Experimental report

15/09/2016

Proposal: **9-10-1436** **Council:** 4/2015

Title: Liquid/liquid neutron reflectivity: the use of fluorinated solvent and Gadolinium cation

Research area: Soft condensed matter

This proposal is a continuation of 9-10-1350

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Instrument	Requested days	Allocated days	From	To
FIGARO User-supplied	7	5	26/05/2016	31/05/2016

Abstract:

Neutron reflectivity on liquid/liquid (LL) interface will be performed to study the distribution of gadolinium cation across the interface. The chosen system will allow to compare two types of incident geometries that can be tested on Figaro. There are also two objectives: a first one that will allow to compare data with previous experiments but using another type of cation in the lanthanide series (Nd has been already studied with a different separation factor). The second is to prepare a future experiment that will allow to couple reflectivity and gamma fluorescence detection to better characterize the cation distribution at the LL interface using only neutrons.

Experimental Report 9-10-1436

Solvent Extraction: Gadolinium at Fluroinated Oil/Water interface

The main purpose of the experiment was to investigate the Perfluoro-toluene/Water (LL) interface with a perfluorinated malonamide (also called diamide or extractant) in the organic phase and Gadolinium nitrate in water phase. The system has been chosen due to the high transmission of neutrons through perfluorinated solvents and to couple reflectometry and γ-ray fluorescence for the localization of Gadolinium[1].

Investigated Samples

We have investigated the LL interface between Perlfuoro-toluene, at various extractant concentration (0.02 M, 0.05 M and 0.08 M), and an aqueous solution of 0.25 M of Gadolinium Nitrate and 2 M of deuterated nitric acid.
Then, for the sample at 0.05 M of extractant in organic phase, we have collected data at various Gadolinium Nitrate concentration in heavy water (0.0 M, 0.05 M, 0.16 M, 0.25 M).
For all these samples we have recorded reflectivity data and, for the samples at 0.05 M of extractant and different concentration of Gadolinium we have collected γ-ray fluorescence intensity.

Reflectometry Results

Thanks to the high transmission through perfluoro-alkanes, we have been able to record reflectivity data in Time Of Flight (TOF) at three different angles (-0.62°, -1.40°, -2.72°) with a resulting Q-range up until 0.2 $\AA^{-1}$.
In Figures 1 we report the data and fits obtained for samples with 0.05 M of extractant with or without gadolinium nitrate in the aqueous phase.

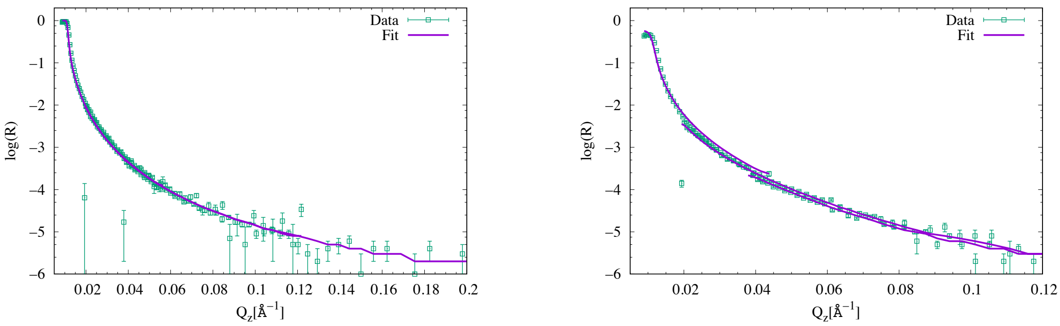

Figure 1: *Reflectivity data for Perfluoro-toluene/Water interface in presence of 0.05 M of diamide in the organic phase.* ***(Left)*** *Data and fits with no Gaolinium Nitrate.* ***(Right)*** *Data and fits with 0.25 M of Gadolinium Nitrate.*

