Experimental report

26/04/2022

Proposal: 9-10-1628 **Council:** 10/2019

Title: H2O Permeability of silica porous liquids

Research area: Chemistry

This proposal is a new proposal

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Samples: HS-350°C
HS-550°C
HS-750°C
HS-Sox-1
HS-Sox-2
HS@1
HS@2
HS-+tri
HS-0tri
PL2
PL1
HS-TMB

Instrument	Requested days	Allocated days	From	To
D33	3	0		
D11	0	3	24/08/2020	25/08/2020
			14/09/2020	15/09/2020
			25/03/2021	26/03/2021

Abstract:

The experiment described in this proposal takes part of a study dedicated to the elaboration of new type of porous liquids and to their application for liquid-liquid extraction. Nowadays, separation of chemical elements is an important stake for many applications.
This project proposes therefore to evaluate a new approach by replacing the organic phases of liquid-liquid extraction processes, with a porous liquid. To form such "liquid material" hollow silica nanospheres are made by sol-gel using a surfactant template. They are further grafted: an organosilane grafting followed by an ionic grafting. This ionic bond gives the interesting property to the nanospheres to become liquid.
Preliminar extraction tests showed the silica hollow spheres can extract small amount of metallic cations in some pH conditions. For extraction application, it is therefore essential to characterize in details the permeability of these nanoparticules. By matching the contrast between H2O/D2O and silica, SANS will be applied to characterize the nanospheres structure and permeability, and determine if water reaches the inside of the cavity or if it is stuck in the microporosity.

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Title: H_2O Permeability of silica porous liquids

3 days allocated: 24-25/08/2020; 14-15/09/2020; 25-26/03/2021

Users: Sandrine Dourdain; Justine Ben Ghozi-Bouvrande

Local contact: Sylvain Prévost

Experimental report

The experiment concerned the characterization of a new type of porous liquids that are synthesized for their application in liquid-liquid extraction. We propose to evaluate a new approach by replacing the organic phases of liquid-liquid extraction processes, with a type I porous liquid [1]. These materials are based on hollow silica nanospheres obtained by a surfactant templated silica sol gel. The surfactant is removed by calcination (**HnS**) (or rinsed by Soxhlet with ethanol (**HnS-SH**)) and monodisperse spheres are made (Figure 1).

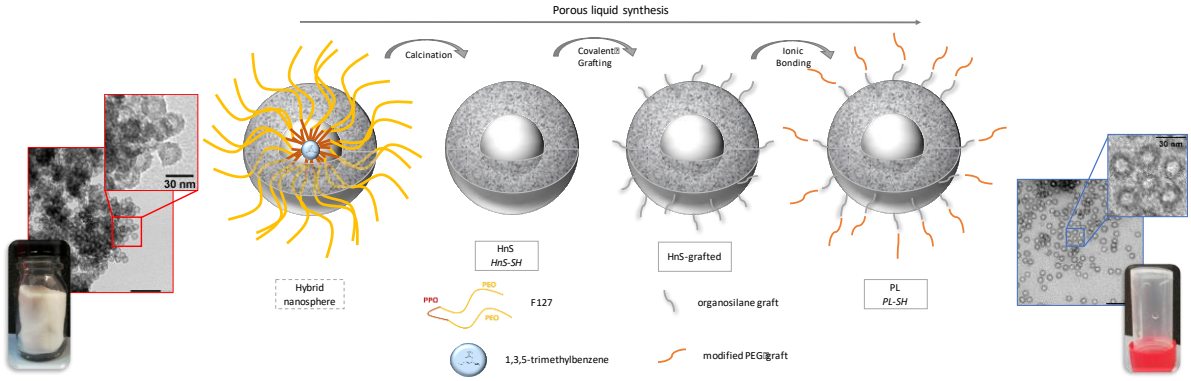

Figure 1: Materials after each step of the synthesis

The spheres are further grafted with an organosilane (**HnSgrafted**) and a PEG interacting thanks to an ionic bond. This ionic corona has the property to turn the solid nanospheres into a liquid material named "porous liquid" (**PL** or **PL-SH**).

An important aim is to evaluate the permeability of these spheres, not only to metallic species but in the first place, to aqueous solutions, in order to consider them for liquid-liquid extraction. We therefore applied SANS experiment to characterize in details the material structure after each step of its synthesis, and their permeability toward aqueous solution thanks to contrast matching experiments.

Dry materials were first analyzed by SANS after each step of the synthesis (Figure).

