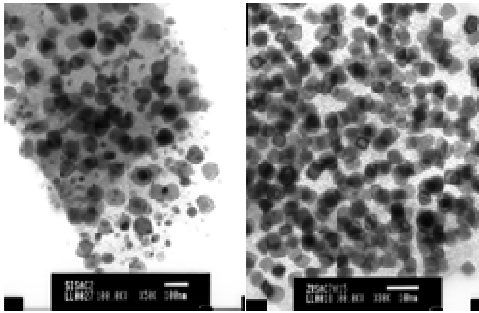


Figure 3: TEM observations of powders pyrolyzed at 1550°C C/M=24, a) P1-type (SiC+C), b) P3-type (ZrC+C).-

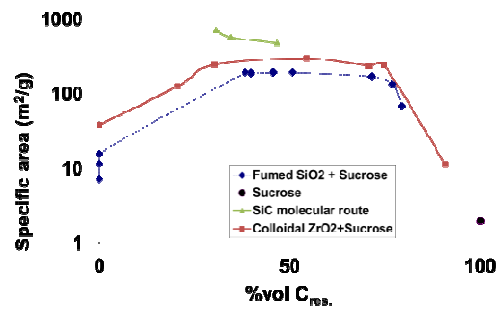


Figure 4: S_{BET} of precursors P1, P2, P3, P4 pyrolysed at 1550°C versus volume fraction of residual carbon. Specific surface area of pyrolyzed sucrose is 2 m²/g.

¹ X. Deschanel, M. el Ghazzal and al., "Synthesis of carbide compounds derived from colloidal oxide and carbohydrate", Progr. Coll. Polymer Sci., 137, (2010), 47-52.

² X. Deschanel and al., "Comparison of two soft chemistry routes for the synthesis of mesoporous carbon/beta-SiC nanocomposites", submitted to J. of Mater. Sci.

³ H-P Martin, E. Müller, Y. Knoll and al., "Silicon carbide derived from silica sol and sugar", J. Mater. Sci. Lett., 14, (1995) 620-622.

Irradiation of mesoporous silica under ionic irradiation

X. Deschanel, S. Dourdain, A. Grandjean, C. Rey, G. Toquer

The objective of the study is to investigate how the damages caused by ions irradiation affect the structure of mesoporous silica. For this purpose, various mesoporous silica samples (Vycor glass and SBA15) were irradiated by swift ions (H, Ar, Xe). It is well known that mesoporous silica is sensitive to damages caused by ions having high electronic stopping power. Such damages result in the formation of amorphous tracks and may give rise to macroscopic deformation leading to the shrinkage of the mesoporosity into Vycor glasses. This phenomenon has been observed by Klaumünzer [1]. Preliminary analyses obtained on vycor glasses indicate a change in the mesoporous structure under irradiation. Their specific surface area decreased from about 10%. No significant change was observed on the pore diameter (Figure 1).

X-ray reflectivity measurements before and after irradiated samples were made on mesoporous silica coated on Si substrate (Figure 2). Structural parameters can be obtained from the Kiessig oscillations observed on these measurements. In all cases, irradiations involve an increase in porosity and restructuring of the mesoporous structure. SEM observations presented in the Figure 3 are consistent with these results. The holes observed on the surface of the samples after irradiation may be the result of the tracks produce by ions bombardments. Indeed, under these conditions of irradiation the electronic stopping power (dE/dx) is greater than the energy threshold leading to the formation of track in silica.

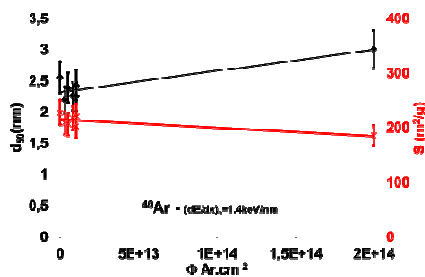


Figure1: Evolution of the mesoporous structure of the samples versus fluence (pore diameter and specific area)

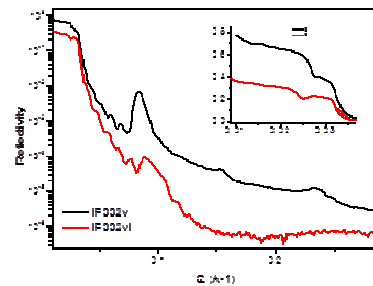


Figure 2: Reflectivity measurement on SBA15 (Black curve : non irradiated, Red Curve : irradiated)

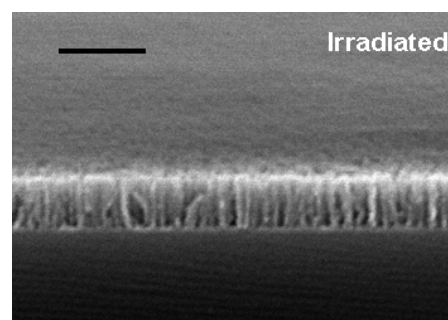
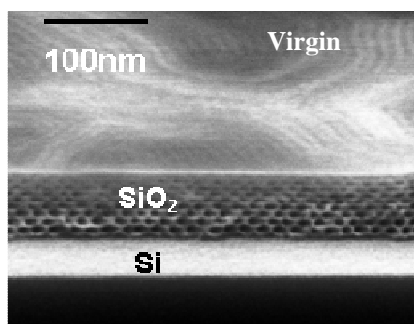


Figure 3: SEM observations of SBA15

Here, the development of analytical techniques suited to characterize the materials after irradiation tests, and the elaboration of well-defined materials and adapted to these characterizations is under study in this team. Note that for practical reasons the amount of tested material is often very low.