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While for the sample without gadolinium (Figure 1 right) we obtain a classical reflectivity curve, in the case with gadolinium (Figure 1 right) we observe a decrease of the intensity below the critical edge and gaps between data at the same Qz but different angles. Those gaps are well underlined by the fitting curve (purple).
In fact, the attenuation at the critical edge is due to the big absorption cross section of gadolinium which, if adsorbed at the interface, reduces the amount of neutron reflected. Nevertheless, the absorption cross section varies as a function of the wavelength: for higher wavelength (lower Q), higher absorption. This effect is particularly evident in a region were data collected at two angles overlap.
For instance, in the Q region between 0.02 and 0.04 $\AA^{-1}$ the reflected intensity at the second angle (higher wavelength) results lower than the one measured at the same Q range but at the first angle (lower wavelength) because neutrons with lower wavelength are less attenuated.
This feature gives us the opportunity to obtain multiple information with only one contrast. The gaps in the reflectivity are related to the amount of adsorbed gadolinium at the interface and the shape of the curve is related to the adsorption of hydrogenated extractant at the Liquid/Liquid interface (Figure 2).
With this knowledge, we designed a Fortran code fitting the reflectivity data in TOF and considering the imaginary part of the SLD which is related to the absorption cross section and varies with the wavelength. This new approach is possible thanks to the COSMOS data reduction producing .lam files.

The data are still under analysis, but we report in Figure 2 the resulting distribution profiles across the LL interface corresponding to data reported in Figure 1.

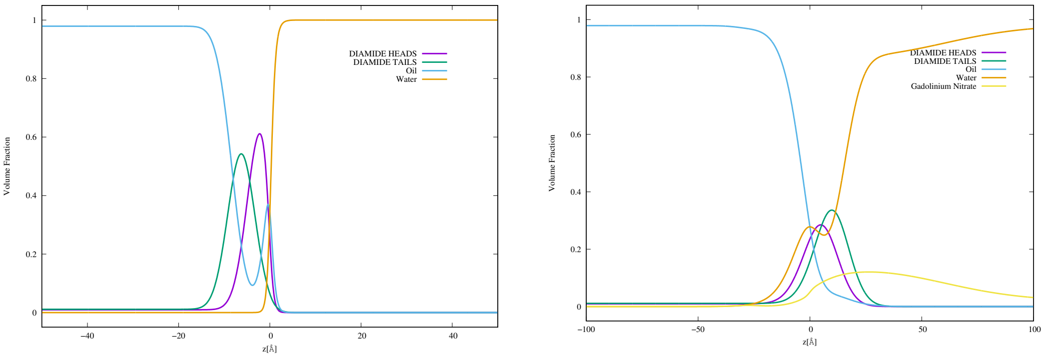

Figure 2: *Distribution profile of species across the liquid/liquid interface for sample with (left) no Gadolinium and with (right) 0.25 M Gadolinium Nitrate in aqueous phase. The results are obtained with a simulated annealing fitting process and the corresponding fits are shown as lines in Figure 1.*

γ-Ray fluorescence

As written above, we have measured γ-ray fluorescence for various samples with and without gadolinium.

The purpose of the experiment (as written in the proposal) was to test the feasibility of this approach. In other words, we wanted to test if the experimental conditions on FIGARO are suitable to detect γ-ray emitted from the samples.

The test has been successful and we have been able to detect the 182 keV peak, corresponding to ^{157}Gd, when Gadolinium was dissolved in the aqueous solution. The results for various samples are reported in Figure 3.

