Permeability of porous liquids

J. Benghozi-Bouvrande, Sandrine Dourdain, S Pellet-Rostaing

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Nom, Prénom : Ben Ghozi-Bouvrande Justine
Responsable CEA : Sandrine Dourdain
Directeur universitaire : Stéphane Pellet-Rostaing
Laboratoire d'accueil : LTSM
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Nowadays, separation of chemical elements is an important stake for many applications. Although liquid-liquid extraction represents the most applied method at industrial scale, it involves many economic and environmental constraints related to the use of large quantities of solvents. There is therefore a growing interest for alternatives as solid-liquid separation and flotation processes which however, require re-designing the actual industrial installations and present limited performances, in terms of extraction capacity and selectivity.

This project proposes to evaluate a new approach allowing to maintain the existing separation installations, by replacing the organic phases of liquid-liquid extraction processes, with a porous liquid. Porous liquids were discovered in 2014 by the Oak Ridge Corporation. They are solid materials made up with hollow nanoparticles of silica, that present the particularity to become liquid when grafted with ionic functions. To date, these materials have only been tested for gas separation. Being at the exact junction between liquid-liquid and solid-liquid extraction processes, porous liquids would allow exploiting the advantages of the two processes.

The first part of the project, based on the article of Zhang and al.[1], is to synthesized nanostructured hollow spheres in both solid and liquid state, and to understand the influence of the different step of synthesis on the morphology and permeability of the nanospheres. An important aspect of this project is therefore to characterize the morphology and the permeability of the hollow nanospheres when they are solid and liquid. For extraction application, it appears indeed essential to optimize the different steps of the synthesis to ensure accessibility of the inside volume of the cavities to hydrophilic solvents, solutes, and metallic cations. For this, the solid and liquid materials were characterized with TEM, BET, and SAXS.

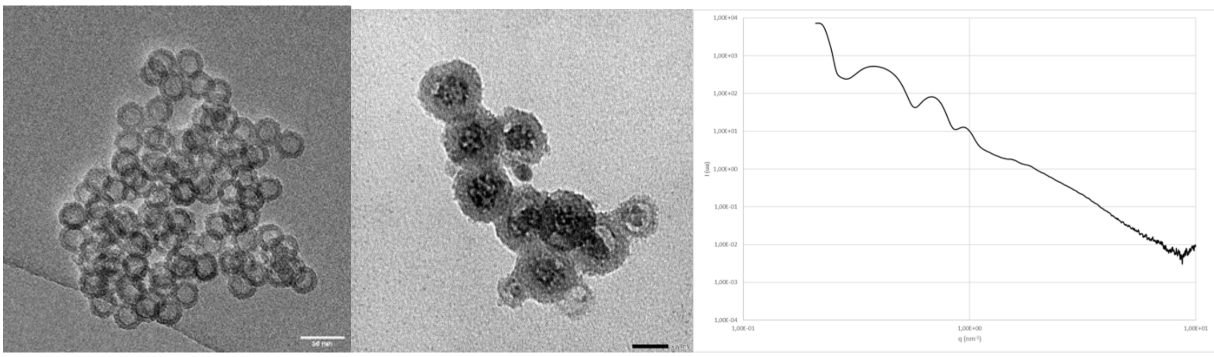

Figure 1 : TEM images of a) hollow silica nanospheres and b) silica nanospheres full of metallic cations and c) SAXS spectra

TEM images and SAXS spectra (Fig. 1) show very well defined and monodisperse hollow spheres with a radius of 17nm. For the solid spheres, gas adsorption indicates an opened porosity with a surface area of roughly 550m²/g. It was also observed that the solid spheres are permeable to water and solutes, as that they can induce the precipitation of metallic cations into the cavities.

When grafted with ionic shell the solid nanospheres become liquid. The challenge is herein to characterize the diffusion of water and solutes when this porous liquid is put in contact with an aqueous solution.

For this we plan to combine SAXS and SANS measurements to identify the contrast variation in presence of water and solutes (contrast matching D_2O/H_2O). NMR and QUENS measurements will also be performed to identify the diffusion and confinement of the various species.

[1] Zhang and al., Angew. Chem., 127 (2015),946-950