Experimental Report

15/01/2014

Proposal:	**9-10-1283**	**Council:**	10/2012

Title: Study of liquid/liquid interface for heavy ions separation neutron reflectivity and scattering

This proposal is a new proposal

Research Area: Soft condensed matter

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Samples:
Oil
D2O
ions
diamide

Instrument	Req. Days	All. Days	From	To
FIGARO User-supplied	3	3	10/06/2013 05/08/2013	12/06/2013 06/08/2013

Abstract:

At the molecular level, the description of the ion transfer through an active interface is still fully opened to exploration. As mentioned in a recent paper on surfactant at LL interface, some general accepted picture of molecular conformation or orientation can be reconsidered when specific studies are carried out [10]. Its study is essential for progressing in fundamental understanding of factors governing the separation process. This is certainly a highly challenging problem that cannot be totally solved in a three year program. However, we propose an original approach coupling complementary experiments and modelling in focusing on this interface specifically.
Liquid/liquid interface will be probed by neutron reflectivity (beamtime requested on FIGARO) in order to determine at equilibrium (controlled by chemical potential regulation) the extractant molecule distribution that will allow to extract metal cation from aqueous up to organic phase.
In parallel, SANS experiment (on D22) will be performed to characterize nanoaggregation of the extractant molecules in the same thermodynamical conditions.

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.

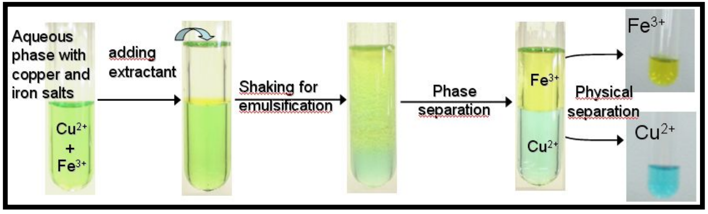

***Figure 1**: Visual demonstration of copper/iron selective solvent separation as proposed for a laboratory experiment for students*

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 JUNE 2013

We decided to focus on the behavior of one extractant, Diamide, $C_{27}H_{54}N_2O_2$ in protonated or not protonated Toluene, C_7H_8/C_7D_8.
To study the liquid/liquid interface, we have designed a new cell with edges at the interface to minimize or, at least, reduce the meniscus. Differently from previous experiments, we decided to pass the neutron beam through either the bulk water or organic phase [7].
For the first experiment on June 2013 we tested the new cell, shown in figure **3.**

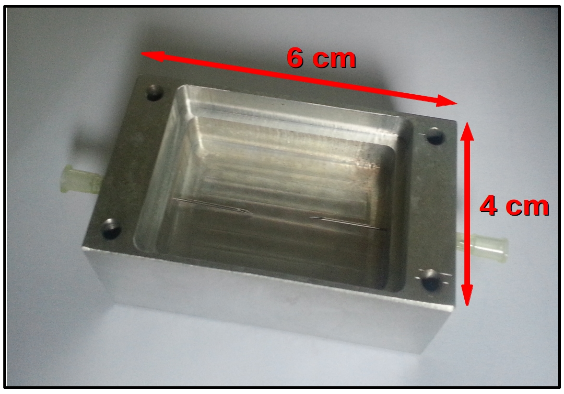

Figure 3:** Liquid-Liquid cell for neutron reflectivity experiment.**

We measured four samples:
a – $D_2O - Air\ interface$
b– $D_2O + LiNO_3 - C_7H_8$
c – $D_2O + LiNO_3 - C_7H_8 + Diamide$
d – $D_2O + LiNO_3 - C_7D_8 + Diamide$

SAMPLES a AND b

In figure **4** we report the fits and SLD profiles for the samples **a** and **b**. Watching the SLD profile we see the expected SLD profile for sample **a** but not for sample **b**.