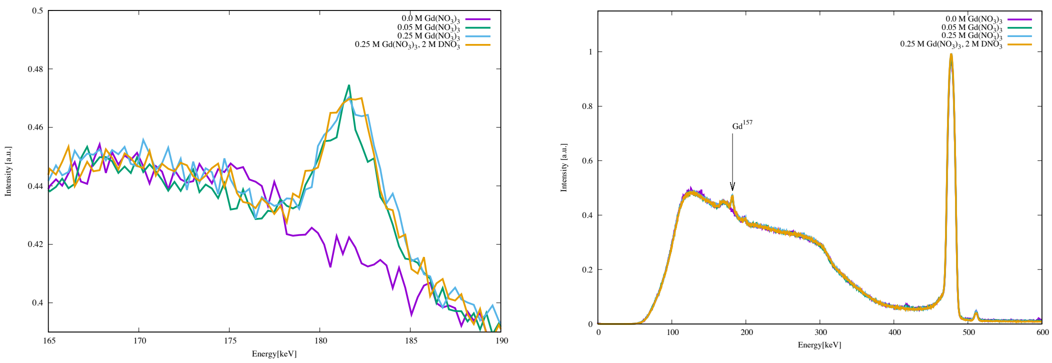

Figure 3: ***(Left)*** . ^{157}Gd *peak appearing when gadolinium nitrate is dissolved in the aqueous phase.* ***(Right)*** *Gd peak standing on the Boron Background.*

Despite we have been able to detect the presence of Gadolinium, we have concluded that for a complet information, in future experiments we will need to collect fluorescence data in list-mode (as a function of wavelength) and with a better shielding to increase the signal to noise ratio. With these king of information we would be able to use the fluorescence spectra as a constraint in the fitting process and fitting at the same time fluorescence and reflectivity curves.

Data are still under process but we are confident to be able to write a publication.

Lipids at Fluorinated Oil/Water interface

We have measured reflectivity at the perfluoro-octane/heavy water interface when hydrogenated lipid vescicles of POPC or DSPC at 0.5 mg/ml were dissolved in the water phase. Moreover, in the case of POPC after a first injection of vescicles we have applied an osmotic pressure by injecting a Sodium Chloride solution to reach 100 mM NaCl solution. Data, fits and SLD profiles are shown in Figure 4.

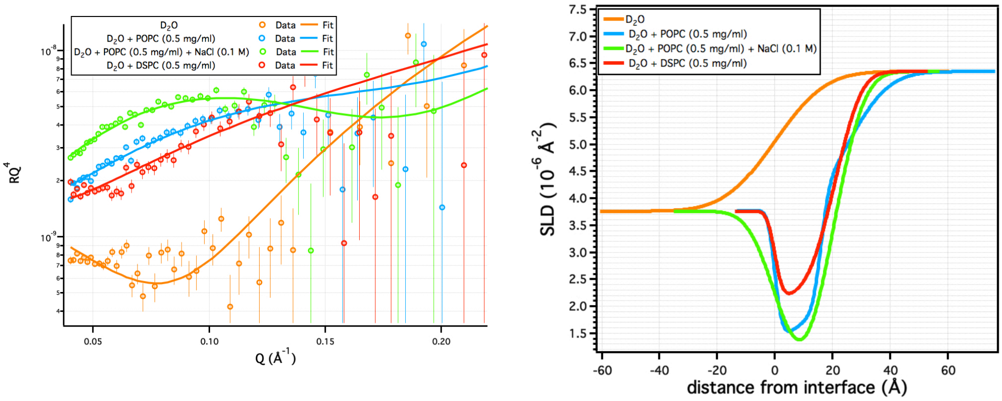

Figure 4: *(**Left**) Data and fits for the (orange) pure perfluoro-ocate/water interface, with POPC vescicles (blue) without or (green) with 100 mM of NaCl and (red) DSPC vescicles. (**Right**) Corresponding SLD profiles using a 1-layer model.*

First of all we are able to observe differences in reflectivity curves collected at the LL interface between water/oil with or without lipids. Moreover, between different lipids produce different interfacial structures as resulting by the SLD profiles shown in Figure 4 right. In fact, the SLD profiles show a clear adsorption of hydrogenated compounds (lipids) at the LL interface.

Despite that, due to the timing of the experiments we have been able to record data with only one water contrast (heavy water) which does not allow us to model data with more than one layer. Future experiments would allow to resolve better the structuration of lipids at soft interfaces.

1. E. Schneck, M. Jentschel, C. Gege, M. Tanaka an B. Deme, Langmuir 29 (2013) 4084