Experimental report

26/04/2022

Proposal:	**6-07-70**	**Council:**	4/2020

Title: Permeability of Silica Porous Liquids thanks to coupled in situ SANS experiments and N2 sorption isotherm

Research area: Materials

This proposal is a new proposal

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Samples:
Nanospheres 1
Nanospheres 2
grafted nanospheres 2
Porous liquid 1
Porous liquid 2
Grafted nanospheres 1

Instrument	Requested days	Allocated days	From	To
D16	5	4	03/06/2021	07/06/2021

Abstract:

The experiment described in this proposal takes part of a study dedicated to the elaboration of new type of material, porous liquids, and to their application for liquid-liquid extraction. Separation of chemical elements is an important stake for applications as broad as ore mining, metal recycling or pharmaceutical industry. Although liquid-liquid extraction represents the most applied method at industrial scale, it involves many economic and environmental issues related to the use of large quantities of solvents. There is therefore a growing interest for alternative process as solid-liquid and flotation separation, which however, would require re-designing the actual industrial installations. The present project proposes to evaluate a new approach by replacing the organic phases of liquid-liquid extraction processes, with a porous liquid.

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4 days allocated: 3/06/21-7/06/21
Users : Sandrine Dourdain; Justine Ben Ghozi-Bouvrande
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Experimental report

The aim of this proposal was to characterize and to understand the permeability of some silica porous liquids to gaz, thanks to in situ SANS and sorption isotherms experiments. This experiment takes part to a project dedicated to the elaboration of such new type of material, and to their application for liquid-liquid extraction. In a previous experiment, we characterized the permeability of these materials to aqueous phases (Exp 9-10-1628), which allowed us to identify the synthesis routes giving rise to permeable porous liquids for liquid-liquid extraction.

Here, we wanted to investigate in more detail the porous structure and the permeability of these materials by performing combined gaz sorption and SANS experiments, in order to understand the pores filling mechanisms. Previous studies on silica materials have reported the powerful combination of SANS and N_2 sorption, as the scattering length density of liquid N_2 matches amorphous SiO_2.[1,2,3,5] We therefore proposed to study our materials by in-situ SANS the sorption of N_2 (thanks to the experimental set up (gas sorption analysers) available at the ILL). One of the main challenges of this project concerns the porous liquid itself. Performing a conventional gas sorption isotherm has never been performed on such a liquid material because N_2 sorption requires low temperatures that damage the porous liquid. We therefore took benefit of the whole set up to perform sorption isotherms with C_5F_{12}, a gaz having liquid-to-gaz transition at room temperature and a SLD which is also comparable to the one of silica, in order to follow silica extinction with neutron scattering during the pores filling.

The powder of hollow silica nanospheres were first characterize with N_2 sorption and SANS.

Then C_5F_{12} sorption was applied to the same powder to calibrate the sorption measurement with this new gaz, to finally apply C_5F_{12} sorptions on the porous liquid. The two measured samples are illustrated in figure 1.

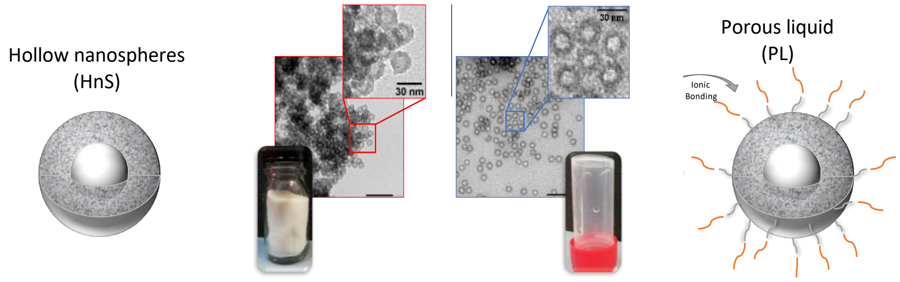

Figure 1 : Illustration and TEM micrographs of NS and PL

The first sample, named HnS in the following, corresponds a powder of hollow silica nano-spheres. The second sample, named PL in the following, corresponds to the same nanosphere that are rendered liquid after the grafting of an organic shell.