[1] S. Klaumünzer, Nucl. Instr. And Meth. In Phys. Res. B, 166 (2000) 459.

[2] S. Dourdain, X. Deschanel, G. Toquer, C. Grygiel, I. Monnet, S. Pellet-Rostaing, A. Grandjean, "Radiation damage of mesoporous silica thin films monitored by X ray reflectivity and Scanning electron microscopy" Journal of Nuclear Materials, 427, (2012) 411.

Specific Characterisation of nanostructured materials

C. Rey, A. Grandjean

The ICSM possess various pieces of equipment for the characterisation of new and novel materials. The management of these equipments is undertaken by a number of groups including the Laboratory of Nanomaterials for Energy and Recycling (LNER).

The LNER research group is in charge of: a gas adsorption-desorption device (BET), a high temperature thermal analyser (TGA/DTA) which can be coupled to a gas analyser. This group also manages a Carbon-Sulfur and an Oxygen-Nitrogen-Hydrogen analyser, as well as a capillary ionic chromatography device. The management of these devices includes the planning, maintenance and development of measurement methods for materials which are synthesised in all the team of the Institute.

The Gas Adsorption-Desorption device can be used to characterise the surface shapes and surface areas of adsorbents and the porosity of various nanomaterials. The example illustrated below (Figure 1) shows a nitrogen adsorption-desorption isotherm from a sample of Vycor Glass.

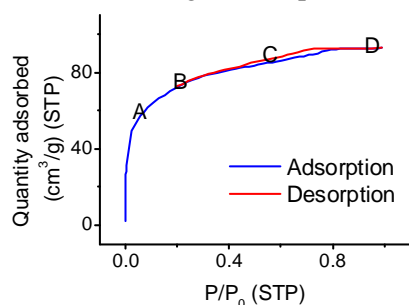


Figure 1: Nitrogen Adsorption-Desorption Isotherm of Vycor Glass (A) Microporous stage $P/P_0 < 0,05$ (B) Gas pressure increased to form a monolayer and the surface area determined using the BET method, $P/P_0 < 0,3$ (C) Gas pressure increased to form a multilayer which allows us to determine pore diameter. (D) Total adsorption on external surface

Adsorption and desorption analyses using different gases such as water vapour or krypton (for materials with low surface area) are also performed as well as micropore. In the future we plan to develop chemisorption analyses.

High temperature thermal analyses, (TGA/DTA), provides us with the ability to measure temperatures ranging from the ambient (thermocouple S, B) to as high as 2400 °C (thermocouple W).

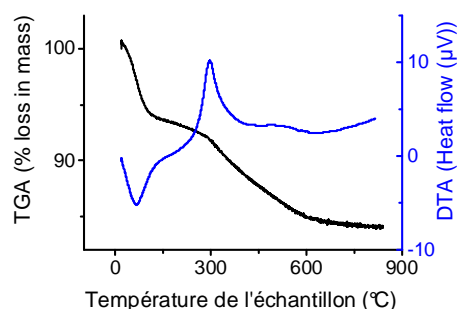


Figure 2: TGA (black line) measures the variation in the mass of a sample as the temperature is increased (i.e. 100°C and 400°C respectively). The DTA (blue line) detects transformations in the sample structure, i.e. fusion, crystallisation, etc. Recently, the LNER group has been equipped with a gas analyser which allows us to identify the emitted vapours and therefore better understand the transformation mechanisms which occurs during the thermal

Combined with a carbon and an oxygen-nitrogen-hydrogen analyser, we are also able to characterise materials functionalised with organic molecules.

Once these materials have been characterised, we then test their capacity for extraction thanks to an ionic chromatography device which can simultaneously detect the presence of cations (alkaline and earth alkaline; organic acid) and anions in solution.

The above mentioned equipment allows the LNER group to not only characterise the materials which we synthesis but also to analysis the efficiency of these materials.

