Liquid-Liquid (LL) or solvent extraction is a separation process [1] which is based on the transfer of a solute from a solution 1 towards an immiscible phase 2, the contact with which can be enhanced by emulsification (see figure 1). In other terms, it is a partitioning method used to separate compounds based on their relative solubility in two different immiscible liquids, usually water and an organic solvent. The solubility is enhanced via the use of complexing molecules (an extractant) either hydrophilic or lipophilic, that are slightly amphiphilic [2,3]. The ultimate aim for application is to develop a selective transfer more cheaply and more quickly, although a trade-off always exists between selectivity and kinetics.

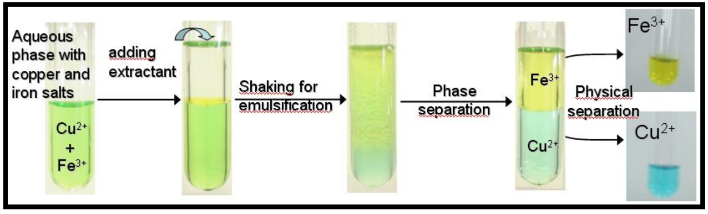

***Figure 1**: Visual demonstration of copper/iron selective solvent separation as proposed for a laboratory experiment for students*

The extraction mechanisms as well as their kinetics at molecular scale across the interface are still poorly understood even if attempts have been made [4,5]. In any case, the hydrated or solvated species (as a function of the transfer direction) have to explore various crossing configurations – very often different from those existing in bulk - associated to energy barriers that determine a part of the kinetics. Several unknown variables are left to quantify the energy barrier of the ion sorption and desorption at the active interface and in a complex association with the extractant molecules [6]. In other words, the interfacial concentration and distribution (of ions and extractants) at equilibrium but also out of equilibrium have to be determined during the ion transfer process.

Experiment November 2014

During the experiment on November 2014 on ID10 at ESRF we have studied the structuration of a ligand (DMDOHEMA) at the water/dodecane interface when contacted with different aqueous solutions. To be able to compare the results with another type of extractant (DMDBTDMA), previously investigated by x-ray and neutron reflectivity [7], we have chosen to work with aqueous solutions with or without nitric acid or lithium and neodymium nitrate.

We have investigated the liquid/liquid interface at various concentrations of DMDOHEMA in dodecane (0.002 M – 0.1 M). The collected data (normalized) as the corresponding SLD profiles obtained via fitting process are shown in Figure 2, for the system with pure water, in Figure 3, for the system with nitric acid and in Figure 4 for the system with lithium and neodymium nitrate.

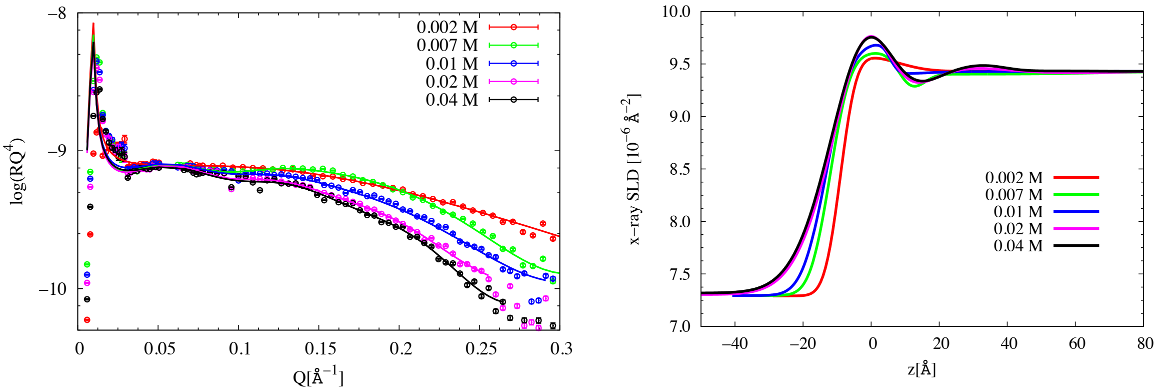

***Figure 2**: (Left) Data collected at the water/dodecane interface at various extractant concentrations in oil (shown in the legend). (Right) Corresponding SLD profiles obtained via best fit modelling.*

