Experimental report

03/07/2017

Proposal: **9-12-444**

Council: 4/2016

Title: Dynamics of Water in ZIF8 and gateopening

Research area: Materials

This proposal is a continuation of TEST-2526

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Samples: $C_8H_{12}N_4Zn$

Instrument	Requested days	Allocated days	From	To
IN13	10	0		
IN6	5	5	30/11/2016	05/12/2016
IN5	5	4	31/08/2016	05/09/2016

Abstract:

Water transport and dynamics in hydrophobic nanopores is of general interest for industrial applications and microscopic systems such as proteins. Among the Metal Organic Frameworks, the ZIF-8 material is a promising candidate because of its large porosity, strong hydrophobicity and water stability. However, water dynamics inside ZIF8 has not been studied yet essentially because of the high pressure required for water intrusion inside pores. In addition, ZIF-8 presents specific selectivity mechanism due to the flexibility of 3Å gates separating the 12Å cavities.

The goal of this proposal is to model the dynamics of water inside cavities, to understand the transport through ZIF-8 gates and measure diffusion coefficient. The goal of this proposal is also to study the flexibility of the gates, that are considered critical to transport and ZIF-8 hydrophobicity.

Experimental Report: 9-12-444

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Confined water has been extensively studied, but up to now in hydrophilic confinement or confinement with moderate hydrophobicity such that a water vapour spontaneously condensate within the confinement. The goal of this experiment is to study the dynamics of water in strongly hydrophobic nanometric confinement that remains empty of liquid water even immersed in liquid water at ambiant pressure. The filling of the pores is obtained by the pressurisation of the surrounding liquid. The material used in this experiment is the water stable Metal Organic Frameworks ZIF-8 that presents a porosity of 50% in volume fraction, and a strong hydrophobicity. ZIF-8 presents 12 Å cavities interconnected through 3 Å gates. ZIF-8 behaves as a molecular sieve and do not let ions penetrates into the nanoporosity. Water dynamics inside ZIF8 has not yet been studied essentially because of the high pressure of 24 MPa required for water intrusion inside the pores. The pressure has to be supplied with a significant change in volume of the sample during the intrusion process of the order of 25% of the initial volume.

Instruments

Quasi-elastic neutron scattering experiments are done with two complementary time-of-flight spectrometer in order to cover a larger Q range. The IN5 line is used at $\lambda = 10$ Å giving access to a resolution of 11 µeV or a typical time window of 10 ps and a Q-range [0.1-1.0] $Å^{-1}$. The IN6 line is used at $\lambda = 5.1$ Å giving access to a resolution of 80 µeV or a typical time window of 100 ps and a Q-range [0.3-2.0] $Å^{-1}$.

Equipment

Experiments are carried out with high pressure equipments developed by the SANE service. The 13PL25TZ12 TiZr cell has been used in combination with an aluminium (AW-7049A-T6 alloy) insert. The insert comprises a rectangular slit of 1.1 mm thickness, 10 mm width and 46 mm depth. This combination of TiZr cell and aluminium insert is able to sustain both pressure and temperature. The pressure is applied through the "Louise" cabestant pump, that can handle our pressure precision requirements. For our soft matter experiment we must control pressure between 20 MPa and 40 MPa with a maximum deviation of 3 MPa. The temperature is adjusted between 10°C and 80°C using a orange cryofurnace. The drawback of this setup is the absence of mechanical separator between our sample, made of a nanoporous powder suspended within an aqueous solution and the fluorinert, used as a pressurisation fluid. The separation of the two fluids rely only on their low miscibility and capillary effects.

Samples and measurements

Water does not adsorb spontaneously in ZIF8[1]. The pure water intrusion starts at 25 MPa and is completed at 33 MPa while its spontaneous extrusion starts at 22 MPa and is completed at 15 MPa. Samples are prepared in advance. The powder of ZIF-8 (BASF) is suspended in water and submitted to a cycle of intrusion/extrusion to remove any air bubble and obtain a slurry of ZIF8. This slurry is injected with a 1

1. M. Michelin-Jamois et al. (2015). Giant osmotic pressure in the forced wetting of hydrophobic nanopores, *Phys. Rev. Lett.* **115**, p. 036101.

mm in diameter syringe in the aluminium insert. The powder volume fraction is 50% for the experiments on IN5 and 30% for the experiments on IN6. We check in the dry ZIF that no QENS arised from the ZIF matrix in the probed temperature range. This result is further confirmed comparing the signal obtained with native hydrogenated ZIF-8 and deuterated ZIF-8.