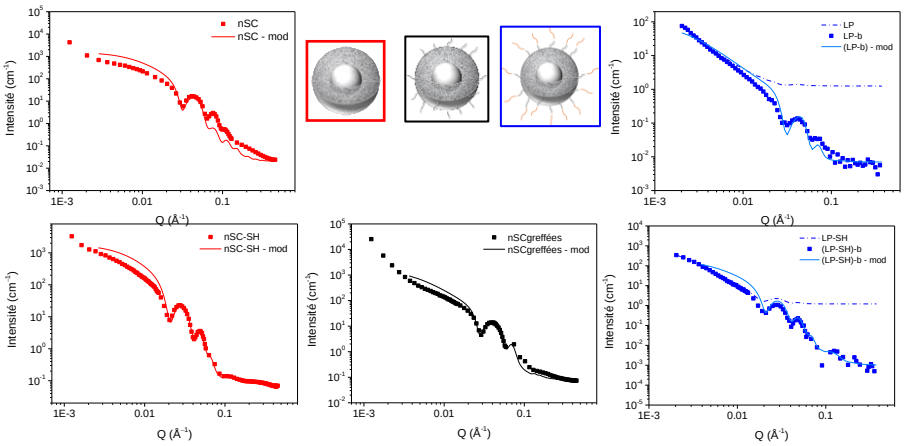

Figure 2 : SANS measurements of samples at each step of the synthesis without any solvent

Incoherent (b) was substracted to the data to highlight the oscillations. Preliminary fit of the data was performed. Results are consistent with monodisperse hollow spheres having a core radius of 6 to 7 nm and a silica shell of 5.5 to 6.6 nm for the calcinated materials. The materials that were rinsed with ethanol to release the organic templates (**HnS-SH)** give bigger hollow spheres with core radius of 12 nm and a silica shell of 7.2 nm.

Contrast matching measurements performed on calcinated hollow nanospheres **HnS** (1st step of the synthesis) are presented in Figure 3. The dry powder (in black) shows oscillations that are typical of monodispersed nanospheres. When the contrast matching solutions are mixed with the powder, the intensity of the scattering intensity is decreased until a minimum at 61.4% of D_2O (inset of Figure 33a).

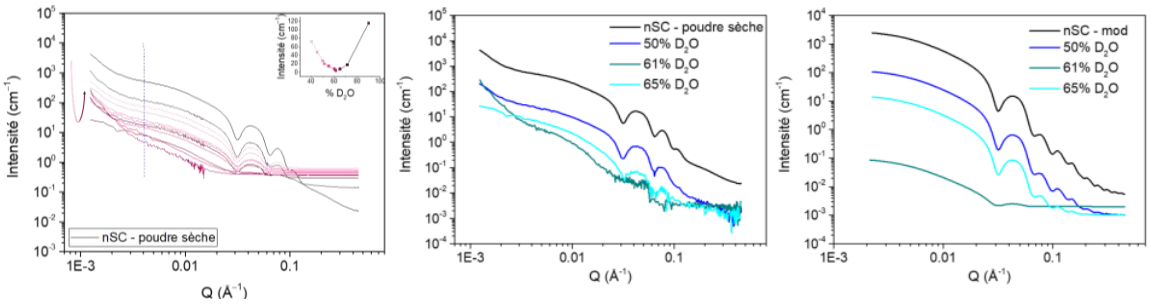

Figure 3: Spectra of SANS H_2O/D_2O matching contrast experiment of HS before (a) and after incoherent signal (b). Sasview simulation of the matching experiment (c).

As simulated with Sasview, such extinction is consistent with a scattering length density (SLD) of 3.68×10^{10} cm^{-2}. As this value matches the SLD of silica, this experiment shows that the silica shell is fully permeable and that the solution penetrates the entire cavity of the hollow spheres. The remaining signal was assigned to bigger spaces between agglomerates of spheres that could not be filled with the solution.

The matching contrast measurements performed with the material which was rinsed with ethanol **HnS-SH** are presented in Figure 4 (Ethanol rinsing was applied instead of calcination to remove the surfactant template without removing some grafted functional groups). Contrary to the HS, the oscillations are not fully extinguished. The minimum of intensity is obtained for 31% of D_2O. To better understand this result, some simulations were performed with SasView (Figure 4).

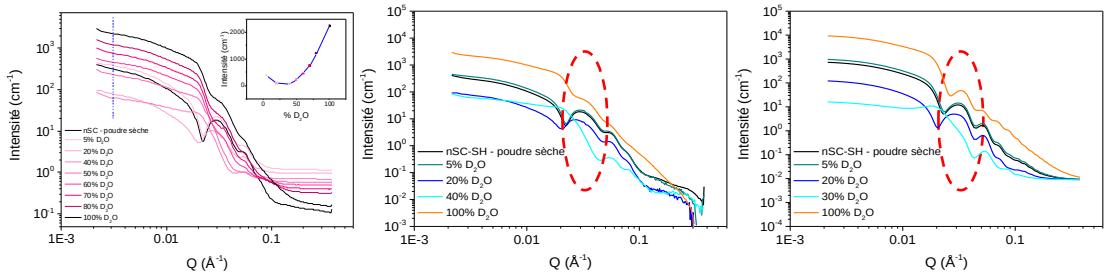

Figure 4: Spectra of SANS H_2O/D_2O matching contrast experiment of HS-SH before (a) and after incoherent signal (b). Sasview simulation of the matching experiment (c).

