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Determination of the structure in organic solution combining experimental characterization and molecular dynamic simulation

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In the frame of the nuclear fuel recycling, various solvent extraction processes have been developed using mono- or di-amide extractants in an aliphatic diluent. In order to better understand the extraction mechanisms involved in such extraction processes, a detailed description of the organic phases is essential. The properties of the solvent extraction system have traditionally been understood from concepts rooted in coordination chemistry. However, since the researches done by Osseo-Assare in the beginning of the 90s^[1], it is now well established that, due to the extractants amphiphilic properties, the organic phases involved in such processes (especially at high solute concentrations) are not molecular solutions of extractants but, rather, structured solutions with an organization at the supramolecular scale. The speciation in organic phase after solvent extraction remains therefore challenging since both level of description have to be assessed concomitantly. To overcome this issue, a new approach, combining experimental studies with molecular dynamic (MD) simulations has been developed.

The solutions were first prepared at the laboratory and characterized in order to obtain: (i) the phases composition (quantitative analysis of all the organic phase constituents) that allowed us to build virtual solution “boxes” for the MD simulations with precisely the same composition than the experimental ones, and (ii) the structural data related to this experimental phases (manly: densities and Small and Wide Angle X-Ray Scattering – SWAXS). Molecular dynamic simulations were then performed and the structural data were computed from the simulation trajectories. As soon as these computed data match the experimental ones (Figure 1), the simulated solution is assumed to be representative of the experimental one. The MD simulation can then be accurately analyzed to describe the structure of the solution at both the molecular and the supramolecular levels.

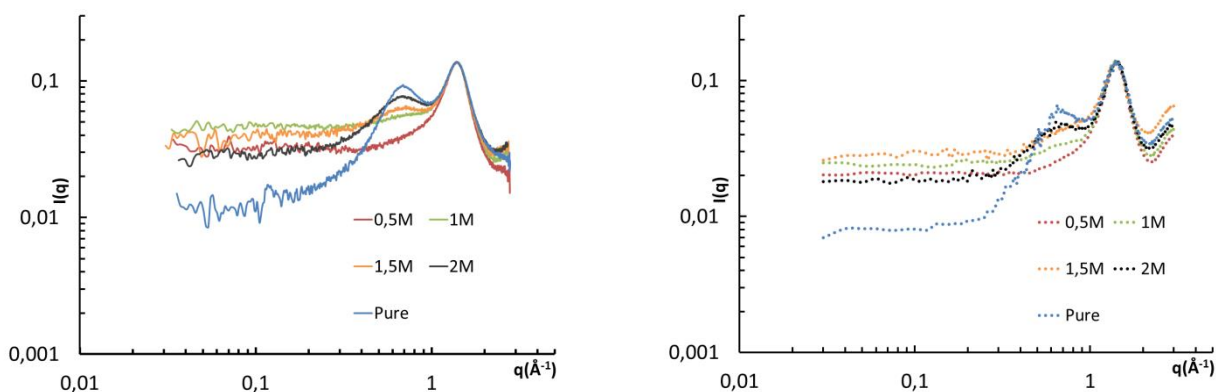


Figure 1: Experimental (left) and calculated (right) SWAXS intensities for organic solution of DEHBA in *n*-heptane after water extraction with increasing extractant concentration.

These simulation results, coupled with analysis of additional experimental data (ESI-MS spectrometry, IR spectroscopy) give information about the environment of the species and allows to get visual representations of the structures at both the molecular and the supramolecular levels.

This paper presents the application of this methodology to the extraction of water and uranium(VI) from

nitrate media by monoamide and malonamide extractant in an aliphatic diluent. The effect of the structure of extractant molecules on the speciation in the organic phases was investigated.

1 Osseo-Asare, K., *Advances in Colloid and Interface Science*, **37**, 123-173 (1991).

Key words: Uranium, monoamide, malonamide, speciation, aggregation, molecular dynamic simulation, SWAXS characterization