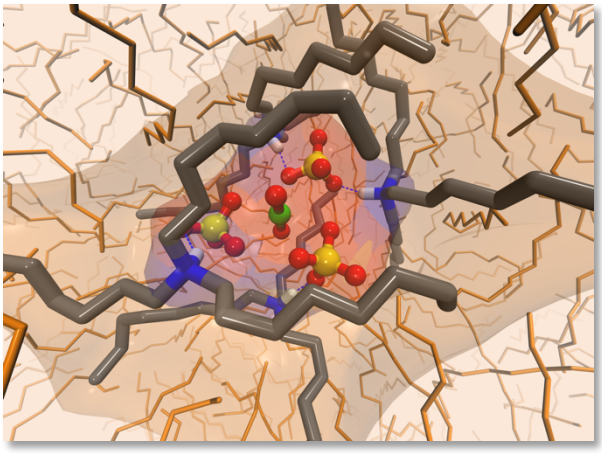
## Open PhD thesis at
## Institut de Chimie Séparative de Marcoule (ICSM), Bagnols-sur-Cèze, France
## Ecole doctorale 459 Sciences Chimiques Balard (University of Montpellier)

# Simulation of the synergetic phenomena in ionic solutions involved in the uranium extraction processes

***Starting date: October 2023***



The proposed thesis aims to **understand and quantify**, through **theoretical approaches**, the **impact of structural effects on uranium extraction performance**. In this context, the extraction of uranium from ore is classically done by a liquid-liquid extraction process using tertiary amines from sulfuric solutions resulting from ore leaching[1]. Despite its application on an industrial scale, this process still faces several problems: 1/ the selectivity of uranium extraction with respect to competing elements (zirconium, molybdenum), 2/ the need to use a phase modifier to prevent the formation of a third phase, 3/ the degradation of tertiary amines by homolytic cleavage catalyzed by vanadium in the presence of the phase modifier, and 4/ the loss of the formulated solvent by entrainment (formation of dross and evaporation).

To overcome these problems, recent studies carried out at the ICSM's Ion Separation using self-assembled Molecular systems Laboratory (LTSM) have shown the high potential of using **ionic solutions** composed of **mixtures of amphiphilic ion pairs**, including protonated trioctylamine sulfate $(TOAH^+)2SO_4^{2-}$ and protonated trioctylamine N-methyl-bis-(trifluoromethylsulphonyl)imide $(TOAH^+)NTf_2^-$: loading capacity increased by 10, selectivity to-wards zirconium increased by 4, selectivity towards vanadium increased by 30, no phase modifier, solvent loss by evaporation decreased by 20[2,3]. This very promising system, which consists of a **mixture of extractants without diluent**, also shows non-linear performances in terms of uranium and water extraction and viscosity which remain to be elucidated in order to generalize these performances to other extraction systems.

As no experimental approach has yet allowed us to fully describe the structural organization of extraction phases that can be assimilated to ionic liquids, the objective of this thesis will be to implement **molecular modelling approaches in connection with the experiments** carried out over the last few years at ICSM to characterize these solutions (EXAFS, SAXS, SANS) in order to propose models that describe the multi-scale structure of these phases (complexes, aggregates, ionic liquid structures). This approach will thus provide crucial insights into the **impact of structural effects on extraction performance**, as we have recently done for other ionic liquids[4], on the **non-linear viscosity** of these mixtures and, for the first time, on the **synergy between solutes** based on a molecular model. These results can be compared with the mesoscopic approaches developed in recent years at the ICSM's Mesoscopic Modeling and Theoretical Chemistry Laboratory (LMCT)[5].

In an attempt of **predicting the structural and dynamic properties** of these solutions on uranium extraction performances in order to **help in the choice of new and more efficient extraction systems** in connection with the themes developed at ICSM, the PhD thesis will focus on the modelling of uranium extraction in such solutions ($TOAH^+$ / $SO_4^{2-}$ / $NTf_2^-$). Depending on the progress of the project, we may also be interested in understanding the efficiency of this system with respect to uranium extraction,

[1] T. Sukhbaatar et al., Chem. Commun. 55, 7583 (2019). DOI: http://doi.org/10.1039/C9CC02651G
[2] E. Guerinoni et al. Green Chem., submitted (2022).
[3] Z. Lu et al. (2021) Patent FR3116936A1, WO2022117942A
[4] S. Le Crom et al., J. Phys. Chem. B 126, 3355 (2022). DOI: http://doi.org/10.1021/acs.jpcb.2c01123
[5] M. Špadina et al. ACS Nano 13, 13745 (2019). DOI: http://doi.org/10.1021/acsnano.9b07605

by comparing, for example, the differences in structural and dynamic properties of these solutions in the presence of other competing ions such as vanadium or zirconium in order to propose a theory explaining the **selectivity between the ions**.

The **theoretical and numerical methods** developed during the thesis can be **adapted and transferred to other industrial applications** involving ionic solutions. During the course of the thesis, the PhD student will be required to disseminate his/her scientific results through publications in scientific journals and communications at national and international conferences.

**Profile:** We are looking for a highly motivated candidate with solid theoretical knowledge in physical chemistry. You have a Master's degree in chemistry, physical chemistry, chemical physics, theoretical chemistry or physics, or equivalent. You have an interest in programming and computer science, and ideally, you already have a basic knowledge of code (e.g., Python, Fortran, … languages, Linux environment, Shell scripts ...). You also have good written and oral communication skills. You have the ability to work in a team while having the necessary autonomy to carry out your own research topic.

**Secured funding:** The Ph.D. thesis is funded by the French Alternative Energies and Atomic Energy Commission (CEA, Energies Division).

Net salary: ~1650 € / month (Gross salary: ~2100 € / month)

**Further information:** The successful candidate will join the LMCT group of ICSM and will be enrolled at the doctoral school ED459 Sciences Chimiques Balard of the University of Montpellier (France).

**Contact:** To apply, please send a cover letter, a detailed CV, and references to Dr. Magali Duvail (magali.duvail@cea.fr) and Dr. Sandrine Dourdain (Sandrine.dourdain@cea.fr) before April 26, 2023.

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