<u>Nitrogen sorption in hollow nanosphere powder HNS</u>

According to this type IV isotherm (IUPAC classification), adsorption in the micropores occurs between points A and A'. Then, the mesopores (here the internal cavities) gradually fill with a mono-, then a multi-molecular layer up to point D, after which the capillary condensation induces the filling of the remaining empty volumes of the mesopores (D to E). The 2nd hysteresis loop is attributed to the filling of the interparticle spaces between the silica shells (E to F'). Desorption follows the same path with hysteresis during the desorption of the interparticle spaces between the shells (G-G') and the desorption of the mesopores (H-I).

SANS spectra corresponding to the different stages of the nitrogen adsorption and desorption stages are presented in Figure 2b and c. The oscillations typical of the hollow silica nanopheres are still present at the points A, A', B and C of the sorption, with an accentuation of two oscillations between 0.1 and 0.2 $Å^{-1}$. From point D, all the oscillations are attenuated until almost extinction at points E and F. The remaining signal is attributed inter-particular region that may not be filled with nitrogen, and to the close but not exactly equal SLD of silica and nitrogen (SLD of nitrogen is 3.25×10^{10} cm^{-2} at 77 K while SLD of dense silica is 3.68×10^{10} cm^{-2}).

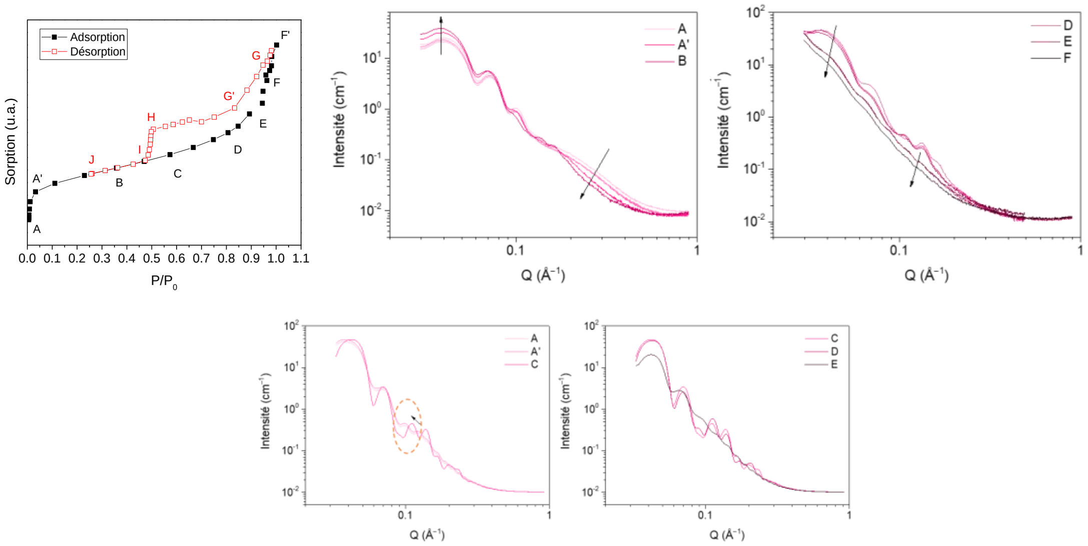

Figure 2 : (a) Nitrogen adsorption-desorption isotherm and SANS spectra of HNS. Experimental (b, c) and (d, e) c*alculated SANS data during nitrogen sorption*

To interpret these qualitative observations, SANS data were simulated at the different stages of sorption. Considering that the HNS material has a silica shell with 5% microporosity (value determined by previous experiments), the SLD of the silica shell was set at 3.45×10^{10} cm^{-2} in the absence of gas and found to be 3.65×10^{10} cm $^{-2}$ when the microporosity of the shell is filled with N_2. In the simulation of the experiment (using Sasview), the parameters were varied in order to reproduce the evolution of the SANS data (Figure 2 d). The obtained nanosphere filling mechanism is illustrated in Figure 3.

