Experimental report

30/09/2024

Proposal:	**6-07-90**	**Council:**	4/2021
Title:	Water dynamics in mesopores with aperiodic distribution of ionic surface charge		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: water-filled BETVA(+)-PMOs (silica with organic surface molecules)

Instrument	Requested days	Allocated days	From	To
IN16B	3	3	27/08/2021	30/08/2021

Abstract:

The dynamics of liquid water in spatially confined geometry has been extensively studied, especially using mesoporous silica as a model system. According to the abundant QENS literature, it appears that the chemical nature of the surface of nanoporous materials can be envisioned as a driving parameter of water dynamics.

Our aim is to make use of this phenomenon in order to tune the interfacial mobility of nanoconfined water from a spatially controlled activation/deactivation of the surface electrostatic charge of the mesopores. The rationale of the project relies on our capability to design nanochannels that exhibit a periodic succession of neutral/charged nanodomains comprising inorganic and organic cationic units, which are perfectly localised along the main pore axis at the molecular scale.

Our measurements at IN16B will complement those data to be acquired during an already scheduled beamtime at SHARP.

6-07-90 Water dynamics in mesopores with a periodic distribution of ionic surface charge

Summary The proposal aimed at characterizing the dynamics of water in nanoporous materials with strongly interacting surface adsorption sites. These highly polar sites are obtained by introducing either electronegative halogenic or ionically charged ammonium groups in the pore wall.

QENS experiments were successfully performed on IN16B for 2 different Periodic Mesoporous Organosilicas (PMOs). Three different hydration levels (dry, 33%RH and 75%RH) were studied for the ionically charged PMO, and two different hydration levels (dry and 75%RH) for the fluorinated one. QENS spectra were acquired at three temperatures (243, 258, 278K) were selected.

The data reduction has been finalized. All the results have been modelled and interpretated. On the timescale of IN16B, the quasielastic broadening seen in hydrated PMOs could be attributed to water molecules that exhibit translational diffusion. The motion is consistent with jump-diffusion model. The obtained values of the diffusion coefficients and residence times demonstrated that incorporating polar adsorbing sites led to a considerable slow down with respect to pure porous silicas and hydrophobic PMOs that were studied previously.

QENS experiments were performed on IN16B during 3 days, from 27/08/2021 to 30/08/2021. The main objective of the proposal was to determine the impact of ionic neutral/charged nanodomains on nanoconfined water dynamics. For that purpose, Periodic Mesoporous Organosilicas PMOs comprising a quaternary ammonium cation (BTEVA+) and Fluorobenzene bridging unit were successfully synthesized. The perfect triangular arrangement of mesopores and the perpendicular periodic distribution of ionic sites were confirmed by SAXS and WAXS, respectively (cf. Figure 1). The porosity was further characterized by BET and IR, and the nanoconfined water by DSC. The structural parameters of the ionically charged PMO are pore diameter (3.8 nm), pore volume (0.816 cm^3g^{-1}), surface area (1200 m^2g^{-1}), and longitudinal period of cationic sites (1.17 nm).

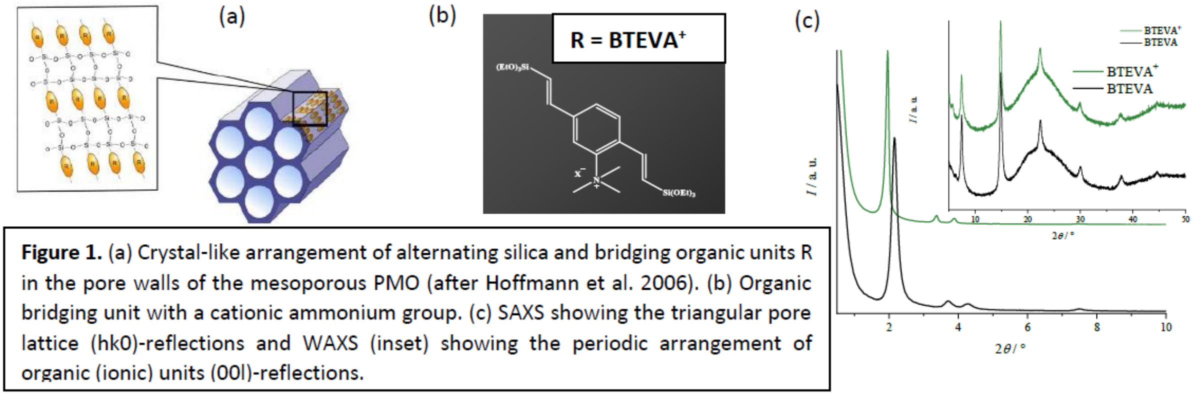

Figure 1. (a) Crystal-like arrangement of alternating silica and bridging organic units R in the pore walls of the mesoporous PMO (after Hoffmann et al. 2006). (b) Organic bridging unit with a cationic ammonium group. (c) SAXS showing the triangular pore lattice (hk0)-reflections and WAXS (inset) showing the periodic arrangement of organic (ionic) units (00l)-reflections.

The PMOs were synthesized at the University of Hamburg. The different samples were prepared and filled in flat aluminum cells well in advanced at the university of Rennes. In total, 5 samples were prepared, hydrated in controlled humidity chamber and hermetically sealed in neutron cells: i.e. dry, 33%RH, 75%RH for ionically charged PMO, and dry, 75%RH for F-PMO, respectively.