Synthesis of nanoparticles using colloidal routes

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

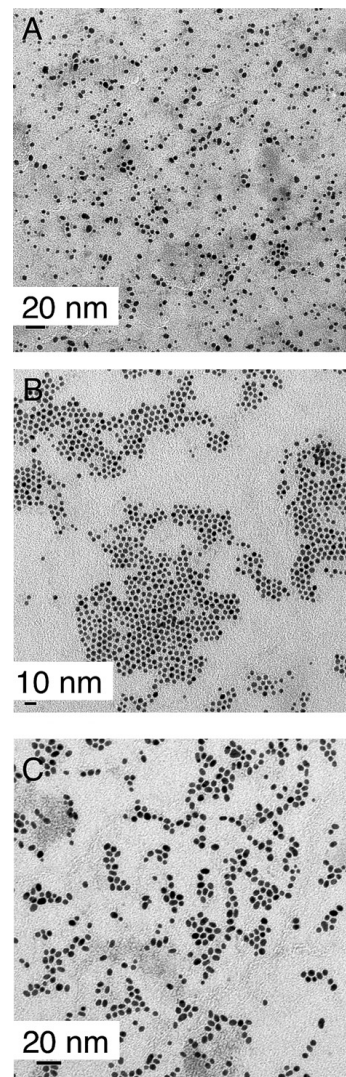
Among various synthesis procedures, the use of reverse micelles is an effective route for yielding a wide range of nanoparticles of different chemical nature, size and shape. The inner core of the reverse micelles acts as a nanoreactor and the nanoparticles are obtained by mixing two microemulsions containing 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 involved¹.

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 – Evolving interfaces in materials

L'équipe est constituée de :

- 1 Professeur des Universités, responsable d'équipe (Pr. N. Dacheux),
- 2 chercheurs CNRS (Dr. N. Clavier ; Dr. A. Mesbah à compter du 01/12/2012),
- 1 chercheur CEA (Dr. S. Szenknect),
- 4 doctorants (D.T. Costin, F. Crétaz, J. Martinez, F. Tocino).



Le laboratoire d'étude des Interfaces de Matériaux en Evolution (LIME) a pour objectif de décrire et de comprendre les phénomènes siégeant aux interfaces solide/solide et solide/liquide, aussi bien au cours d'étapes de frittage (densification) que de dissolution (ou d'altération) sous contraintes de matériaux d'intérêt pour le nucléaire du futur.

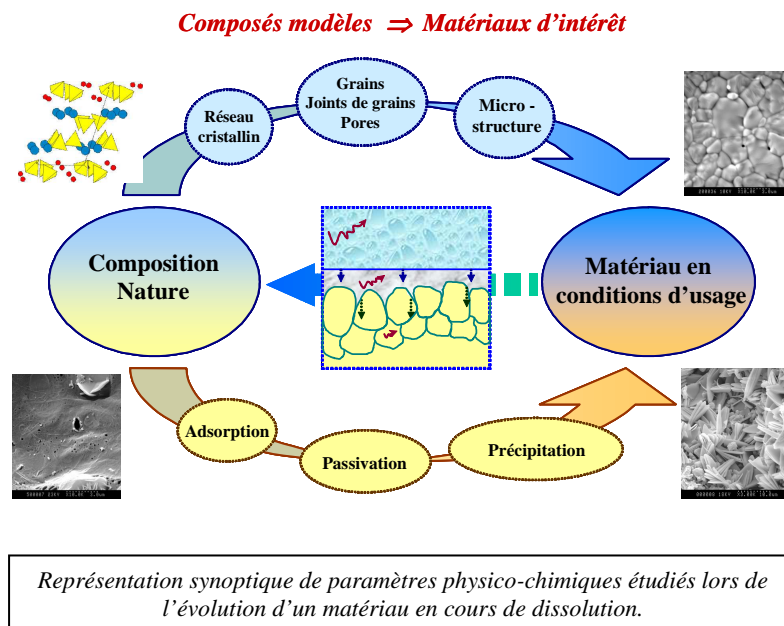
Les expérimentations relatives aux interfaces solide/solide s'inscrivent dans l'étude du frittage à travers les divers mécanismes intervenant lors de la densification d'un matériau (consolidation de l'objet, grossissement de grains, réduction de la porosité). Dans ce cadre, le couplage d'expérimentations *in situ* et *ex situ* permet non seulement d'analyser les différentes étapes de la densification et d'obtenir des données généralement uniquement accessibles par modélisation mais également d'aboutir à l'obtention de cartes de frittage (taille de grains vs. taux de densification) dans un délai très court. Il en découle une optimisation des conditions expérimentales en fonction de la microstructure désirée. Concernant l'évolution des interfaces solide/liquide, 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. En particulier, cette démarche consiste à appréhender et à comprendre les liens étroits reliant d'une part, la morphologie d'un solide et d'autre part, sa propension à se dissoudre ou s'altérer.