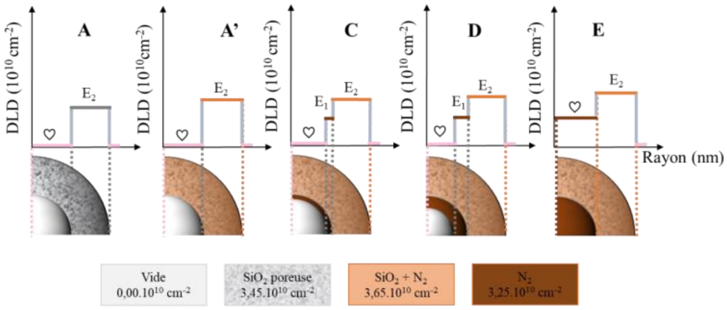

Figure 3: Nitrogen filling mechanism of the hollow nanospheres HNS

This simultation of the evolution of the SANS data is in agreement with the interpretation of a type IV sorption isotherm according to the IUPAC classification: the microporous silica shell fills with nitrogen at low pressures, then the core begins to fill with the formation of a mono then multi-molecular layer of liquid nitrogen on its surface. Finally, the remaining heart of cavities is filled by capillary condensation. The small oscillations between 0.1 and 0.2 Å^{-1} are therefore characteristic of the presence of a layer of liquid nitrogen at the surface of nanospheres cavities. Desorption was also monitored by neutron scattering, showing the same desorption mechanisms.

<u>Perfluoropentane sorption in the powder of hollow nanospheres HNS</u>

The sorption of perfluoropentane was carried out on HNS at 276 K. The adsorption-desorption isotherm is presented in Figure 4 together with SANS spectra. The isotherm has a similar shape with two hystereses: a first between 0.35 and 0.6 P/P$_0$ and a second between 0.6 and 1 P/P$_0$. The rise A-A' corresponding to the filling of the microporosity at low pressure is less marked and spread over a wider range of pressure, due to the larger perfluoropentane molecules. The two hystereses that are attributed (as with nitrogen), to sorption in the mesopores and in the interparticle spaces, are also widened. Desorption branche occurs at lower pressures than with nitrogen because of the larger size of the perfluoropentane molecules. SANS spectra shows the same filling patterns as with nitrogen, showing that:

- The nanospheres are fully filled and therefore permeable to perfluoropentane;

- Perfluoropentane molecules can penetrate the spheres through their microporosity despite their larger size;
- The nanospheres filling and emptying mechanisms established during nitrogen sorption are also valid with perfluoropentane.

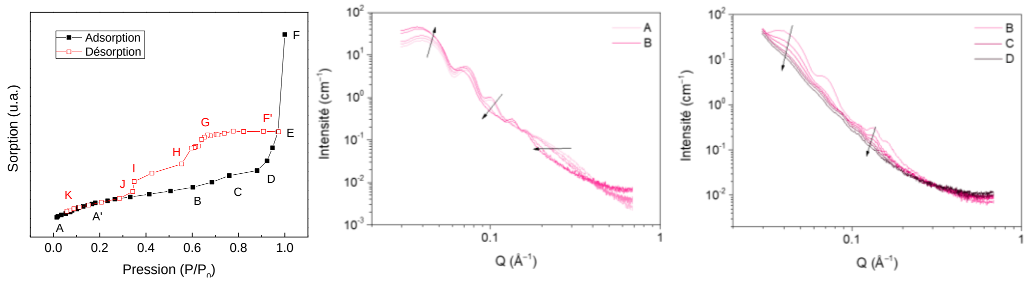

Figure 4 : Sorption isotherm of C5F12 in HNS ; SANS spectra measured during adsorption

