Experimental report

06/05/2020

Proposal: **EASY-537** **Council:** 4/2019

Title: Water diffusion into ZIF-8 hydrophobic nanopores

Research area: Materials

This proposal is a new proposal

Main proposer: **Marie PLAZANET**

Experimental team: Marie PLAZANET
Jerome GIRAUD
Julie WOLANIN
Cyril PICARD
Benoit COASNE

Local contacts: Jean Marc ZANOTTI

Samples: ZIF-8

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	48	72	18/02/2020	21/02/2020

Abstract:

Water dynamics in highly hydrophobic nanopores is almost unexplored experimentally but relevant for a large number of confining systems and applications. The Metal Organic Frameworks, ZIF-8 is a promising candidate for such a study because of its large porosity, strong hydrophobicity and water stability. Liquid water is present within the nanopores only above 240 bars.
The goal of this proposal is to complete a previous experiment in the aim of quantifying the diffusion coefficients of water confined within ZIF-8 cavities from QENS measurements. This characterization relies on a comparison between measurements at low pressure in presence of bulk water only around nanoporous ZIF-8 particles and measurements at high pressure with both confined water within the nanopores and bulk water around the ZIF-8 particles.

Experimental report

Context

Only little is known on the water dynamics in hydrophobic nanopores contrary to hydrophilic systems. The proposed study is focused on the zeolitic imidazolate framework 8 (ZIF-8: Figure 1), a particularly interesting candidate for energy storage applications. This material has a pore opening of 3.4 Å and cages of 11.6 Å and presents key characteristics as a large porosity, a strong hydrophobicity and water stability.

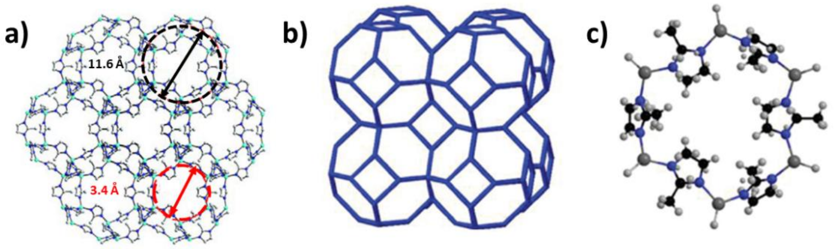

Figure 1: a) ZIF-8 structure: spherical cages connected by narrow gates, with diameters of 11.6 and 3.4 Å, respectively b) Global organization of the cages c) Inter-cages gates structure

It has been previously experimentally measured [1] that water penetrates inside the nanopores above 250 bars (ZIF-8 intrusion pressure) at ambient temperature. The aim of the proposed study is to experimentally measure the diffusion coefficients of water trapped in the ZIF-8 nanopores. It is already known that below 250 bars, there is only bulk water around ZIF-8 particles, whereas above 250 bars, two water populations, inside and outside the nanopores are present.

Results

Experiments were performed using a homemade high-pressure cell made of 7075 aluminium alloy. The sample is contained in a parallelepipedic flat cuvette, the dimensions of which are 30 x 20 x 0.2 mm. The internal surface of the aluminium cell has been coated by a thin gold layer to avoid corrosion of the surface by ZIF-8 (Figure 2).

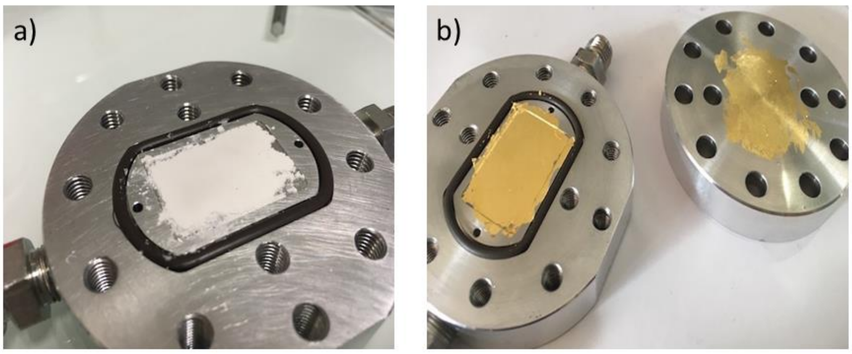

Figure 2: a) Picture of the filling of the cell with ZIF-8 (test before coating) b) Gold coated cell