Dans ce but, la première étape de l'étude consiste à développer ou optimiser les conditions de synthèse de combustibles modèles ($\text{Th}_{1-x}\text{U}_x\text{O}_2$, $\text{Th}_{1-x}\text{Ce}_x\text{O}_2$, $\text{U}_{1-x}\text{Ce}_x\text{O}_2$, $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$, $\text{Th}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$, ...) en privilégiant l'usage de précurseurs cristallisés oxalate, hydroxyde, ... de manière à améliorer l'homogénéité, la réactivité et la capacité de frittage des oxydes préparés à haute température. Les étapes de conversion des précurseurs en matériaux oxydes ultimes sont alors examinées à travers le couplage de nombreuses techniques (thermiques, diffraction, microscopiques, spectroscopiques). Il en découle l'identification des transformations et des intermédiaires réactionnels successifs intervenant lors de la conversion. Plusieurs structures cristallines ont ainsi été précisées. A titre d'exemple, pour les solutions solides $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$, 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 des oxydes mixtes $\text{Th}_{1-x}\text{U}_x\text{O}_2$, $\text{Th}_{1-x}\text{Ce}_x\text{O}_2$ et $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ 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. Par ailleurs, des premières expériences mettant en œuvre l'observation *in situ* des phénomènes de densification ont été menées par microscopie électronique à balayage environnementale à haute température (HT-MEBE). Des données inédites relatives à la cinétique de croissance granulaire ou à la mobilité des joints de grains ont ainsi été déterminées pour CeO_2 et ThO_2 jusqu'à 1400°C. De plus, le couplage de ces résultats avec ceux issus de l'analyse dilatométrique a permis de construire rapidement des trajectoires de frittage permettant *in fine* de contrôler la microstructure des matériaux céramiques considérés.

Des expériences de dissolution ont été entreprises en conditions de faible ou de fort renouvellement. Pour les solutions solides $\text{Th}_{1-x}\text{U}_x\text{O}_2$, une étude multiparamétrique a été développée afin d'évaluer l'influence relative de chaque paramètre sur la durabilité chimique des matériaux. A ce titre, l'amélioration de la distribution 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 étroits 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. Par ailleurs, la progression de la réaction de dissolution est généralement associée à une modification significative de la surface réactive. Dans le but de corriger le biais en découlant, une méthode de suivi *in operando* de cette évolution par ESEM a été développée.



Concernant les solutions solides $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$, 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 $\text{Th}_{1-x}\text{U}_x\text{O}_2$, les tests de dissolution menés sur les composés $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ ont montré 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 $90-100 \text{ kJ.mol}^{-1}$) qu'à travers la saturation des sites actifs de surface au-delà de 2M en acide nitrique. Ces travaux initiés au cours des thèses de Laurent Claparède (Bourse CTBU, ICSM – DRCP/LC2A, 2008-2011) et de Denis Horlait (Bourse MENRT sur thème prioritaire, ICSM, 2008-2011) sont actuellement poursuivis dans le cadre de la thèse de Florent Tocino (Bourse CTBU, ICSM – DRCP/LED, 2012-2015). Un aspect particulier du travail consiste à étudier le rôle des réactions rédox à l'interface solide/solution à partir de la comparaison des systèmes $\text{An}_{1-x}\text{Ce}_x\text{O}_2$ et $\text{An}_{1-x}\text{Ln}_x\text{O}_{2-x/2}$ (An=Th,U) et $\text{Th}_{1-x}\text{U}_x\text{O}_2$.

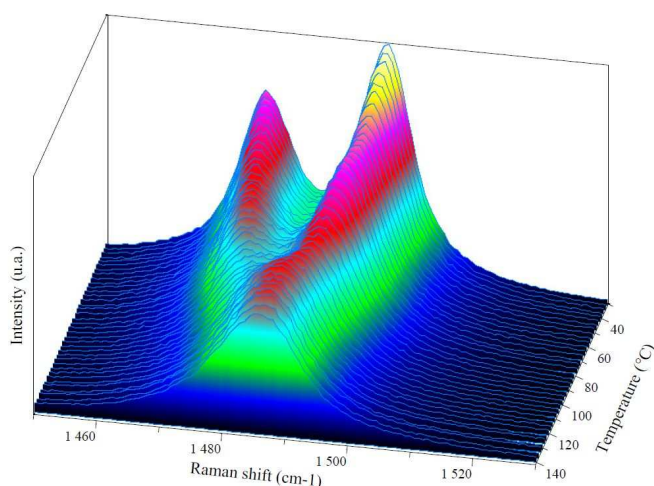
Un second axe de recherches, en lien avec l'amont du cycle, a été initié en partenariat avec le DRCP (CEA Marcoule) dans le cadre de deux thèses (Dan T. Costin : 2009-2012 et Fanny Crétaz : 2010-2013). Les premières études ont porté sur le système thorium – uranium – silicate, à travers la préparation de solutions solides d'uranothorite $\text{Th}_{1-x}\text{U}_x\text{SiO}_4$ en conditions hydrothermales. Des méthodes de purification des échantillons, par séparation chimique des phases oxydes $\text{Th}_{1-y}\text{U}_y\text{O}_2$ et SiO_2 présentes en tant que phases secondaires pour les forts taux d'incorporation d'uranium ont été mises au point. En revanche, les tentatives de synthèses de coffinite USiO_4 ont, à ce jour, toujours conduit à des échantillons polyphasés au sein desquels la phase coffinite est demeurée minoritaire. 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 l'ensemble de ces systèmes, 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 , $\Delta_R H^\circ$, $\Delta_R G^\circ$, $\Delta_R S^\circ$) nécessaires pour évaluer le comportement de ces phases minérales lors de leur mise en contact avec une solution. Pour le système actinide-silicate, des données ont d'ores et déjà permis d'apporter des conclusions sur la réaction « d'uranothoritisation » en fonction des conditions d'altération et de la nature des solides. Une comparaison directe entre échantillons modèles et réels a été entreprise 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 $\text{Th}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ 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 elements¹. 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 years², reliable data concerning their crystal structures and their stability range are often lacking.

