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Structure of Liquid/Liquid interface during Solvent Extraction combining X-ray and Neutron Reflectivity Measurements

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We have resolved the molecular structure of a bulk oil/water interface that contains amphiphilic ligand molecules using a combination of x-ray and neutron reflectivity measurements for the first time. This milestone impacts on the field of ion separation by phase transfer, i.e. liquid/liquid extraction.

Glenn T. Seaborg, Nobel prize in chemistry for the discovery of transuranium elements, stated in the eighties: "In the future, chemistry will be called upon to extend our natural resources of copper, lead, zinc, and other non-ferrous metals by making it possible to recover these metals more economically from low-grade ores or to recycle materials now discarded as waste".[1] As resources in chemical elements become scarce, and the demand is expected to rocket, recycling becomes crucial. The key point in recycling from waste is separation.[2-4] For this purpose, liquid-liquid (LL) or solvent extraction partitioning methods have been developed to separate compounds based on their different solubilities in immiscible liquids, usually water and an organic solvent ("oil phase"). Among the many solvent extraction technologies,[4-10] those used for metal recovery are quite challenging due to the poor solubility of inorganic ions in oils. Metal extraction thus requires the use of lipophilic extractant molecules to complex the cations and solubilise the complex in the oil phase.[11] In practice, there is a trade-off between selectivity, kinetics and efficiency, in keeping with cost constraints. However, despite all the attention solvent extraction has received the molecular structure of the LL interface remains quite elusive and, as a result, the mechanisms of complex (ion + extractant molecules + counterions) formation and transfer, all of which influence the kinetics of extraction, are not well understood. Ion-extraction can be referred to as a diffusion-limited or a reaction-limited process depending on the height of the energy barrier at the LL interface.[12-15] To tackle this highly challenging problem, as a first step we obtained coherent nanometer scale structural information of the interface at equilibrium.[16] We propose in this paper to analyze the molecular structure of the buried liquid/liquid interface in such complex systems using for the first time a combination of x-ray and neutron reflectivity and data analysis aided by Monte-Carlo simulations. As described in a recent paper, Schlossman et al. have coupled other techniques such as x-ray reflectivity and x-ray fluorescence measurements in order to gain insight into the ligand and ion distribution at the interface in similar systems but at much lower concentrations.[17,18] Reflectivity measurements are well suited to the probing of interfacial structures with nm to sub-nm resolution[19]. By combining neutron and x-ray reflectivity measurements it is possible to obtain two fundamentally different scattering contrasts to obtain complementary scattering length density profiles of the mixture at the LL interface.[20,21] Neutrons provide greater contrast for observing the organic species in deuterated environments[22] and the the measurements were possible thanks to the unique 'reflection down' option on the versatile time-of-flight reflectometer, FIGARO, at the Institut Laue-Langevin (Grenoble, France). X-rays on the other hand are more sensitive to the distribution of high Z number ionic species.[23,24] The LL cells developed for this work, as well as the experimental procedures and the method of data analysis, are described in the supplementary information (SI1-2). Regarding metal ions, we focused on rare earth Ln^{n+} elements because of their importance in industry. They are considered as critical or strategic elements due to their high values in many applications from catalysis to energy.

For these purposes, one system was selected using a malonamide ligand, the DMDBTDMA (or N1,N3-dimethyl-N1,N3-dibutyl-2-tetradecyl-malonamide – see its chemical structure in the SI3). This diamide extractant is well known to complex lanthanide cations.[25-27] Such a molecule has amphiphilic[28] and surfactant properties[29,30] that allow first a complexation of the ligand with ions at the interface and second an increase in efficiency of the emulsification that occurs during the solvent extraction process. We worked using 0.25M of $NdNO_3$ and 2M of $LiNO_3$ salt in water, the Li cation extraction by malonamide being negligible and allows an increase

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the lanthanide chemical potential.[31] We present data for a concentration in diamide in dodecane between 0.01-0.1 M, a concentration range below its critical concentration aggregation concentration of about 0.1M in these conditions and for which we have shown in previous work that the separation coefficient is not too high and the rate of ion transfer is maximized.[32]

In figure 1, two series of reflectivity profiles varying concentrations of diamide in dodecane are shown: the upper series for x-rays and the lower series for neutrons.