In order to compare the fully empty state and the fully filled state of ZIF-8, samples are submitted either to a pressure of 10 MPa (empty state) or a pressure of 40 MPa (filled state) to keep a safety margin with respect to intrusion and extrusion pressures. The pure water case with ZIF8 is studied on IN5 at 280, 300, 313, 323, 336, 346 and 356 K. The pure water case with ZIF8 is studied on IN6 at 283, 305, 323, 343,and 383 K. The behavior of ZIF8 with pure water is compared to the behavior of ZIF8 in 5 M LiCl solution characterized on IN6 at 293 K. Because of the shift of intrusion pressure due to the osmotic effect, a 60 MPa pressure is used for this last experiment. For correction purposes and normalisation, the signals given by pure solvent samples as well as vanadium and cell with dry ZIF-8 are also acquired both on IN5 and IN6.

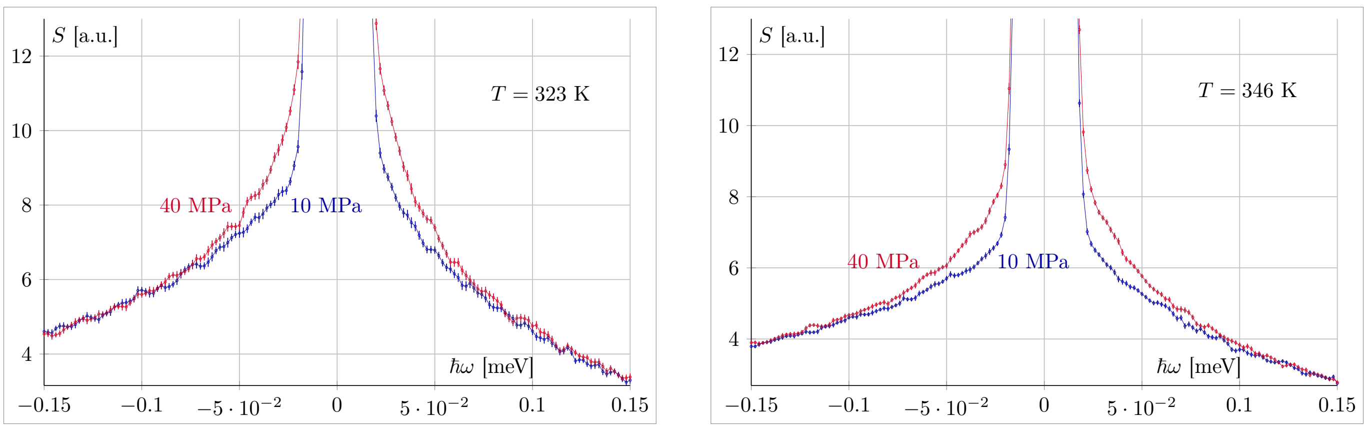

FIGURE 1 – Dynamical structure factor for $q = 1$ Å^{-1} measured at 10 MPa in absence of confined water and at 40 MPa in presence of confined water into ZIF8.

The figure 1 shows, for a wave vector $q = q = 1$ Å^{-1} and two different temperature, the structure factor obtained from measurement carried out on IN5 with a slurry of ZIF8 particle dispersed in water. At a pressure of 10 MPa, lower the intrusion pressure, water is only present outside of the particle, but not inside the pore. The quasi-elastic contribution of the structure factor, shown in blue, is associated to the water surrounding particles, that should behave mainly as a bulk water if the impact of the surface of the particle is neglected. At a pressure of 40 MPa, larger than the intrusion pressure, part of the water has migrated into the pores. The structure factor, shown in red, demonstrate a visible discrepancy of its quasi-elastic contribution with respect to the case at low pressure. This difference can be attributed to the specific behavior of the water confined into the pores.