A study was then focused on the system based on $\text{Th}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ 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 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 cohesion³. 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.

Finally, the transformation of anhydrous oxalate into dioxide was investigated by TGA studies and *in situ* HT-Raman in order to elucidate the possible 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, 400-406.

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 $\text{Th}_{1-x}\text{U}_x(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ solid solutions", *Inorg. Chem.*, 2010, 49, 1921-1931.

Dynamic aspects of ceramic sintering

Nicolas CLAVIER, Renaud PODOR, Johann RAVAUX, 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 as well as intergranular 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. A specific methodology was then developed, using the new opportunities offered by Environmental Scanning Electron Microscopy (ESEM) implemented with a high temperature device. It was then possible to directly observe the sintering mechanisms of ceramics at the sub-micrometer scale ¹.

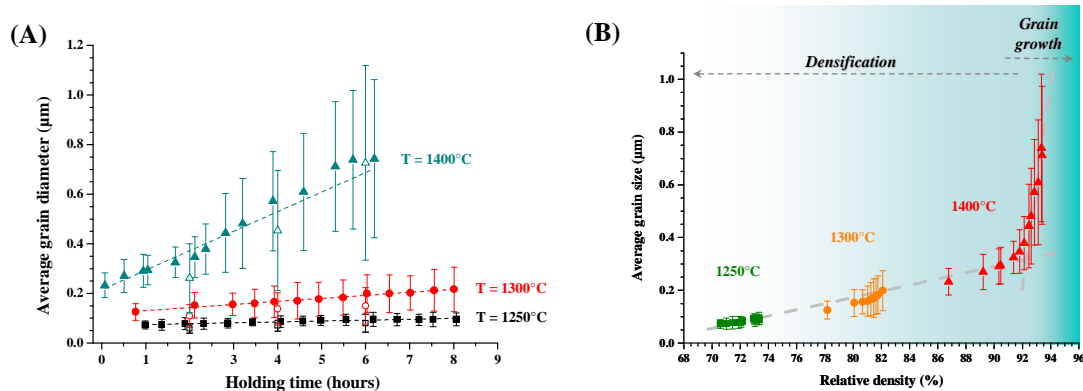


Fig.1: (A) Evolution of the average grain size during heat treatment at various temperatures in *ex situ* (open symbols) or *in situ* (full symbols) conditions. (B) Sintering trajectory of ThO₂ obtained from the HT-ESEM/dilatometry combined approach.

The CeO₂ sintering was studied directly in the ESEM chamber from 1000 to 1400°C ². The morphological modifications of a single grain population were observed for 6 to 8 hours and good quality images were recorded. Kinetic parameters were then 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. From the image series, kinetic parameters such as grain boundary velocities were also determined.

This methodology was then extended successfully to the study of ThO₂ sintering. In this case, the data determined from *in situ* HT-ESEM images (Figure 1A) was correlated to *ex situ* dilatometric measurements, and the sintering map for ThO₂ was obtained ³ (Figure 1B). On the basis of these first results, the combination of these two techniques appeared as a very promising way to control the microstructure of ceramic materials, including nuclear fuels.

1 R. Podor, N. Clavier, J. Ravaux, L. Claparède, N. Dacheux, D. Bernache-Assolant, "Dynamic aspects of cerium dioxide sintering- HT-ESEM study of grain growth and pore elimination", J. Eur. Ceram. Soc. 32 (2012) 353-362.

2 R. Podor, N. Clavier, J. Ravaux, L. Claparède, N. Dacheux, "In situ HT-ESEM observation of CeO₂ grain growth during sintering", J. Am. Ceram. Soc. 95 (2012) 3683-3690.

3 N. Clavier, R. Podor, L. Delière, J. Ravaux, N. Dacheux, "Combining *in situ* HT-ESEM observations and dilatometry: an original and fast way to the sintering map of ThO₂", Mater. Chem. Phys. doi:10.1016/j.matchemphys.2012.10.003 (2013).

Influence of structural and microstructural parameters on fluorite-type (An,Ln)O₂ mixed oxide dissolution

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Actinides mixed dioxides are currently used in PWR nuclear reactors and considered as reference fuels for several Gen III and Gen IV concepts. Moreover, they could act as matrices for the recycling of minor actinides, either directly in the reactor core or in fertile blankets. In these conditions, the consequences of the incorporation of trivalent elements, such as americium or curium (and lanthanides as surrogate elements), in the fluorite-type structure of MO₂ should be carefully assessed when dealing with key-steps of the nuclear fuel cycle, such as reprocessing. This study was then focused on the dissolution of (An^{IV},Ln^{III})O_{2-x} and (An^{IV},An^{IV})O₂ samples (An^{IV} = Th, U ; Ln^{III} = La-Yb) as model compounds for future mixed oxides fuels. Since the influence of conventional parameters such as temperature or acidity was mainly described in the literature, a particular attention was paid to structural (chemical composition and homogeneity, crystal structure...) and microstructural (crystallization state, density, pore size and distribution, ...) parameters.

