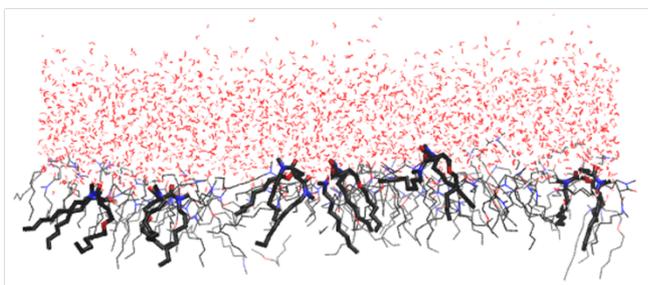


**Open PhD thesis at
Institut de Chimie Séparative de Marcoule (ICSM), Bagnols-sur-Cèze, France
Ecole doctorale 459 Sciences Chimiques Balard (University of Montpellier)**

**Solvent extraction:
Study of ion transfer kinetics at water/oil interfaces containing
mono- or diamide ligands by coupling techniques probing
the interfacial domain.**

Starting date: September 2023



One of the ways presented to slow down the primary demand for mineral raw materials is to optimize their recycling from end-of-life goods and materials. This recycling usually involves grinding, dissolving into solution ions, and finally separating the ions, most often by liquid-liquid (LL) extraction or solvent extraction. This liquid-liquid extraction is the key process used in various industrial hydrometallurgical applications, in particular in the reprocessing process of nuclear

fuel and materials or assemblies containing strategic metals. The term "solvent extraction" refers to the distribution of a solute between two immiscible liquid phases in contact with each other, i.e., a two-phase distribution of a solute.

In order to better understand the transfer of ions between these two phases, it is important to understand:

1. the speciations of the different ionic and molecular species respectively in each of the two phases in contact, which correspond to the differences in chemical potential between the two phases.
2. all the molecular and supramolecular interaction phenomena at the interface which are at the origin of the potential barriers that can influence the ionic transfer kinetics.¹

Our work over the last 10 years²⁻⁸ has demonstrated the interest and complexity of understanding LL interfaces at the molecular level in order to understand the ionic transfer phenomena in cases where the aggregation in the organic phase impacts their kinetics.

Numerous experimental results on speciation and molecular organization in each of the phases exist and can now be interpreted structurally from molecular dynamics simulations. However, this same experimental/simulation approach correlated at the interface containing ligands and in equilibrium with adjacent volumes has been little explored. Indeed, probing by innovative methods the liquid/liquid (LL) interfaces involved in ion-assisted extraction from water to an organic oil phase and vice versa remains a challenge. Although the two-phase solvent extraction process is the basis for many large-scale industrial hydrometallurgical applications for recycling strategic metals, the molecular and supramolecular mechanisms that may determine the transfer kinetics are still relatively unknown, despite decades of research. This is due to the fact that probing buried, fluid, and therefore dynamic nanoscale interfaces remains a challenge.

We have demonstrated by reflectivity techniques that it is possible to analyze interfacial structures rich in diamide ligands, and to describe their organization as interfacial monolayers or interphases. We were able to show how these different interfacial structures explain the different regimes of ionic transfer qualified as either diffusional or kinetic. Finally, we were able to explain why the energy barrier for a system comprising DMDOHEMA is higher than for DMDBDMA, two diamides associated with very different ionic transfer mechanisms⁹. The interfacial structure can, in fact, strongly impact the entropic gain to the formation of inverse ligand aggregates, aggregates that allow the solvating of hydrated ion pairs in the organic phase. Atomic force microscopy (AFM) measurements on these



same interfaces have recently revealed force jumps at contact and during ion transfer kinetics, physical characteristics that can be correlated to lateral inhomogeneities (or raft) responses already observed on immersed biological membranes. Finally, nonlinear optical analyses of second harmonic generation (SHG), a technique suitable for probing buried fluid interfaces, suggest molecular orientation fluctuations characterized by correlation lengths.

These numerous observations are severely lacking in statistics and the variety of chemical parameters in terms of ligand nature or solvent has not yet been explored to define reliable correlations.

This is the purpose of this Ph.D. thesis, which focuses on families of malonamides and monoamides on which we have collected a large number of macroscopic data and average interfacial responses at the CEA and ICSM, and for which our approaches must be systematized. Measurements of acid and trivalent ion transfer kinetics will be correlated with AFM measurements, interface rheology measurements (oscillating drop method), neutron reflectivity measurements (possibility of experiments in Japan), SHG measurements on systems without chromophores but also on ligands of the same family carrying chromophores (work based on J. Wang) and this, by varying the concentrations on both sides of the critical aggregation concentrations. It is indeed recognized that the structure of these interfaces must be studied as a function of several thermodynamic parameters in order to determine the associated energy landscape¹⁰. Finally, the "stripping" aspect, i.e., the ionic transfer from the organic phase to the aqueous phase, will also be specifically studied, a point almost never developed from a structural point of view at the LL interfaces.

1. Zemb, T. et al. Recycling metals by controlled transfer of ionic species between complex fluids: en route to "ienatics". *Colloid and Polymer Science* **293**, (2014).
2. Diat, O. et al. Structure of a liquid/liquid interface during solvent extraction combining X-ray and neutron reflectivity measurements. *Phys. Chem. Chem. Phys.* **17**, 15093–15097 (2015).
3. Scoppola, E. et al. Solvent Extraction: Structure of the Liquid–Liquid Interface Containing a Diamide Ligand. *Angew. Chemie - Int. Ed.* **55**, (2016).
4. Pham, T. T. et al. Analysis of the second harmonic generation signal from a liquid/air and liquid/liquid interface. *J. Chem. Phys.* **146**, (2017).
5. Martin-Gassin, G. et al. Second harmonic generation monitoring of nitric acid extraction by a monoamide at the water-dodecane interface. *Phys. Chem. Chem. Phys.* **13**, 19580–19586 (2011).
6. Malloggi, F. et al. X-ray standing waves and molecular dynamics studies of ion surface interactions in water at a charged silica interface.
7. Paquet, A. et al. P. Aggregation in organic phases after solvent extraction of uranyl nitrate: X-ray scattering and molecular dynamic simulations. *J. Mol. Liq.* **277**, 22–35 (2019).
8. Wang, J. et al. Synthesis and Characterization of a Chromo-Extractant to the Probe Liquid-Liquid Interface in a Solvent Extraction Process. *J. Phys. Chem. C* **124**, 10916–10923 (2020).
9. Simonin, J.-P. et al. Kinetics of Liquid/Liquid Extraction of Europium(III) Cation by Two Malonic Diamides. *Solvent Extr. Ion Exch.* **32**, 365–377 (2014).
10. Luo, G. et al. Ion distributions near a liquid liquid interface. *Science (80-)*, **311**, 216–218 (2006).

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 L2IA group of ICSM and will be enrolled at the doctoral school ED459 Sciences Chimiques Balard of the University of Montpellier (France).

Education and skills required: Master's degree in condensed matter, optical physics, physical chemistry of solutions, or separation chemistry

Contact: To apply, please send a cover letter, and a detailed CV to Pr. Luc Girard (luc.girard@cea.fr) et Dr. Olivier Diat (olivier.diat@cea.fr).

Ions at Active Interfaces Laboratory
(L2IA)
ICSM UMR 5257 – BP 17171
Site de Marcoule
F-30207 Bagnols sur Cèze, France
https://www.icsm.fr/icsm_eng/l2ia_en.html