

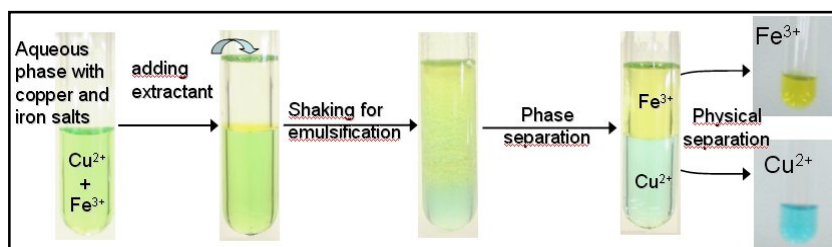
## Report for beam time at ESRF SC3766 – Experimental Method

### Proposal Summary (should state the aims and scientific basis of the proposal) :

Using x-ray reflectivity we intend to probe the structure of a buried liquid interface between water and oil through which ions are transferred via organic and complexant molecules. This is a challenging problem, extremely important for metallic cation recycling.

### Scientific background :

Liquid-Liquid (LL) or solvent extraction is a separation process [1] which is based on the transfer of a solute from a solution 1 toward an immiscible phase 2 whose contact can be enhanced by emulsification (see figure 1). In other terms it is a partitioning method in order 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 and giving some very interesting results [4]. In any cases, 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. It remains many unknown variables to quantify the energy barrier of the ion sorption and desorption at the active interface and in a complex association with the extractant molecules [5]. In other words we have to determine the interfacial concentration and distribution (of ions and extractants) at equilibrium but also out of equilibrium during the ion transfer process [6].

### Samples:

During our experiment on ID10 we tested a new liquid/liquid cell developed at ILL and we measured the presence of Diamide at water/oil interface at equilibrium at different diamide concentrations and changing the subphase.

We have been trying to record the differences in the diamide adsorption at interface and/or Neodymium Nitrate extraction in presence of different water activity and pH. For this purpose we used the following subphases:

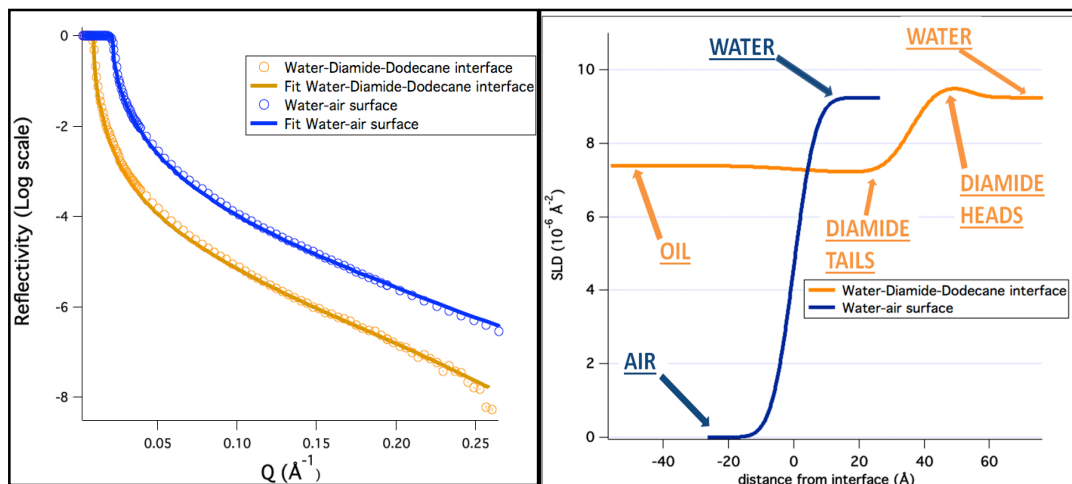
- Pure water;
- Water with 2 M of Nitric Acid and 0.25 M of Neodymium Nitrate;
- Water with 2 M of Lithium and 0.25 M of Neodymium Nitrate;

The first one has been used to understand the difference between pure Diamide adsorption at interface, and Diamide adsorption to extract Neodymium Nitrate. The last one is the case of the last two composition of subphase, where we used the same activity in both but we changed the pH working with acid (Nitric acid) or neutral salt (Lithium Nitrate).

On the other hand we have been working at different diamide concentrations, below and over the CMC (0.1 M, depending on water activity and pH). Indeed we investigated samples with a concentration of extractant in oil between 0.01 and 0.3 M.

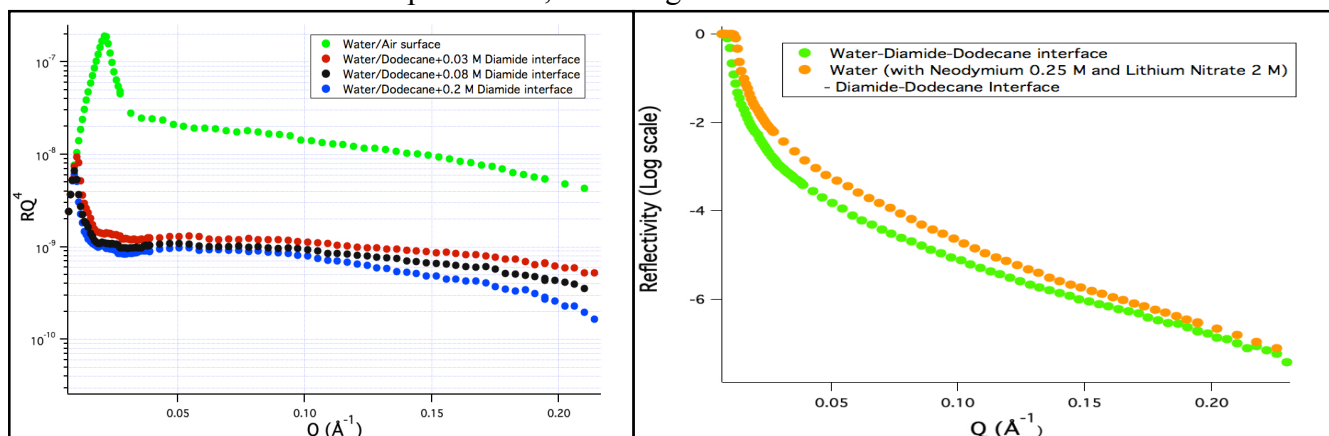
## Recorded Data and Data Analysis:

The data analysis request more time, but for the moment we analysed the adsorption of diamide (0.2 M in Dodecane) at the pure water/oil interface, as shown in **fig. 2**. The fits demonstrate we are able, with this technique, to see the diamide at water/oil interface. We are not able to present the water/oil reference curve because, due to the curvature of the interface (the presence of diamide reduces the curvature since it has a surfactant behaviour).



**Figure 2:** (Left) Data – corrected for footprint correction and normalized to direct beam - and fits for free water surface and water-oil interface with a two layer model of Diamide. (Right) SLD Profiles obtained by fitting procedures.

In addition, the data shown in **fig. 3** shown the difference of reflectivity curve increasing the concentration of diamide in dodecane contacted with pure water, or adding salt in the water.



**Figure 2:** (Left) Data – corrected for footprint correction and normalized to direct beam - and fits for free water surface and water-oil interface with increasing concentration of Diamide in Dodecane (from 0.03 M up to 0.2 M). (Right) Reflectivity curves of diamide at water oil interface with or without Neodymium and Lithium Nitrate.

The analysis of this data (and other data we are not presenting in this report) is still in process. (Experiment performed on the end of January 2014 – beginning of February 2014).