Experimental Report

17/02/2015

Proposal:	**9-10-1350**	**Council:**	4/2014

Title: Study of Liquid/Liquid interface for heavy ions separation

This proposal is continuation of: 9-10-1283

Researh Area: Chemistry

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Samples:
Neodymium Nitrate
Dodecane
Water
Gadolinium Nitrate
$C_{27}H_{54}N_2O_2$ (Diamide)
Lithium Nitrate

Instrument	Req. Days	All. Days	From	To
FIGARO User-supplied	5	5	03/10/2014	08/10/2014

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. 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

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.

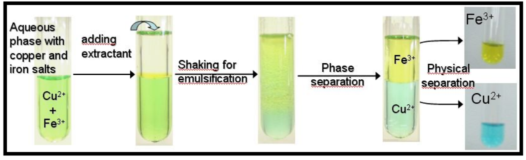

***Figure 1**: Visual demonstration of copper/iron selective solvent separation as proposed for a laboratory experiment for students*

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 OCTOBER 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, J-PARC on March 2014, FIGARO on July 2014) useful to improve the cell geometry and details. 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.**

Ernesto Scoppola 16/10/14 16:12
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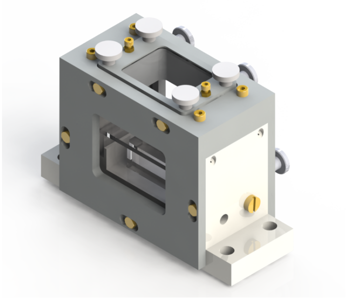

***Figure 3:** Cell for neutron reflectometry experiments. With this cell we have been able to cross 3.5 cm of deuterated water. The interior reservoir for water has a length of 3.5 cm and a width of 6 cm.*

We measured three samples. We contacted a water solution of D_2O with and without $LiNO_3$ (2 M) and $Nd(NO_3)_3$ with an organic phase with dodecane (hydrogenated/deuterated) at different concentrations of extractant: 0.02 M, 0.04 M, 0.07M, 0.09 M and 0.1 M.
The purpose was to measure changings in the interfacial structure between concentrations below and above the CMC (0.1 M).

RESULTS

In this report we show the data of liquid-liquid interface between pure deuterated water contacted with oil at three different concentration of diamide in oil: 0.04 M, 0.09 M and 0.15 M.

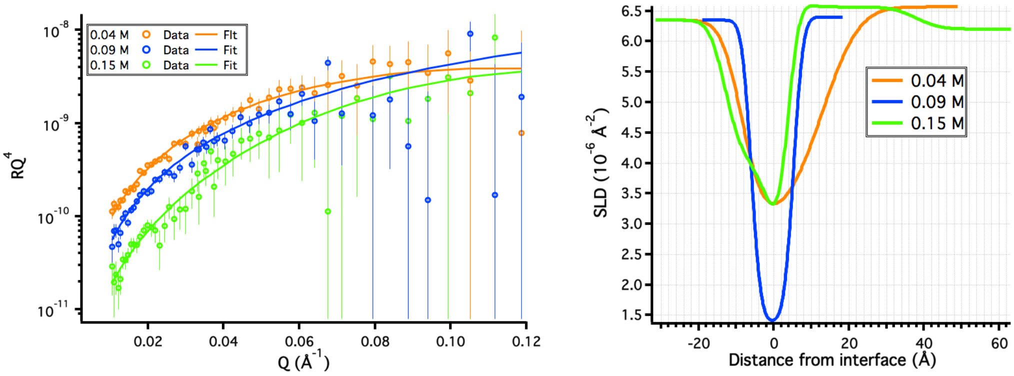

Figure 4: (Left) *Fits of the reflectivity data for samples***.** ***(Right)*** *SLD profile for samples* ***obtained with best fitting process.*** In the legend we show the molar concentration of diamide in organic phase. The SLD profiles show an hydrogenated layer at the interface between water (for distances from interface smaller than zero) and oil (for distances from interface greater than zero)

With these fits it is clear a formation of an hydrogenated layer (Diamide) at the interface between water and oil. The data, collected to understand the interfacial structuration of diamide during the water extraction process without ions, show a different behavior if compared with the one collected in previous experiments (See experimental reports from July 2014) but further data analysis will be necessary to obtain a complete model.

It is clear we are able with our cell and with the powerful flux and instrument settings on FIGARO, to catch changings at the liquid-liquid interface for different systems.

The cell used for previous experiments (ISIS and JPARC) was 5 cm long and the signal attenuation was much higher. Thanks to the test on July and this experiment on October we collected data at the Liquid-liquid interface crossing only 3.5 cm of water, with a better signal to noise. 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 on different systems (fluorinated samples) would be very useful to improve the cell and to understand better the interfacial interaction between two immiscible liquids with and without extractants/surfactants.

1 J. Rydberg et al, Solvent extraction principles and practice. (Marcel Dekker, New York, 2004).
2 Z. W. Zhu and C. Y. Cheng, Hydrometallurgy 107 (1-2), 1 (2011).
3 G. Cote, Technique de l'Ingénieur J2762 (1998).
4 G. Martin-Gassin, P. M. Gassin, L. Couston, O. Diat, E. Benichou, and P. F. Brevet, Physical Chemistry Chemical Physics 13 (43), 19580 (2011) and J. Chem Phys. 2012.
5 C. D. Wick and L. X. Dang, Chemical Physics Letters 458 (1-3), 1 (2008).
6 F. Testard, L. Berthon, and T. Zemb, Comptes Rendus Chimie 10 (10-11), 1034 (2007).
7 A. Zarbakhsh, J. Bowers and J. R. P. Webster Meas. Sci. Technol. 10 (738-743) , (1999).