Perfluoropentane Sorption in the porous liquid

The porous liquid being very hygroscopic, a long degasing was carried out until the level of incoherent signal of (due to the presence of hydrogens from the sorbed water) reached a minimum value. Figure 5 shows the sorption isotherm of perfluoropentane in the porous liquid. No hysteresis is present around $P/P_0=0.5$. Only a vertical hysteresis similar to a Type V isotherm is present. The high pressures of this hysteresis indicates that to the sorption of the gas occurs in the interparticle spaces between the nanospheres but not in the micro and mesopores of the silica nanospheres.

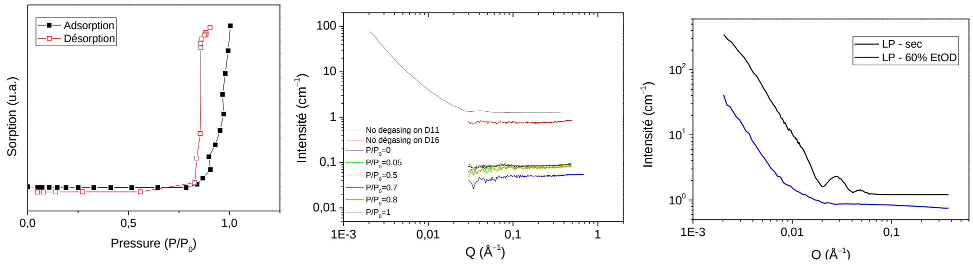

Figure 5: Adsorption-desorption isotherm of perfluoropentane on porous liquid PL ; SANS spectra obtained during degassing and sorption of perfluoropentane in the porous liquid ; SANS spectra of a monidisperse and dry porous liquid measured on beamline D22, and after its immersion in EtOD.

This might be due to several hypotheses: i) The LP is not completely degassed and water is still present, making the pores inaccessible; ii) The LP is not permeable to C_5F_{12}. The gas molecules therefore accumulate around the material. Neutron data acquired during this sorption experiment are also disappointing. Oscillations typical of the porous liquid could not be observed. This problem can be explained by several reasons: i) in order to fill the neutron cell, a large volume of material had to be used, which required mixing several synthesis batches. This had the effect to increase the polydispersity of the measured sample and therefore to smooth the intensity of its oscillations; ii) insufficient degasing, leaving a quantity of water in the sample might fill the pores, and inducing a high level of incoherent signal compared to the oscillations to be measured. For comparison and to show the expected oscillations, a dry and monodisperse porous liquid measured on D22 is presented in figure 5c, as well as the same sample after its immersion in a EtOD solution.

In conclusion, gas sorption in the porous liquid did not give interpretable results. However, this experience allowed to evaluate a large number of essential parameters and constraints to take into account. In particular, a longer degassing would need to be applied to ensure emptying total porosity of the porous liquid. A large volume of sample from the same synthesis batch should also be used to ensure sufficient monodispersity and concentration of silica shells. Finally, this experiment will have to be carried out on a neutron line allowing to reach smaller values of Q in order to better follow the extinction of the signal at smaller angles. A new experiment will therefore be proposed at the ILL as soon as possible in order to evaluate the permeability of the LP but also to study the one of the nanospheres that are grafted by thiols for metal extraction.

[1] S. Ozlem, A. Brandt, D. Wallacher, M. Thommes, B. Smarsly. Langmuir 23, 9, 4724-27.

[2] M. Simone, D.Wallacher, A. Kuschel, S. Polarz, G. A. Zickler, A. Timmann, B. M. Smarsly. Langmuir 26, 9, 6583-92.

[3] J. Dirk, M. Paradiso, D. Wallacher, A. Brandt, M. Hartmann ChemSusChem 2, 2 (2009): 161-64.