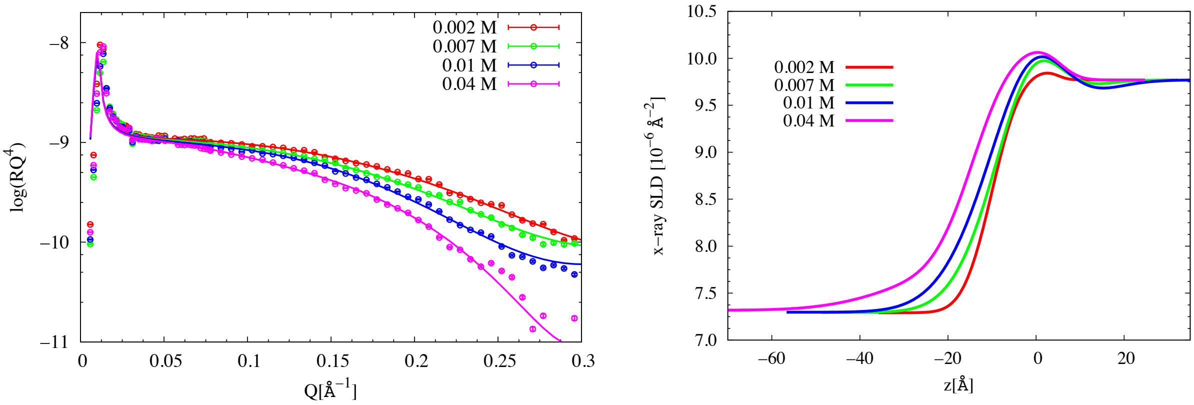

***Figure 3**: (Left) Data collected at the water/dodecane interface at various extractant concentrations in oil (shown in the legend). The aqueous phase was a Nitric acid aqueous solution (2 M). (Right) Corresponding SLD profiles obtained via best fit modelling.*

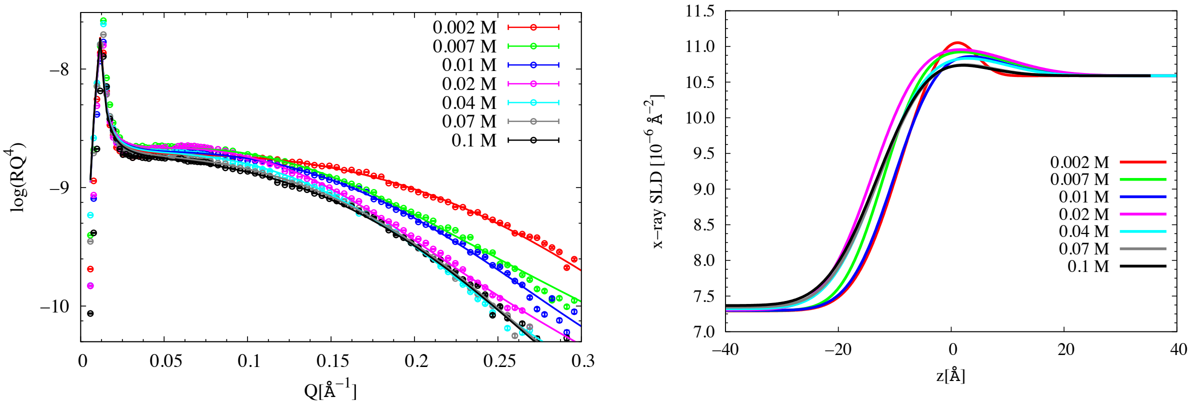

***Figure 4**: (Left) Data collected at the water/dodecane interface at various extractant concentrations in oil (shown in the legend). The water phase was a Lithium Nitrate (2 M) and Neodymium Nitrate (0.25 M) aqueous solution. (Right) Corresponding SLD profiles obtained via best fit modelling.*

Thanks to this experiment we have been able to achieve the following goals :
1 – We have been able to detect different interfacial structure depending on the aqueous solution composition (pure water phase, nitric acid, lithium and neodymium nitrate) for the DMDOHEMA ;
2 – We have been able to compare these results with those obtained for DMDBTDMA (another extractant used for Lanthanides extraction).
3 – We have been able to measure the equilibration time by fixing the angle and recording the reflected intensity over the time. This information can be obtained only by x-ray reflectivity and very useful for complementary measurements (as neutron reflectivity).

Moreover, the combination of these data with those collected on FIGARO at ILL, allowed us to obtain a clear and detailed picture of the liquid/liquid interface. In fact, with neutron reflectivity we can work with isotopic contrast and highlight the distribution of extractant and solvents. On the contrary, with x-ray reflectivity we are more sensitive to the salts distribution across the interface. Combining the two we have shown that is possible to solve the structure of the interface [8]. For further details please refer to the Ernesto Scoppola's PhD Thesis « *Extraction par solvant : étude d'une interface liquide/liquide contenants des ligands en associant des mesures de réflectivité de rayons X et de neutrons* ».

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