Experimental report

09/02/2016

Proposal: **TEST-2526** **Council:** 4/2015

Title: Dynamics of water in nanoporous materials

Research area:

This proposal is a new proposal

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Samples:

Instrument	Requested days	Allocated days	From	To
IN13	4	4	16/10/2015	20/10/2015

Abstract:

Experimental Report: Test 2526

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Instrument: IN13
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Users: Loïc Michel (LiPhy, PhD student), Cyril Picard (MCf UGA)

The first objective of the test was to demonstrate the feasibility of elastic incoherent neutron scattering on ZIF8 samples in solution and under pressure. The second objective was to measure the motion of the so called "gates" found in ZIF8, a microporous Metal Organic Framework (MOF). ZIF8 is made of spherical cages of 1.2 nm diameter interconnected by gates of 0.3 nm. The flexibility of the gates, thought to be critical to the selectivity of ZIF8 upon organics adsorption, is studied spectroscopically. In particular the goal of this study is to understand the low water affinity and high water stability of ZIF8 in contrast to other MOF material. Most MOF indeed spontaneously adsorb water vapour and are unstable in water. We hypothesize that the water intrusion in ZIF8 that is initiated at a pressure of 250 bars is related to the gate motion. This motion would be the key to understand the effective hydrophobicity of ZIF8.

Equipment

Experiments are carried out with a specific pressure cell developed by the SANE service. Pressure is applied through the "Louise" cabestant pump, that is the only one available that could handle our pressure precision requirements. For our soft matter experiment we must control pressure between 20 bar and 400 bar with a maximum deviation of 10 bar.

Instrument

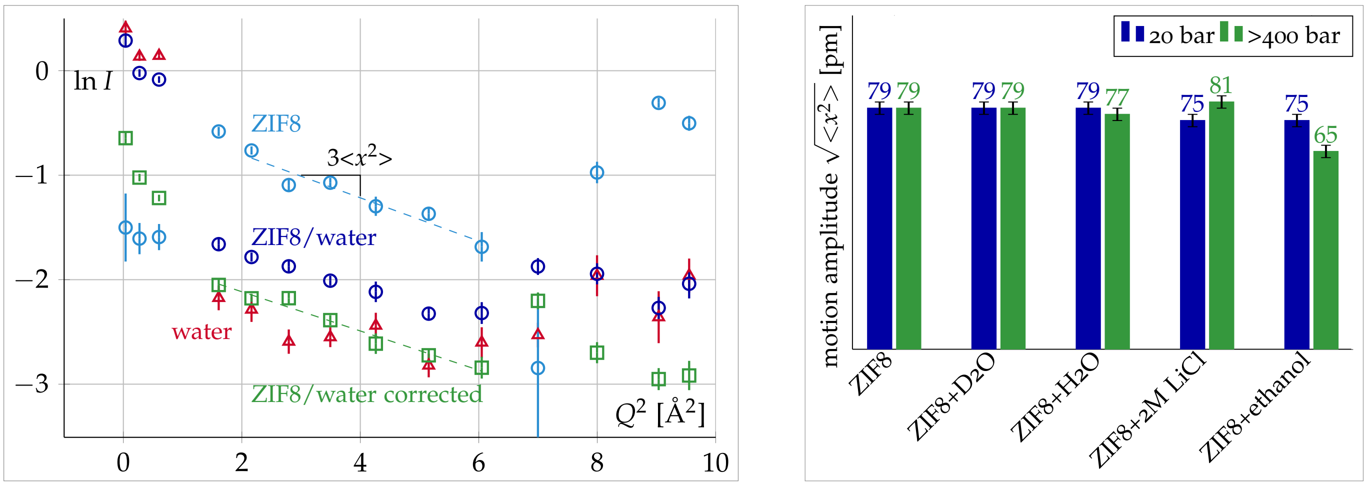
IN13 is a backscattering spectrometer that gives access to the high Q range (0.2 to 4.9 $Å^{-1}$) with a high resolution of 8 µeV that let us probe the 100 ps time window. This time window lets water diffuse on a 2.5 nm scale that is beyond the space scale we probed, so water signal does not screen the range of Q or interest of this sample between 1.2 $Å^{-1}$ and 2.5 $Å^{-1}$. This range lets us measure the mean square displacement of 2-methlImidazole protons contained in the ZIF8 gates.