On the one hand, the incorporation of trivalent lanthanides in both CeO₂ and ThO₂ matrices was found to drastically increase their normalized dissolution rates, due to the formation of oxygen vacancies weakening the crystal structure¹ (Figure 1). As instance, the normalized dissolution rate of Ce_{1-x}Ln_xO_{2-x/2} was increased by 4 orders of magnitude when shifting from Ce_{0.9}Ln_{0.1}O_{1.95} to Ce_{0.5}Ln_{0.5}O_{1.75}². On the contrary, the nature of tetravalent cation did not induce great modifications in the chemical durability of the ceramics. Another significant effect of composition was found to arise from the cationic homogeneity of the solid solutions considered. Such effect was particularly observed for Th_{1-x}U_xO₂ samples, whose dissolution is often promoted by redox reactions involving U(IV). In these conditions, the kinetics of alteration was generally slowing down when improving the distribution of cations at the microscopic scale, namely by using wet chemistry routes of preparation³.

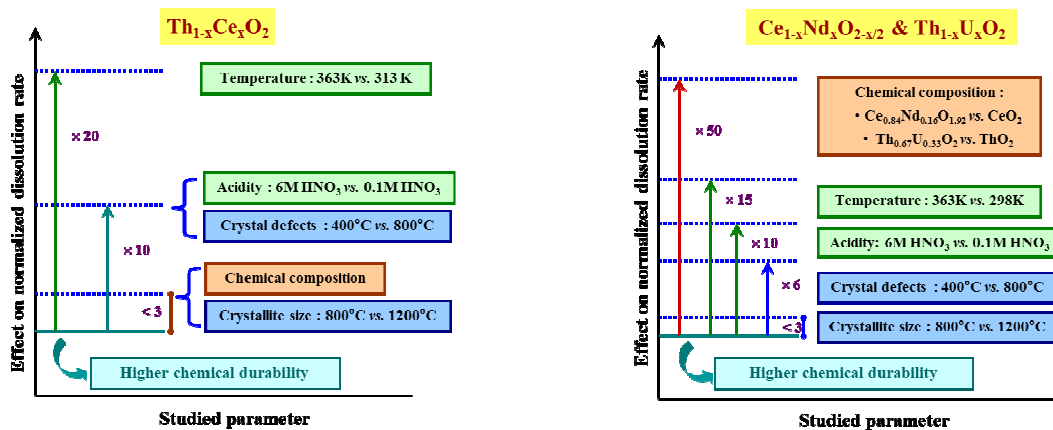


Fig. 1: Relative effect of parameters affecting oxide dissolution.

¹ D. Horlait, N. Clavier, S. Szenknect, N. Dacheux, V. Dubois, "Dissolution of cerium(IV)-lanthanide(III) oxides : comparative effect of chemical composition, temperature and acidity" *Inorg. Chem.*, 51 (2012) 3868-3878.

² D. Horlait, F. Tocino, N. Clavier, N. Dacheux, S. Szenknect, "Multiparametric study of Th_{1-x}Ln_xO_{2-x/2} mixed oxides dissolution in nitric acid media" *J. Nucl. Mater.*, 429 (2012) 237-244.

³ N. Hingant, N. Clavier, N. Dacheux, N. Barré, S. Hubert et al. "Preparation, sintering and leaching of optimized uranium thorium dioxides", *J. Nucl. Mater.*, 385 (2009) 400-406.

On the other hand, micro-structural parameters were generally found to be significant only for samples of high chemical durability, *i.e.* ThO₂, CeO₂, and derived solid solutions⁴⁻⁵. In these conditions, the crystallization state of the samples could influence the kinetics as much as the acidity of the leachate while density or grain size remain second order parameters. Nevertheless, these latter parameters must be taken into account when studying the evolution of the solid/solution interface. Indeed, ESEM observations performed *in operando* during the dissolution process allowed imaging the preferential alteration zones for several solids which can be located either within the grain boundaries, triple junctions or through intragranular corrosion pits (Figure 2). Also, it allowed pointing out the effect of surface heterogeneities on the dissolution kinetics as well as the strong evolution of the reactive surface during the dissolution of the ceramics. This information appears of main importance when working with normalized dissolution rate and led to consider limit cases for using such variables.