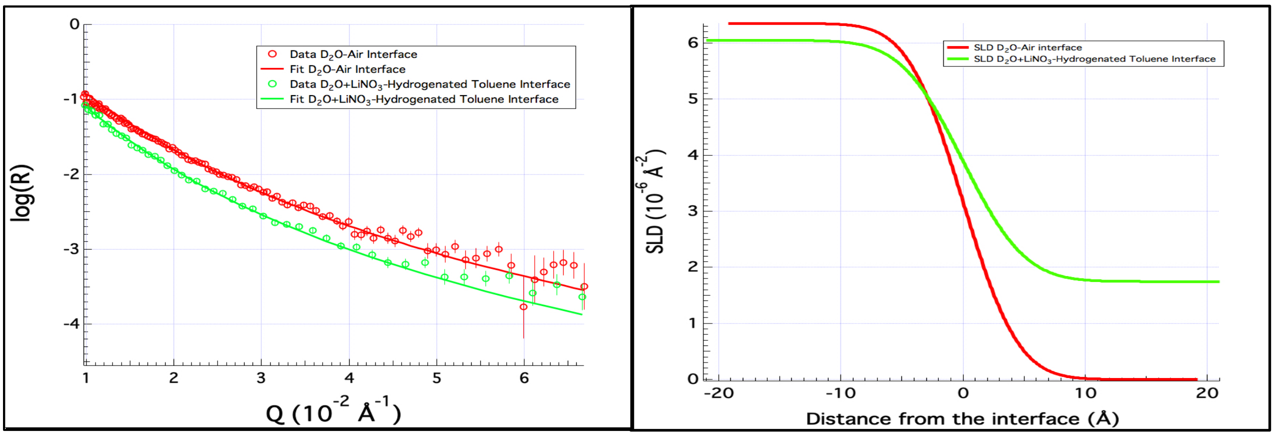

Figure 4:* (Left)** *Fits of the reflectivity data for samples* ***a *and* ***b*. (Right)** *SLD profile for samples* ***a*** *and* ***b*.**

With these fits it seems a large amount of water dissolves in toluene when we contact them. The ratio between the two liquids, in the oil phase would have to be 14% of water and 86% of toluene. This result is not in agreement with the solubility of water in oil or vice-versa. We have reason to believe that we have been able to see the interface but this one was not completely flat. The curvature of the interface produced a shift in ***Q*** of the reflectivity curves, depending on the meniscus shape, and this could explain the difference between the modeled SLD values and the expected ones. We are trying to calculate the ***Q*** shift as a function of the interface shape to correct the data.

SAMPLES b, c AND d

In figure **5** we report the fits and SLD profiles for samples **b, c** and **d**.