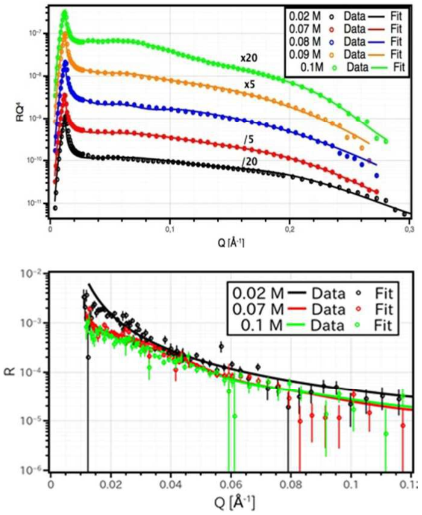

Fig. 1 (Top) X-ray reflectivity curves in the RQ4 vs Q representation for the 2M LiNO3, 0.25M NdNO3 water solution - dodecane interface in presence of 0.02 to 0.1M diamide. Each curve is shifted with a suitable factor (0.05, 0.2, 5 and 20) for clarity; (Bottom) Neutron reflectivity curves in the logR vs Q representation for the same systems and a lower number of diamide concentrations. Data collected on ID10b at the ESRF and FIGARO at the ILL.

The RQ^4 versus Q representation of the x-ray data, where R is the reflectivity and Q the wave vector transfer, was chosen to emphasize the deviation from an ideal Q^{-4} decay at a sharp interface of the x-ray reflectivity. By increasing the diamide concentration, first we observe a more pronounced decrease of the reflected intensity at large Q-values which can be crudely interpreted as an increase of the interface roughness or the presence of larger amplitudes of capillary waves. Some features, like the weak intensity bump that grows at low Q, however, indicate liquid structuration at larger length scales than those corresponding to a simple monolayer formation. The diffuse or incoherent scattering from capillary waves that contributes to the specular reflection was not considered. We have a variation of the surface tension of the LL interface from about 25 to 10 mN/m by varying the diamide concentration. From this variation we calculated a roughness amplitude variation from 4 to 10 Å.[33] This variation can partially explain the decrease of the reflected intensity at large Q-values and are taken into account within the layer overlapping in the sigma parameters (see fitting parameters tables in SI4). Through the use of a classical model of data analysis[34] which involves a series of stratified layers of variable scattering length density (SLD) that are parallel to the interface, SLD profiles as a function of the (z-) direction normal to the interface are obtained (see continuous lines in fig. 1, with parameters and details in the SI.3). Through the combination of neutron and x-ray reflectivity data, thereby exploiting both the nuclear and electron density contrasts, two sets of SLD profiles for the same system were obtained. These SLD profiles are plotted in figure 2.

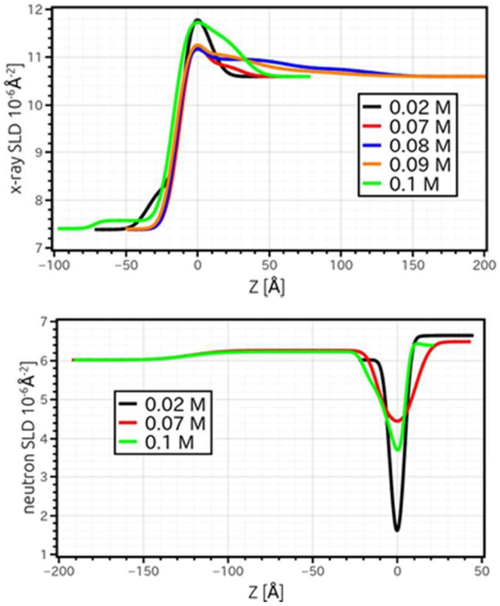

Fig. 2 SLD profiles from x-ray (Top) and neutron (Bottom) measurements as a function of depth perpendicular to the water/oil interface for various diamide concentrations between 0.02 and 0.1M. For x-ray SLD profiles, the organic phase corresponds to the negative z-values and the aqueous phase to the positives. Vice versa for neutron SLD profiles.