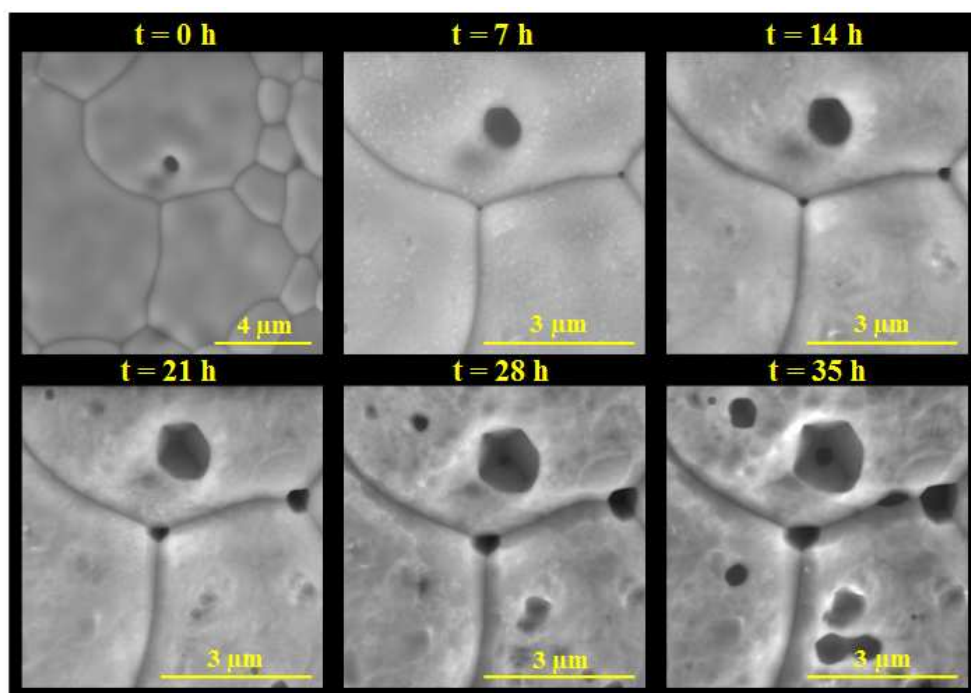


Fig. 2: *In operando* ESEM observations performed during the dissolution of Th_{0.5}U_{0.5}O₂ (2M HNO₃, T = 90°C).

⁴L. Claparede, N. Clavier, N. Dacheux, P. Moisy, R. Podor, J. Ravaux, "Influence of crystallization state and microstructure on the chemical durability of cerium-neodymium mixed dioxides" *Inorg. Chem.*, 50 (2011) 9059-9072.

⁵L. Claparede, N. Clavier, N. Dacheux, A. Mesbah, S. Szenknect et al., "Multiparametric dissolution of thorium-cerium dioxide solid solutions" *Inorg. Chem.*, 50 (2011) 11702-11714.

Thermodynamic Properties of $\text{Th}_{1-x}\text{U}_x\text{SiO}_4$ solid solutions from solubility measurements

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Secondary phases which could be formed during radwaste leaching represent important sinks for U and other radionuclides, and thus control the subsequent mobility and the ultimate distribution of the radiotoxic elements in the surrounding environment. Sites under investigations for underground repository are for the greatest part located in undisturbed clayrocks exhibiting anoxic conditions and silica-rich environment¹. Such geochemical conditions imposed circum-neutral pH and low-redox potential that favor the formation of U(IV) secondary phases after the dissolution of UO_2 matrix. Under these conditions, USiO_4 coffinite is suspected to precipitate depending on the relative stability

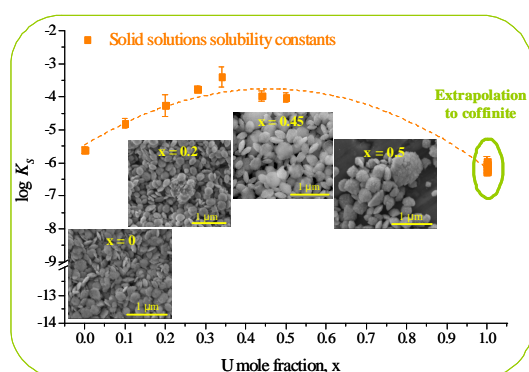


Fig.1: Variation of the solubility constant along the uranothorite series determined by undersaturation experiments at 298 K under anoxic conditions and extrapolation to coffinite.

$x=0.8$ was evidenced from XRD and EDS analyses. However, polyphased samples systematically obtained for $x \geq 0.25$ underlined the kinetic hindering linked with the preparation of uranium-rich silicates, including coffinite. A purification process was developed based on the selective dissolution of secondary phases, that led to a complete removal of the impurities (mixed oxide and amorphous silica).

Finally, a set of experiments on the dissolution of intermediate members of the uranothorite solid solution ($0 \leq x \leq 0.5$) was carried out in hydrochloric acid, at several temperatures and under anoxic conditions, that pointed out the influence of composition, pH and temperature on the normalized dissolution rates. Once the equilibrium was reached, the solubility constant of each compound was determined then allowed the extrapolation to the coffinite end-member (Figure 1). Finally, the determination of $\Delta_R G^\circ$, $\Delta_R H^\circ$ and $\Delta_R S^\circ$ made possible conclusions on the relative stability of uranothorite and uranothorianite solid solutions.