The following measurements have been carried out: empty cell, bulk water, ZIF-8 dry and hydrated ZIF-8. The hydrated ZIF-8 has been measured at four hydrostatic pressures (40, 200, 280 and 380 bars). Based on the ZIF-8 amount contained within the cell, the volume fraction of bulk water is of the order of 30%, below 250 bars; above 250 bars, there is 30% bulk water plus 23% confined water. As expected, the quasi-elastic spectra obtained at 40 and 200 bars on the one hand, and at 280 and 380 on the other hand, are identical. $S(\omega)$ spectra are shown in Figure 3.

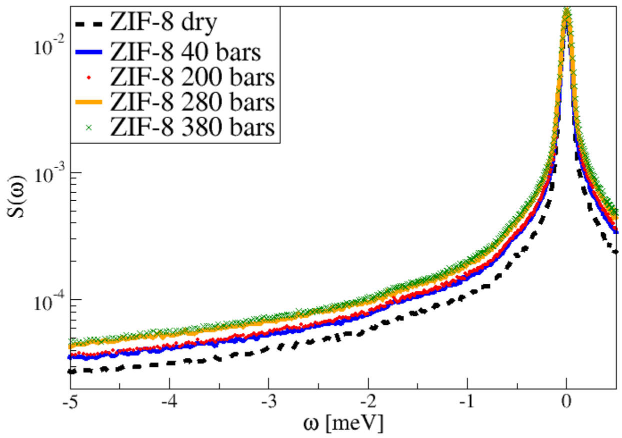

Figure 3: Sum over Q, from 0.6 to 1.9 Å^{-1}, of the quasi-elastic spectra of the ZIF-8 dry and hydrated samples

QENS spectra were fitted by two Lorentzian functions supposing that the first one corresponds to translational motion and the second to rotational one, and assuming that both motions are decoupled. The translational motion was described with the Fick's law.

Bulk water:

Fitting spectra corresponding to bulk water, including the empty cell as a background and a sample transmission of 0.9, gives results in accordance with the literature [2,3]. Indeed, the translational diffusion coefficient was found to be (2.13 ± 0.08)x10^{-5} cm^2/s and the rotational diffusion constant 2.28 ± 0.23 ps^{-1}.

ZIF-8:

Diffusion coefficients of the hydrated ZIF-8 are given in Table 1. The ZIF dry spectra and the ZIF-8 low pressure spectra have been included as background, respectively, for the analysis of the ZIF-8 low pressure and high-pressure data. For both cases, the sample transmission was fixed to 0.95 corresponding to ~ 80 µm of water.

Table 1: Numerical values of the extracted fitting parameters.

	D_T [cm^2/s] - self diffusion coefficient	D_R [ps^{-1}] - rotational diffusion constant
ZIF-8: low pressure (<250 bars)	(1.99 ± 0.15) x10^{-5}	2.5 ± 0.5
ZIF-8: high pressure (>250 bars)	(1.22 ± 0.15) x10^{-5}	2.2 ± 0.3

Water dynamics around the nanopores is similar to that found for bulk water alone. Assuming that the water present outside the ZIF-8 matrix is identical for both low and high pressure, the analysis of the water inside the pores above 250 bars, shows the existence of a non-negligible confinement effect. We can highlight a general slowing down of the water dynamics confined in the ZIF-8 matrix.

QENS experiments have demonstrated a bulk-like behaviour for ZIF-8 below 250 bars and a much slower behaviour for water trapped in the nanopores above 250 bars. It confirms the existence of one water population at low pressure and the existence of two at high pressure.

References

[1] Michelin et al., *Phys. Rev. Lett.* **2015**, *115 (3)*, 036101
[2] J. Teixeira et al., *Phys. Rev. A* **1985**, *31*, 1913 1917
[3] Yoo et al., *J. Phys. Chem. Lett.* **2011**, *2*, 532–536