An ILL cryofurnace was used to control the temperature. QENS spectra were acquired at three selected temperatures 278K, 258K, and 243K. Fixed windows scans at 0 and 3ueV were also acquired during the cooling ramp between these temperatures. Spectra of very good quality were obtained after 5 hours of counting time. They exhibited obvious quasielastic broadening for the hydrated samples with clear Temperature and Q-dependence (cf. Fig. 2), while the neutron scattering intensity was essentially elastic for the dry samples.

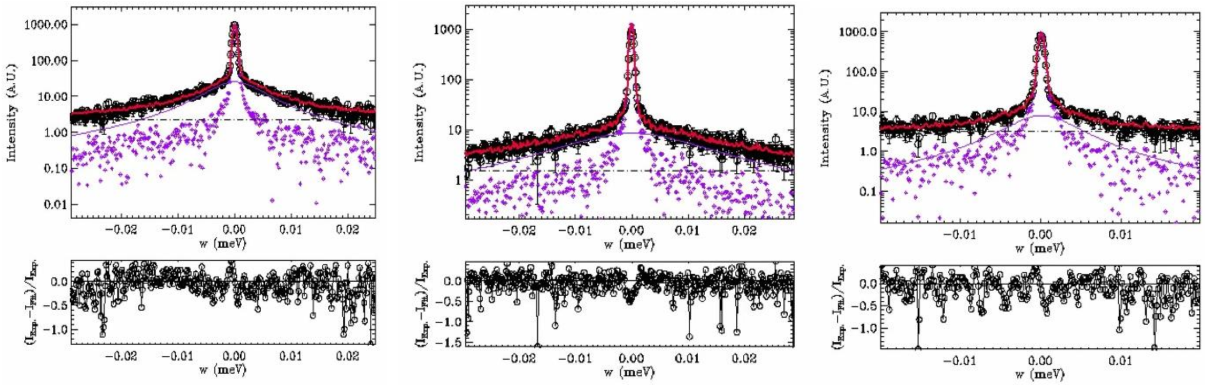

Fig. 2 Spectra of water filled ionically charged PMO (75%RH) at transfer of momentum Q=1.3Å^{-1} and three temperatures 243K, 258K, 278K from left to right. The fitted function (red line) including a Lorentzian term (violet line), a constant background (dash-dotted) and the spectrum of the dry matrix (purple symbol).

The data reduction was performed using Mantid scripts. Then, some models were fitted to the data using the QENSH software. A combination of a quasielastic Lorentzian component with the constant background was applied. The purely elastic contribution from the matrix was accounted for by using the experimental spectrum of the dry matrix. The Q dependance of the quasielastic broadening of the different samples is illustrated in Fig. 3. It indicates that the water molecules actually performed translational diffusive motion, that could be fitted by a jump-diffusion model (solid line in Fig. 3).

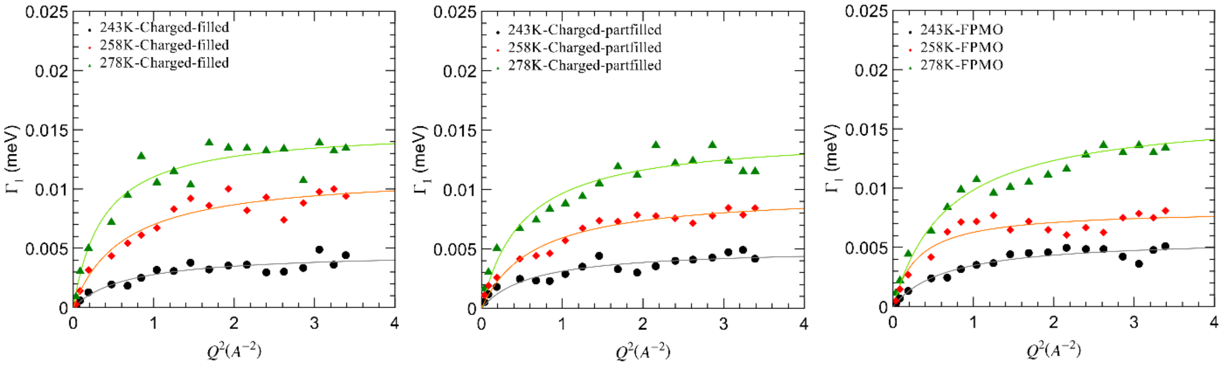

Fig. 3 Quasielastic broadening HWHM of the slow diffusive motion as a function Q and temperature for the water filled (75%RH left panel) and partly filled (35%RH middle panel) ionically charged PMO and water filled F-PMO (75%RH right panel).

Interestingly, the obtained values of the diffusion coefficients and residence times differed markedly from those measured recently on IN16B for water filled porous silica MCM-41 and PMOs with more hydrophobic bridging units [Jani 2021]. It demonstrates that the dynamics of nanoconfined water are extremely sensitive to the presence of ionically charged or highly polar surface sites which lead to a slowdown by a factor ranging from 2 to 5.

[Jani 2021] A. Jani et al. "*Dynamics of water confined in mesopores with variable surface interaction*." J. Chem. Phys. **154** 9 (2021)]