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² Amme, M.; Wiss, T.; Thiele, H.; Boulet, P.; Lang, H. "Uranium secondary phase formation during anoxic hydrothermal leaching processes of UO_2 nuclear", *J. Nucl. Mat.* 341 (2005) 209-223.

³ Costin, D.T.; Mesbah, A.; Clavier, N.; Dacheux, N.; Poinssot, C.; Szenknect, S.; Ravau, J.; Brau, H.P. "Preparation and characterization of synthetic $\text{Th}_{0.5}\text{U}_{0.5}\text{SiO}_4$ uranothorite", *Prog. Nucl. Energy* 57 (2012) 155-160.

⁴ Costin, D.T.; Mesbah, A.; Clavier, N.; Dacheux, N.; Poinssot, C.; Szenknect, S.; Ravau, J., "How to explain the difficulties in the coffinite synthesis from the study of uranothorite?" *Inorg. Chem.* 50 (2011) 11117-11126.

Dissolution of uranyl phosphates and vanadates: from synthetic analogues to natural samples

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Uranyl minerals form as secondary phases within uranium deposits represent potential new uranium resources¹ but also affect the distribution of uranium and others radionuclides and their subsequent mobility under oxidizing conditions encountered in the vicinity of nuclear waste repository settings or at sites of groundwater contamination. Due to their extremely low solubility, uranyl phosphates and vanadates are ubiquitous within uranium ore deposits and strongly affect uranium fate and transport in soils and aquifers under oxidizing conditions². Considering uranyl phosphates and vanadates as potential phases of interest for ore exploitation, it is essential to evaluate their thermodynamic properties, and to acquire reliable kinetic data in the perspective of sustainable ore treatment process development.

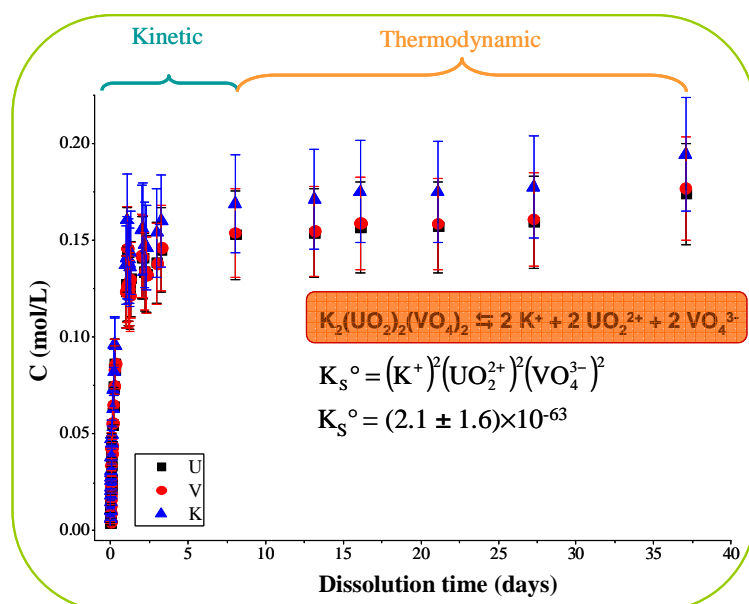


Fig.1 Evolution of elementary concentrations during the dissolution of synthetic carnotite in 1M HCl at 22°C.

Reliable measurements of the Gibbs free energy of formation of a mineral phase can be derived from solubility studies only if the mineral of interest is pure and stable under the experimental conditions. The preparation of synthetic samples is thus usually required. The congruence of the dissolution as well as thorough characterization of the raw and leached solids indicates the stability of the studied phase. Establishment of mineral-water equilibrium is demonstrated by approaching the equilibrium state from undersaturated (dissolution) and oversaturated (precipitation) conditions. This methodology was used to determine thermodynamic

data associated to relevant phases in the {P₂O₅-V₂O₅-UO₂} system. Pure and single phase autunite, Ca(UO₂)₂(PO₄)₂·2-6H₂O, torbernite, Cu(UO₂)₂(PO₄)₂·8-12H₂O, carnotite K₂(UO₂)₂(VO₄)₂·3H₂O and its phosphate analogous ankoleite K₂(UO₂)₂(PO₄)₂·6H₂O were synthesized then exhaustively characterized and finally submitted to dissolution experiments. The determination of solubility constants, K_S[°] (Figure 1) was performed in various media and at several temperatures then associated thermodynamic data (Δ_RG[°], Δ_RH[°] and Δ_RS[°]) were evaluated. The comparison of these values (especially K_S[°]) with that obtained from natural minerals will allow evaluating the behaviour of natural samples during dissolution.

¹ Cuney M., K. Kyser, "Recent and not-so-recent developments in uranium deposits and implications for exploration.", *Short Course Series* 39, 2009, Mineralogical Association of Canada Eds.

² Gorman-Lewis, D., P.C. Burns, J.B. Fein, "Review of uranyl mineral solubility measurements", *J. Chem. Thermo.*, 40 (2008) 335-352.