Samples

Water does not adsorb spontaneously in ZIF8[1]. The pure water intrusion starts at 250 bars and is completed at 330 bar while its spontaneous extrusion starts at 220 bars and is completed at 150 bar. In order to compare the fully empty state and the fully filled state of ZIF-8, samples are submitted either to a pressure of 20 bar (empty state) or a pressure of 400 bar (filled state) to keep a safety margin with respect to intrusion and extrusion pressures. Samples are prepared in advance with a cycle of intrusion/extrusion of water to remove any air bubble and obtain a slurry of ZIF8 in water, that can be injected in the Louise pressure cells. The behaviour with pure water is compared to the behaviour of ethanol, that spontaneously fills ZIF-8 and the behaviour with a salt solution that shifts intrusion/extrusion pressures to higher values due to an osmotic effect[1]. We used a sample of 2 mol/L of LiCl that intrudes at 350 bar and that is studied at 20 bars and 450 bar. For this set of experiments the ZIF8 synthesised by BASF has been used. In each case the solvent volume fraction in the slurry is less than 0.6. For correction purposes and normalisation, the signals given

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

by pure solvent samples as well as vanadium and empty cell are also acquired. The signals are corrected in LAMP for transmission, then empty cell was subtracted and vanadium used for the detector normalisation. The solvent intensity was then subtracted from the sample intensity according to the solvent volume fraction to yield the corrected ZIF8 Intensity. According to the Gaussian approximation[2] $I = I_0\, e^{-\frac{1}{3}<x^2>Q^2}$. Elastic incoherent scattering intensities I are shown in figure 1A as $\ln I$ versus Q^2 plots for water and ZIF8. This lets us appreciate the occurrence of a clear linear tendency in the ZIF8 signal spanning from 1.6 Å^{-2} to 6 Å^{-2}. The signals for Q^2 values smaller than 1.5 Å^{-2} are associated to bound water motions. The ZIF8 signal is attributed to the only protons in the ZIF8 sample located within the 2-Methyl-Imidazole linkers that are submitted to rotational fluctuations[3]. The slope s of the curve is proportional to the mean square displacement of methyl groups related to the motional amplitude around the mean position from crystallographic data. The proton motion amplitude is extracted from the slope s of the curves as $\sqrt{-3s}$. Uncertainties on slopes are estimated from IN13 error bars.



A **B**

FIGURE 1 – A) Elastic incoherent scattering intensities I according to Q values, vertical lines are error bars. B) Motion amplitude from the slopes of the curves in the range 1.6 - 6 Å^{-2}.

The motion amplitudes for the different studied cases are ploted in figure 1B. The effect of pressure on gates fluctuation amplitude is not visible. The presence of water inside pores did not impact the gates fluctuation. This lead us to think of gates motion as independent of water loading. Surprisingly a reduction of 13% is obtained when ethanol is pressurized inside the pores. Currently we do not have any explanation for this result.

Conclusion

This test was successful in demonstrating the feasibility of measurements on ZIF8 samples with water under pressure. We successfully quantified linker rotational motion through the methyl group translation amplitude. This motion is found to be pressure independent and not impacted by water inside pores. The gained knowledge on the ZIF8 gates motion under pressure lay the foundation for further investigations of the impact of this gates motion on the dynamics of water inside pores in order to understand the origin of ZIF8 hydrophobicity. In particular, we would like to investigate now the temperature dependence of such effects on IN13 ad the water/liquid motion by QENS on IN6 and IN5.

2. A. Rahman, K. S. Singwi, and A. Sjölander (1962). Theory of slow neutron scattering by liquids. I*, *Phys. Rev.* **126**, pp. 986–996.
3. M. R. Ryder et al. (2014). Identifying the role of terahertz vibrations in metal-organic frameworks: From gate-opening phenomenon to shear-driven structural destabilization, *Phys. Rev. Lett.* **113**.21, pp. 1–6.