The attenuation of the oscillation at $0.03 Å^{-1}$ and the overall shape of the data could be reproduced by simulating a core filled with organics (0.65×10^{10} cm^{-2}), and a silica shell having a SLD of 1.6×10^{10} cm^{-2}, corresponding to the SLD measured at the minimum of intensity.

This experiment shows therefore that the material HnS-SH, is not fully rinsed by the Soxhlet treatment and that the porosity is not empty of organics, which explains that the material is not permeable and that the core is not accessible.

The permeability of the final liquid material was also characterized by contrast matching. SANS data of the porous liquid **PL** made from HnS are presented dry and in various D_2O/H_2O solutions in Figure 5. As for the dry PL, oscillations are weak and a strong increase of intensity occur at low Q. It is important to notice that an intense correlation peak appears in presence of water around 0.08Å^{-1}. Origin of this peak was attributed to nanodomains of water formed in the PEG that are grafted at the sphere's canopee. To confirm this hypothesis, the contrast matching was performed with EtOH/EtOD which, as an hydrotope solvent, is expected to prevent such domain formation. Results are shown in Figure 5.

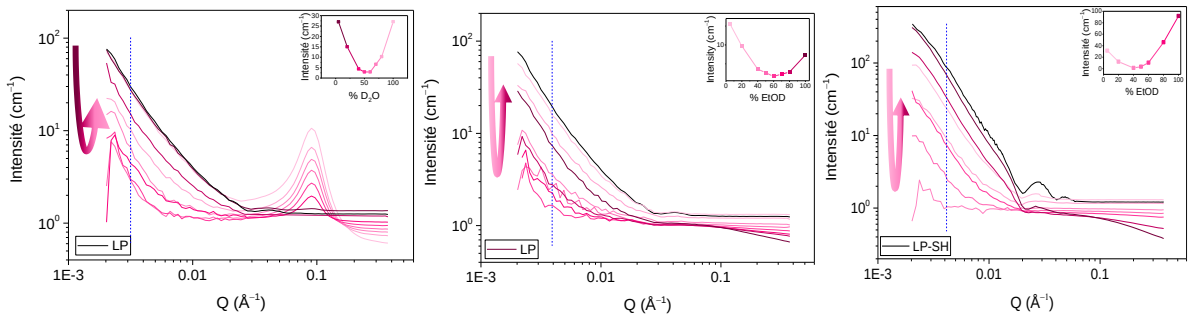

Figure 5: Matching contrast of PL with H_2O/D_2O (a) of PL with EtOH/DEtOD (b) of PL-SH with EtOH/DEtOH (c)

The correlation peak can indeed be removed in EtOH/EtOD solutions, and as shown in the inset of figure 11, the maximum contrast matching was obtained for a EtOD ratio of 60% which is consistent to a SLD of a silica+organic shell material. This results suggests moreover that the solution penetrates the porous liquid and its cavities, and that the PL is permeable to ethanol solutions.

The porous liquid **PL-SH** made from the HnS-SH was further measured in the same conditions. As for the non functionalized porous liquid, extinction seems possible with aqueous solutions but for a D2O ratio below 50%. As for the previous PL, a correlation peak is observed at 0.08 Å^{-1}. A contrast matching experiment was therefore performed with EtOH/EtOD solutions (Figure 5c).
As for the non functionalized porous liquid, the correlation peak disappears in presence of ethanol. The contrast is matched around 45% of EtOD, corresponding to a SLD of $2.65x10^{10}$ cm^{-2}. This low SLD value compare to the one of pure silica indicates that the PL-SH contains a high ratio of organics which is in agreement with the previous results indicating that the Soxhlet rinsing was not efficient to remove all the organic template.
These contrast matching experiments obtained with the porous liquids suggest however that the porous liquids are permeable to the aqueous solution. Proper fit of the data will be necessary to confirm this important result.

As a conclusion, this SANS experiment showed that the porous cavities of the material is accessible at each step of its synthesis (HnS, HnSgrafted and PL). Thanks to this experiment, it was also possible to observe that the Soxhlet rinsing is less efficient than calcination to release the entire porosity of the organic templates. Additional rinsing could further be optimized. This permeability experiment confirms therefore that these new materials are promising for liquid-liquid extraction. These results were presented in the PhD thesis of Justine Ben Ghozi, which defense was on the 14th of January 2022.

[1] Z. Jinshui, S. Chai, Z. Qiao, S.M. Mahurin, J. Chen, Y. Fang, S. Wan, K. Nelson, P. Zhang, S. Dai, Angew. Ch., 3, 2015, 932