MATHILDE COQUIL

will present her Ph.D. dissertation

Energetic contributions for liquid-liquid extraction

The defense will take place on **Monday, December 6th, 2021** at **1.30 pm**

in the ICSM Auditorium

In order to respect the procedures for organizing public events in the ICSM auditorium, people who wish to attend the thesis can register before by sending an e-mail to jean-francois.dufreche@icsm.fr. The health pass and the surgical mask are mandatory.

Despite its importance, the description of liquid-liquid extraction is made difficult because the link between experimental methods and molecular dynamics simulations is not direct due to the existence of organization phenomena. We propose a new methodology combining microcalorimetric measurements and molecular dynamics simulations to better describe the nature and strength of interactions in these complex fluids. In the first part of this work, the study of the contribution corresponding to the evolution of the solvation energy in the organic phase is presented. The dilution enthalpies were obtained by microcalorimetric measurements at 25°C for n-dodecane and n-heptane with N,N-di(2ethylhexyl)isobutyramide and for n-dodecane with N,N-di(2ethylhexyl)butyramide. These results were compared using a new method that we present here, to molecular dynamics simulations carried out on these same systems. In particular, we analyzed the influence of the branching of the alkyl chain in the area surrounding the complexing site of the extractant molecules and the role of the diluent. Overall, the excess enthalpy obtained indicates mixtures that have a behavior like regular solutions, but the detailed results show a significant attraction between the extractants, which can lead to the formation of macromolecular entities favoring extraction. In the second part of this work, the study of multicomponent mixtures in the aqueous phase was carried out for different concentrations. A new methodology based on molecular simulations was proposed and applied to binary mixtures ($LiNO_3$ + H_2O) for which experimental dilution data were available. To complete the study of binary mixtures, the system ($UO_2(NO_3)_2$ + H_2O) was also studied. Finally, the same methodology was applied to ternary solutions ($UO_2(NO_3)_2$ + $LiNO_3$ + H_2O). Thus, the partial molar enthalpies of the different salts could be estimated by molecular dynamics in this reference state. In the third part of this work, we studied the organic phase in the same way as for the charged aqueous phases but for quaternary mixtures ($UO_2(NO_3)_2$ + H_2O + DEHiBA + n-dodecane). The aim of this study was to determine the enthalpy of extraction from the calculated partial molar enthalpies of uranyl nitrate in the aqueous and organic phases and the partial molar enthalpies of the ligand and the complex. The enthalpy of extraction was modelled in two different ways, firstly by a complexation model taking into account the formation of the majority species, and secondly by a global uranyl nitrate transfer model taking into account only the change in solvation of uranyl nitrate. This work has shown that calorimetry was a method of choice for linking experiments and molecular dynamics simulations, particularly in the context of the study of complex liquid mixtures used in nuclear energy. The comparison of these two approaches allows a deep understanding of the measurements by quantifying the energy contributions through simulation. Moreover, it allows to validate molecular models by testing thermodynamic quantities directly related to their force fields.

Keywords: Separation chemistry; Thermodynamics; Molecular dynamics; Theorical Chemistry