

PhD project: Physico-chemical characterisation of biphasic aqueous systems for the recycling of metallic ions.

Laboratoire Interdisciplinaire de Physique, Grenoble, France.

In a world of scarce resources, recycling of metals from used technological objects (mobile phones, automotive catalysts, batteries, permanent magnets etc.) is an urgent task. Liquid phase extraction is one of the well-established methods for metal separation and recycling, for which various routes have been explored. Recently, a breakthrough was proposed on the principle of aqueous biphasic systems, based on the aqueous solution of ionic liquids (IL) and strong acid (Ac). The ternary mixture reversibly changes from monophasic at room temperature to a biphasic state over a few tens of degrees. A very efficient and clean way of separating metallic ions was proved this way, since metals turn to find a preferential phase in between the two when the system is heated up. The aim of the present project is to understand the fundamental mechanisms of metal separation in the biphasic state of the ternary mixtures of IL, Ac and water.

The PhD will be articulated into two main parts. In a first part (mainly LIPhy and large scale facilities), we will focus on the description of the ternary mixtures without the addition of any metal, from a structural, dynamical and thermodynamical point of view. We will combine optical techniques such as UV/vis absorption, light scattering and transient grating spectroscopy to describe the appearing (vanishing) interface during the phase separation (mixing). Scattering of shorter wavelength radiation such as X-ray and neutrons will then provide structural information on the organization of solution in each of its phases, in particular the nanoscale structures potentially formed by the IL in water and its interaction with acid. Measurement of the diffusion coefficients of the three species from the microscopic scale by Quasi-elastic neutron scattering (giving also access to diffusion mechanisms) to macroscopic distances by Dynamic Light Scattering will enable to quantify the energy barriers leading to the phase separation and its kinetics.

In a second time, we will focus on metallic complexation and formation of coordination compounds in the solution. At the macroscopic scale, the partition coefficient of each chemical species in the biphasic state will be determined by Atomic Absorption Spectroscopy (metals), classical pH-meter (acid), ion selective electrode or ionic chromatography (counterion Cl^-), and NMR (cation of the ionic liquid). By means of X-ray absorption technique (EXAF), we will then characterize the microscopic properties such as complexation of metals with ionic liquid or acid molecules and determine the properties leading to the migration of metals in its preferential phase. The results will enable the determination of optimal concentrations, temperature and species (IL, Ac) for the metallic separation, in view of direct applications for metal recycling.

The PhD student will be in charge of the large scale facilities experiments (diffraction, small angle scattering, quasi-elastic neutron scattering). In between those well scheduled experiments, he/she will perform laboratory characterization of chemical species (Atomic Absorption Spectroscopy, pH-meter titration, ion selective electrode or ionic chromatography and NMR) and physico-chemical properties by UV/vis absorption/fluorescence or Light Scattering to quantitatively determine the partition coefficients, long-range diffusion coefficients, density, viscosity etc., i.e. collecting data in the different phases to complement the microscopic investigations.

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Contact : Marie Plazanet, LIPhy, Grenoble, marie.plazanet@univ-grenoble-alpes.fr

Isabelle Billard, LEPMI, Grenoble, isabelle.billard@grenoble-inp.fr