Across the LL interface, an excess of ions and extractant molecules results in a maximum in the x-ray SLD profiles and a minimum in the neutron SLD profiles, which are inverted due to the different scattering contrasts of the species involved. For x-rays, the electron density (and respectively the SLD) is greatest for the high Z number ions and the data are most sensitive to the concentration of these species at the interface. For neutrons, the diamine is fully protonated (with a low SLD compared to the other deuterated or partially deuterated compounds) and the data are most sensitive to the diamide concentration at the interface. Even though the experimental resolution and statistics of the neutron measurements are poorer, a complementary structural description emerges from the two analyses. At low diamide concentration a dense and sharp distribution of the extractant molecules is observed at the interface which becomes slightly more diffuse as the diamide concentration increases and reaches the CAC. Simultaneously, a wider distribution of ion enrichment is observed at the interface. While an excess of molecular complexes at the interface and its dependence on bulk concentration was expected from LL surface tension measurements, which also point out an strong accumulation of amphiphilic extractants at the LL interface with increasing concentration up to the CAC,[32] the distribution of the species at the interface has to date been unknown.

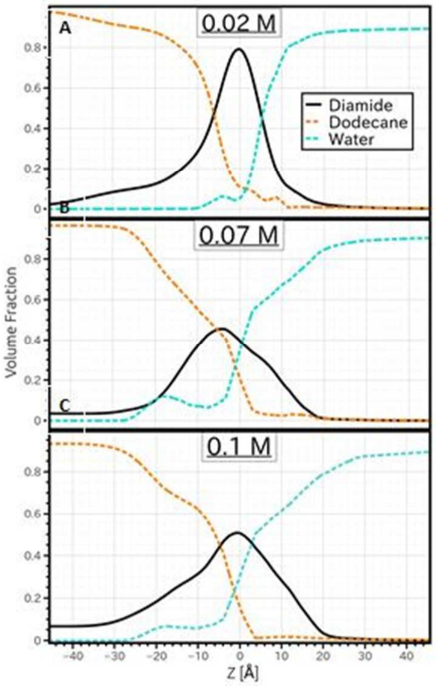

Fig. 3 Volume fraction profiles across liquid/liquid interface for three concentrations of diamide in dodecane (A) 0.02, (B) 0.07 and (C) 0.1M respectively obtained via a Monte Carlo sampling of the location of the ions and molecules in order to described accurately the neutron and x-ray SLD profiles. The orange and cyan dashed lines represent the oil and water volume fractions. The diamide distribution is shown in black (widths of these distributions are given in SI5).

Although the studied system is complex, knowledge of the distribution of specific molecular species across the interface would shed light on the ion extraction mechanism. A molecular dynamics approach could be a suitable approach and has already demonstrated its relevance for the understanding of oil structuration using extractant molecules[30] as well as the interfacial molecular organization in similar systems.[35] However, this method has some limitations in terms of the time required for calculation due to both the large number of molecules that have to be taken into account in a diphasic system and the long range interactions resulting from the presence of ionic charges. As a result of these limitations, we have used a Monte-Carlo sampling method here to obtain the depth-dependent concentration of each molecule. Taking into account the x-rays and neutron scattering length of each species, we designed an algorithm to produce the optimal distribution across the interface that fits both SLD profiles. Details of this analysis are given in the Methods and in SI.5. Figure 3 shows the volume fraction variation as a function the perpendicular z-coordinate across the interface for water, dodecane and diamide species and for three extractant concentrations for which we had both neutron and x-ray measurements. In figure 4, the distribution of (A) lithium, (B) neodinum and (C) nitrate ions across the interface are plotted for three diamide concentrations. For another comparison are superimposed in the SI. 5 the diamide and nitrate distributions as a function of the z-coordinate and for the three different diamide concentrations. Due to the low resolution of the data (limited Q-range), structural details in the distribution below nanometer length scales are difficult to obtain. Nevertheless, a general behavior in the evolution of the distribution of each species can be discussed.

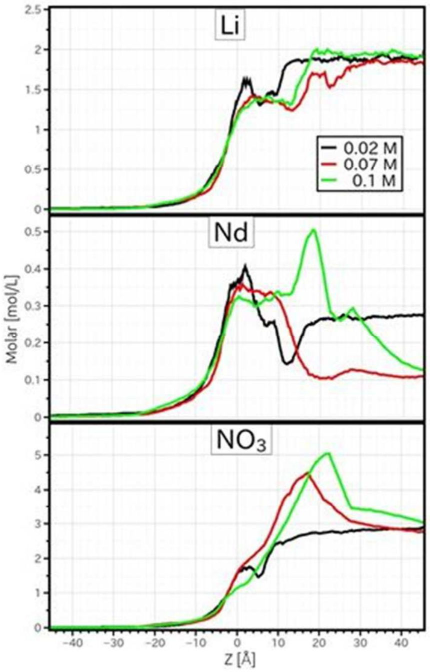

Fig. 4 Distribution of ions - (A) for lithium, (B) for neodinum and (C) for nitrate in molar concentration - as a function of the perpendicular distance z across the interface obtained via a Monte Carlo sampling of the location of the ions and molecules in order to described accurately the neutron and x-ray SLD profiles; Black, red and green lines correspond to the averaged distribution of ions at 0.02, 0.07 and 0.1 of diamide in dodecane respectively (widths of these distributions are given in SI5).

