Experimental Report

23/10/2014

Proposal:	**TEST-2340**	**Council:**	4/2014
Title:	Solvent Extraction and Liquid/Liquid Interfaces		

This proposal is a new proposal

Researh Area:

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Samples: H_2O
D_2O
$C_{27}H_{54}N_2O_2$
$C_{12}D_{26}$
$C_{12}H_{26}$

Instrument	Req. Days	All. Days	From	To
FIGARO	6	6	15/07/2014	16/07/2014
			18/07/2014	19/07/2014
			20/07/2014	22/07/2014
			11/12/2014	12/12/2014

Abstract:

ABSTRACT

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.

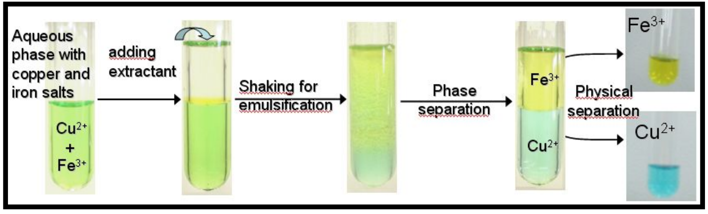

***Figure 1**: Visual demonstration of copper/iron selective solvent separation as proposed for a laboratory experiment for students*

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.

In our laboratory we have used (in collaboration with ILM team from Lyon university) a non linear optical technique (SHG for Second harmonic generation) that is specific for studying (buried) interfaces and we have shown on two examples that i) the variation of the SHG signal which is in our case proportional to the distribution of water dipoles orientation is first correlated to the surface tension variation and ii) that the transfer rate of an ionic species is correlated with the amplitude of the SHG signal fluctuation (see fig. 2 top from ref 4).

EXPERIMENT JULY 2014

We decided to focus on the behavior of one extractant, Diamide, $C_{27}H_{54}N_2O_2$ in deuterated Dodecane, $C_{12}D_{26}$.
To study the liquid/liquid interface, we have designed a new cell with edges at the interface to minimize the meniscus. We tested this cell during previous experiment (ISIS on February 2014 and J-PARC on March 2014). Thanks to the concept behind FIGARO we have been able to increase the statistic (if we compare to experiments in other facilities) shining the sample passing from the water phase. With this setting we avoid to shine through the organic phase where hydrogenated material is dissolved.
For the experiment on July we use the cell, shown in figure **3.**

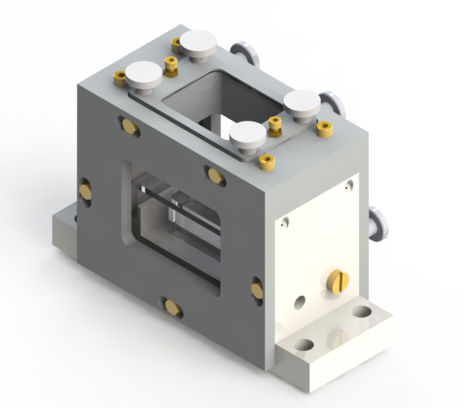

Figure 3: *Cell for neutron reflectometry experiments. With this cell we have been able to cross 3.5 cm of deuterated water. The interior reservoir for water has a length of 3.5 cm and a width of 6 cm.*

We measured three samples. We contacted a water solution of $\mathrm{D_2O}$ with $\mathrm{LiNO_3}$ $(2\ \mathrm{M})$ and $\mathrm{Nd(NO_3)_3}$ with an organic phase with deuterated dodecane at three different concentrations of extractant: 0.02 M, 0.07 M and 0.1 M.
The purpose was to measure changings in the interfacial structure between concentrations below the CMC (0.02 M and 0.07 M) and above the CMC (0.1 M).

RESULTS

In figure **4** we report the fits and SLD profiles for the samples three samples measured.

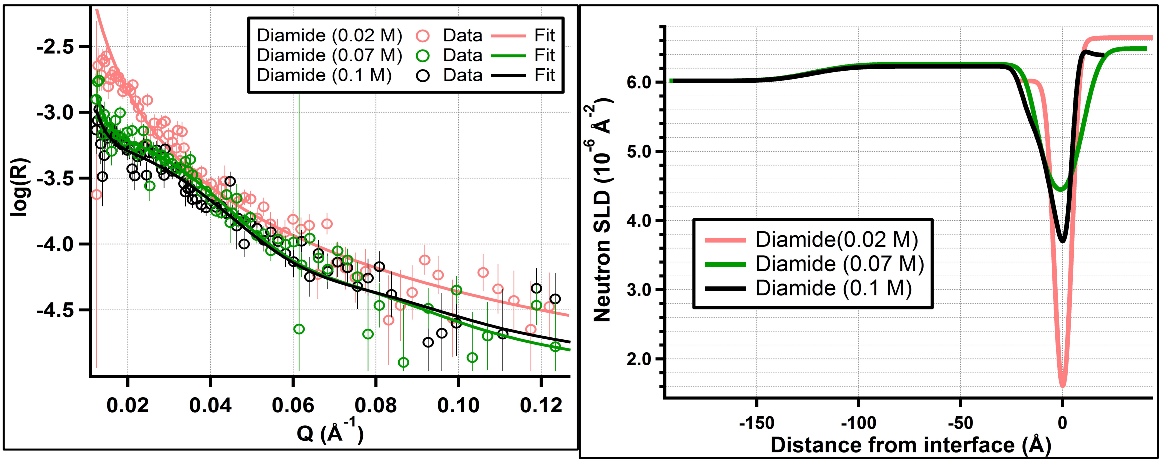

Figure 4:* *(Left) *Fits of the reflectivity data for samples*. ***(Right)*** *SLD profile for samples* ***obtained with best fitting process.***

With these fits it is clear a formation of an hydrogenated layer (Diamide) at the interface between water and oil. In addition to the layer of diamide, we have been able to record also a layer with an higher density of ions (mostly Neodymium) for the samples with diamide at 0.07 M and 0.1 M.

This experiment has been a test for future measurements since we changed the sizes of the water reservoir. The cell used for previous experiments was 5 cm long and the signal attenuation was much higher. We can now obtain flatter surface with the help of the diamide which reduces the interfacial tension between the two immiscible liquids.

This characteristic allows us to employ smaller cell when we have surfactants or extractants increasing the signal to noise and bigger cell (5 cm long) for the pure liquid/liquid interface.

Further measurements we will give us the chance to completely exploit the isotopic substitution to measure the same interface at different contrast, obtaining more information about the interfacial structure.

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