In order to extract the properties of water attempts were made to fit the quasi elastic contribution. After several tests of various functions, we concluded that the most physical and suitable model to be fitted is composed of an elastic peak, a rotational-translational component of bulk water, and an extra lorentzian component accounting for non-bulk water population. This population is associated to the water confined in ZIF and in contact with ZIF grain surface. The bulk water component was constrained to have a rotational radius of 1 A, a rotational diffusion constant following the Arrhenius behavior given by Teixeira et al (PRA 1985), while the translational diffusion constant and residence time were free parameters (we check that they were close to expected values for bulk water in the given thermodynamic conditions). The rotational, translational diffusion constants and residence time were kept fixed at a given temperature for a pressure of 10 and 40 MPa. Data were reduced and fitted with the LAMP program and str_fit function (model Iri2). No empty can was subtracted, instead the high intensity of the pressure cell was included in the elastic line, with the signal arising from the ZIF material.

The figure 2 shows the translation diffusion coefficient of bulk water in presence and absence of ZIF8

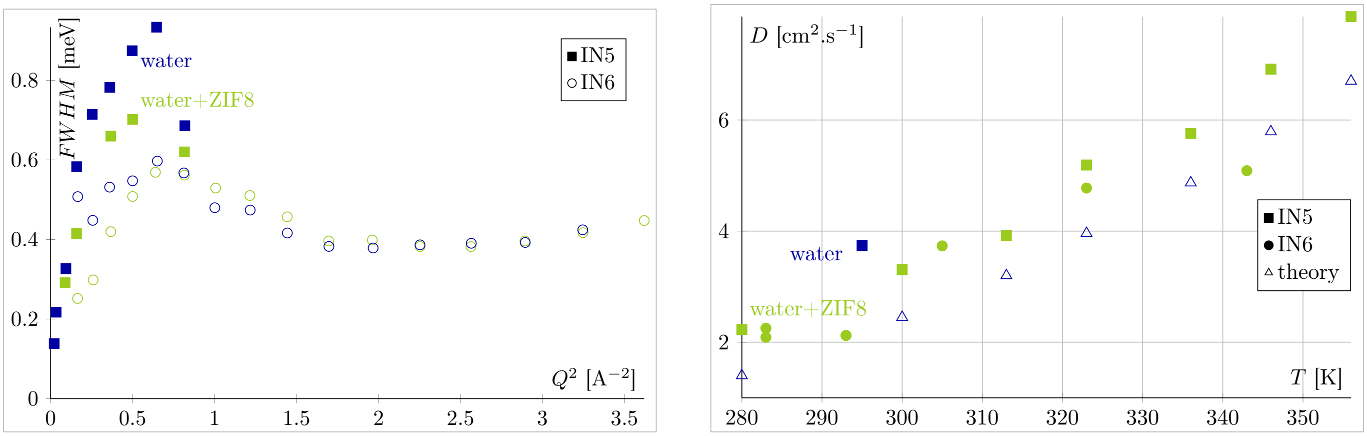

Figure 2 – FWHM of Lorenzian contribution and translational diffusion coefficients for the bulk water in presence or absence of ZIF8.

particles. A slight discrepancy is observed between these two situations. Moreover the experimental pure water case (filled blue symbol) is shifted with respect to the theoretical values (blue open symbol). We attribute this discrepancy to the presence of multiple scattering. This multiple scattering might explain the need of a lorenzian contribution required to fit our data obtained with pure water. We note also a discrepancy between the fit obtained from the data acquired on IN5 and IN6 that could also be attributed to multiple scattering. We are currently correcting our data in order to take into account the contribution of the multiple scattering.

Conclusion

This experiment was successful in demonstrating the feasibility of measurements on ZIF8 samples with water under pressure. We successfully measured QENS signal at low and high pressure respectively in absence and presence of confined water. The raw data shows a deviation in the quasi-elastic contribution according to the pressure level. A fine analysis incorporating the contribution of multiple scattering is on the way in order to characterize the properties of water confined into the hydrophobic cages of ZIF8 according to the temperature.