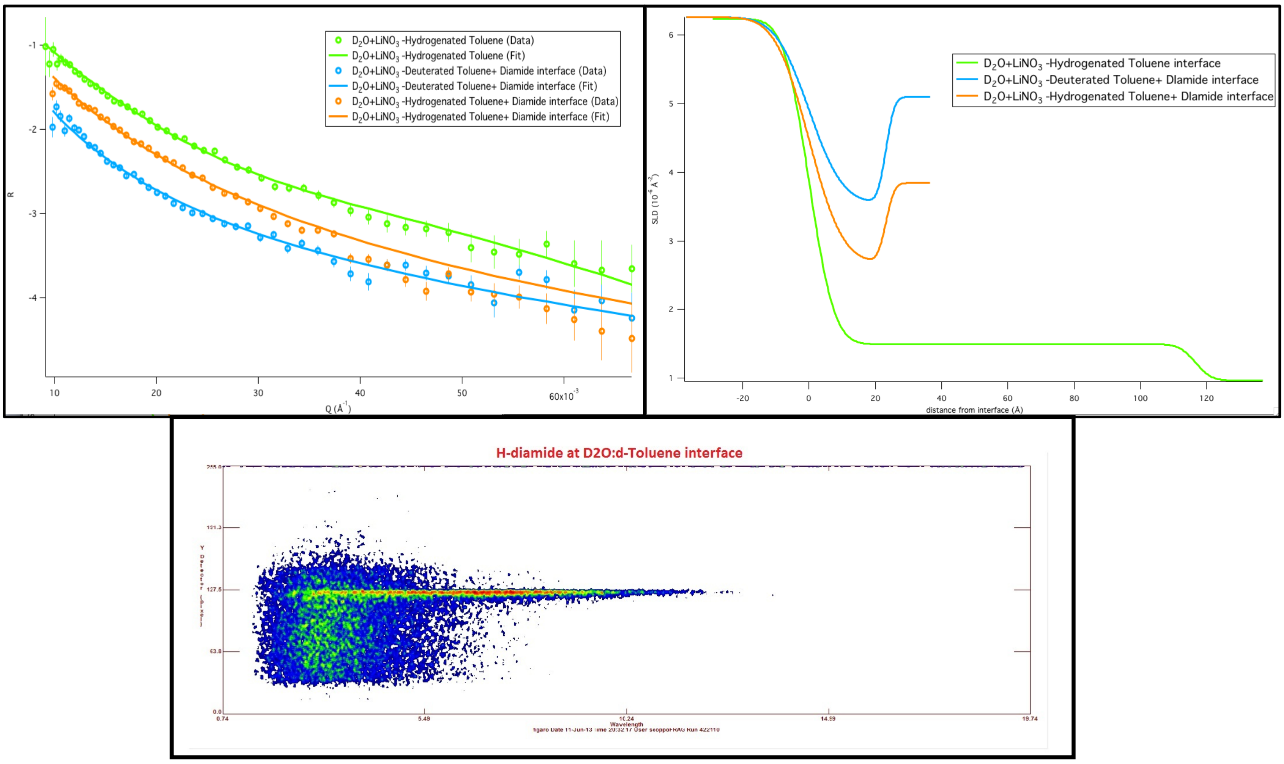

Figure 5:* (Top Left)** *Fits of the reflectivity data for samples* ***b, c *and* ***d*. (Top Right)** *SLD profile for samples* ***b, c*** *and* ***d*.** **(Bottom)** *We show the detector image (****c****) for a sample with a layer of Diamide at the interface between* D_2O *and deuterated Toluene. For technical reasons data from only one angle (0.62°) has been extracted.*

For the sample ***b*** we changed the model, fitting with three layers: the bulk water and oil phases with an interlayer of 10 nm with a mixed SLD.

For samples ***c*** and ***d*** we supposed one layer between the oil and water:
1 (bottom) – Water with Lithium Nitrate
2 (middle) – 2 nm of Diamide layer with 60% of oil
3 (top) – Toluene with Diamide and Water with lithium nitrate.

According to the modeled SLD, for both the contrast (hydrogenated and deuterated Toluene) the ratio between the two liquids in oil is 40 % of water and 60 % of oil. Again, this depends on the possible presence of a small meniscus which might produce a ***Q*** shift affecting the SLD values for this model.

EXPERIMENT AUGUST 2013

On August we conducted a second experiment with an improved cell with an added Teflon coating on the edge (in contact only with the oil face) , as shown in figure **6**, to reduce the meniscus.

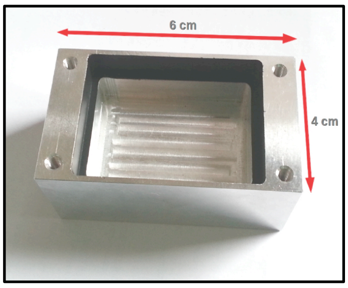

Figure 6: *Liquid-Liquid cell for neutron reflectivity experiment. The black part is the lipophilic (Teflon) coating.*

This idea worked fine and measuring the water-air interface, but it failed for Toluene-Water because the contact angles between the walls and the bulk phases due to the poor affinity between the Teflon and the Toluene. Anyway we saw the lipophilic coating is essential to reduce the water meniscus and changing the type of coating (OTS for example) we can work on the curvature of the interface between water and alkanes. In figure **7** we show the data with fits and SLD profiles obtained with this last cell measuring $D_2O - Air\ interface$.

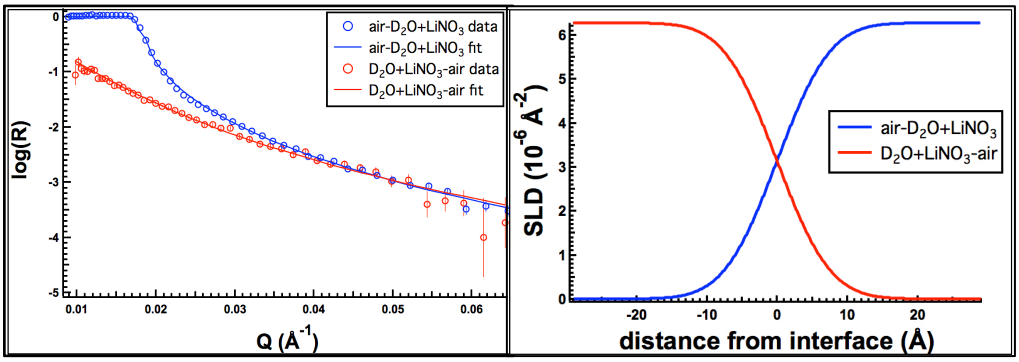

Figure 7: (Left) *Reflectivity data and fits for $D_2O - Air\ interface$.* ***(Right)*** *SLD profiles for $D_2O - Air\ interface$. For both the plots we show in blue the reflectivity curve from the top, in red the one coming from the water. The two SLD profiles are symmetrics around the zero (interface plane) and this demonstrates the equivalent information about the air-water interface can be obtained by shining the neutrons through the water phase and reflecting off the air.*

These plots are important for two reasons:

1. the presence of the plateau (blue line, figure **7**) which is the evidence of the absence of meniscus. Having a total reflection region with the expected critical angle is an evidence of absence of artifact as curvature of surface;
2. we get two SLD profiles describing the interface coming from the air and from the water

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