First, at the lowest concentration of extractant measured, the water and oil phases appear as disjoined phases with the diamide molecules concentrated in a low density monolayer at the interface. When the bulk concentration of the extractant increases, the interpenetration of water and dodecane molecules is more pronounced and a mixed interphase with a wider distribution of extractant molecules is formed.

Concerning the salt distribution, an interesting point is that as the CAC is approached, we observe an increase of neodymium accumulation at the expense of lithium ions. This accumulation is highly correlated to the presence and the spreading of extractant molecules at the interface and more specifically to the mixing of water and extractant molecules within this interphase. For lithium and nitrate, the ionic distributions as a function of diamide concentration converge to the bulk concentration over approximately 5 nanometers across the interface (Fig 4A and C). For neodymium cations, the average bulk concentration is reached at slightly larger distances of ~10 nm (data not shown). The weak fluctuations observed on the graphs depend on the sampling steps but the slight excess or depletion of ions close to the interface is reproducible independent of the sampling resolution (the width of these distributions are shown in SI. 5).

Another way to visualize the condensation of heavy ions at the interface is to calculate the mass density profiles from these distributions using knowledge of the concentration and the mass of each species (see SI6). An excess of density is highlighted that cannot be due solely to an accumulation of diamide at the interface but must correspond to the presence of "heavy" salts, here neodymium. This excess is observed over several tens of nanometers when approaching the CAC. Since there is a broad molecular distribution across the interface, the zero position is arbitrary and difficult to compare as a function of the concentration.

An accumulation of the diamide molecules at the water/oil interface was already evidenced from the surface tension variation as a function of diamide concentration in contact with similar aqueous phases.[32] However, we deduce from the SLD profile simulations an interesting evolution of the interface with significant mixing of oil in water due to the presence of the extractant, a model that seems to be at odds with the current scheme of an amphiphilic monolayer. The formation of an thick interface or an interphase enriched with extractant molecules over several nanometers can be compared to a surface induced pre-transitional effect or a critical adsorption already observed with surfactant close to solid or liquid surfaces.[36] A pre-alignment of the molecules at an interface, or more generally the loss of entropy of the molecules at an interface, can indeed induce such a transition toward a more concentrated phase if it exists in the phase diagram. In the present system, it is known that a third phase transition appears for extractant concentrations above the CAC and characterized by a liquid/liquid demixing in the organic phase (beyond 0.2-0.3 M in the present system).[37] The denser phase is enriched by the extractant molecules and the extracted salt. We can then consider the presence of this interphase as a pre-transitional effect leading to the third phase transition. At high concentration, DMDBTDMA diamide also has the tendency to form disordered lamellar structures[38] but it would be difficult to characterize such an organization in the thin layers observed here at the liquid/liquid interface. The appearance of this interphase warrants further investigation because the kinetics of ion transfer is fully related to the extractant concentration and configuration within this thick extended layer.

Last, the comparison of our reflectivity measurements and MC simulations has allowed us to address for the first time a possible molecular organization at a LL interface under thermodynamic conditions, rather close to those used in real processes. Due to the limited number of fitting parameters and the absolute units of the SLD profiles with different scattering contrasts contributions, the simulation converged to a unique solution independent of the initial conditions. The work paves the way for a range of detailed studies in the future. Further experiments will address varying water activity, ionic strength, pH as well as temperature in order to extract the corresponding potential landscape across the interface. This will be important to understand or predict the various kinetics of ion transfer in solvent extraction processes. Besides solvent extraction, LL interfaces have great interest in many other applications such as phase transfer catalysis[39], electrochemical processes,[35,40,41] and liquid chromatography.[42] More widely, LL interfaces are ubiquitous in biology and for numerous biological process.[43] Our structural approach provides a new tool for the investigation of active interfacial phenomena as well as the potential capability to follow the time-evolution of relaxation phenomena in interfacial systems submitted to external stimuli.

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