Experimental report

30/09/2024

Proposal:	**CRG-2896**	**Council:**	4/2021
Title:	Water dynamics in mesopores with aperiodic distribution of ionic surface charge		
Research area:			

This proposal is a new proposal

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Samples:
BTEVA+PMO : Bromide-trimethyl-divinylaniline bridged Periodic Mesoporous Organosilica (Powder)
BTEVA-PMO : dimethyl-divinylaniline bridged Periodic Mesoporous Organosilica (Powder)
BTEVAP+PMO : Bromide-methy-pyridine bridged Periodic Mesoporous Organosilica (Powder), Water

Instrument	Requested days	Allocated days	From	To
SHARP	4	4	16/09/2021	20/09/2021

Abstract:

CRG 2896 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 ionically charged Bromo Methyl pyridinium group in the pore wall and compared to the neutral pyridine one. QENS experiments were successfully performed on SHARP+ for these 2 different Periodic Mesoporous Organosilicas (PMOs) for two different hydration levels (dry and 75%RH). QENS spectra were acquired at four temperatures (245, 260, 280K, and 300K).

The data reduction has been finalized. All the results have been modelled and interpretated. On the timescale of SHARP+, the quasielastic broadening seen in hydrated PMOs could be attributed to water molecules that exhibit two motions, i.e., localized libration and translational diffusion. The latter 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 SHARP+ during 4 days, from 16/09/2021 to 20/09/2021. 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 either a methyl pyridinium cation or a neutral pyridine bridging unit were successfully synthesized.

The PMOs were synthesized and fully characterized 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, 4 samples were prepared, hydrated in controlled humidity chamber and hermetically sealed in neutron cells. They corresponding to dry and capillary filled (75%RH) PMOs with neutral and ionically charged surface, respectively.

An ILL cryofurnace was used to control the temperature. QENS spectra were acquired at incident wavelength 5.1Å, resolution 70 microeV at four selected temperatures 245, 260, 280K, and 300K.

Spectra of very good quality were obtained after 4 hours of counting time. They exhibited obvious quasielastic broadening for the hydrated samples with clear Temperature and Q-dependence (cf. Fig. 1), while the neutron scattering intensity was essentially elastic for the dry samples.

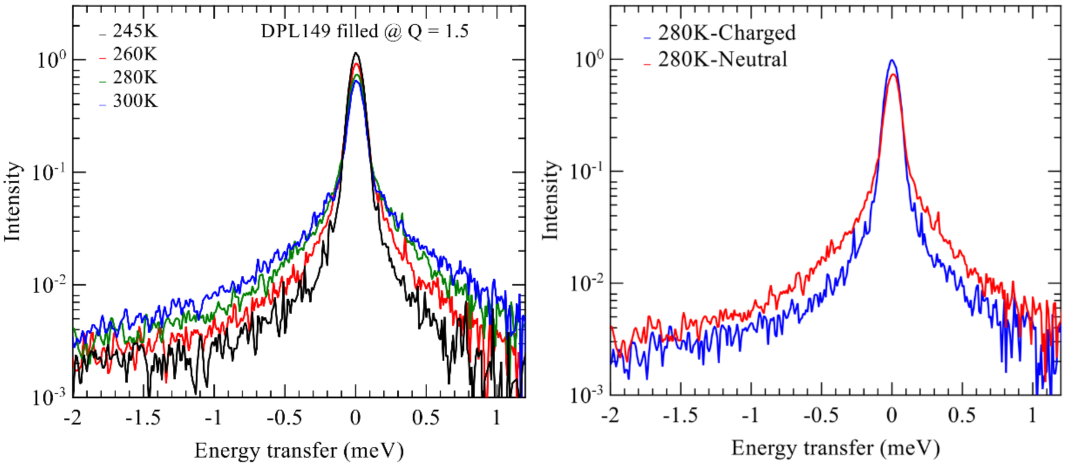

Fig. 1 Spectra of water filled neutral Pyr-PMO (75%RH) at transfer of momentum Q=1.5Å^{-1} and four temperatures 245K, 260K, 280K, and 300K (left panel). Effect of charge surface on the spectrum of water filled Pyr-PMO at transfer of momentum Q=1.5Å^{-1} and T= 280K (right panel).

From the direct visual inspection of the spectra, it is obvious that the water dynamics was much slower when confined in the ionically charged PMO compared to the neutron counterpart (cf. Fig. 1 left panel).

The data reduction was performed using Mantid scripts. Then, some models were fitted to the data using the QENSH software. A combination of two quasielastic Lorentzian components was applied. The purely elastic contribution from the matrix was accounted for by using the experimental spectrum of the dry matrix. The broad component could be attributed to localized libration, as demonstrated by the modelling of its EISF. The Q dependance of the quasielastic broadening of the sharper Lorentzian indicated that the water molecules actually performed translational diffusive motion as illustrated in Fig. 2. It could be fitted by a jump-diffusion model (solid line in Fig. 2).

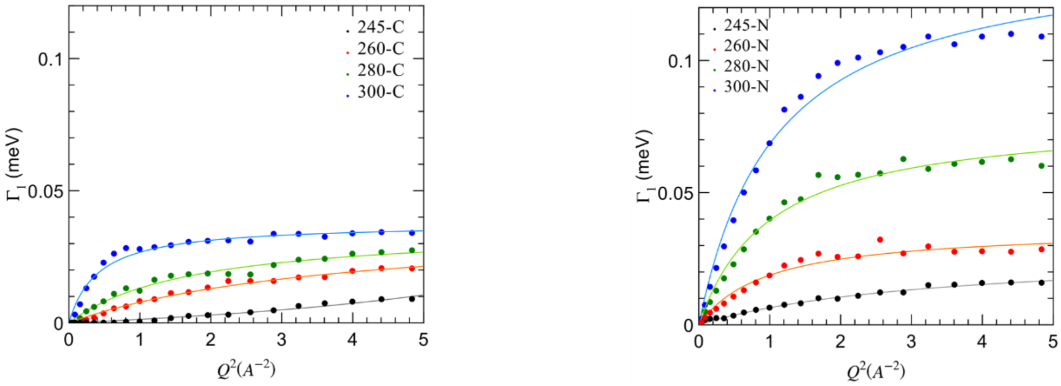

Fig. 2 Quasielastic broadening HWHM of the slow diffusive motion as a function Q and temperature for the water filled 75%RH charged PMO (left panel) and neutral PMO (right panel).

Strikingly, the obtained values of the translational diffusion coefficient, residence time and librational correlation time all demonstrated that the water dynamics are extremely sensitive to the nature of the organic bridging sites (neutral vs charged). It demonstrates that the dynamics of nanoconfined water are extremely sensitive to the presence of ionically leading to a global slowdown by a factor 2 to 5.

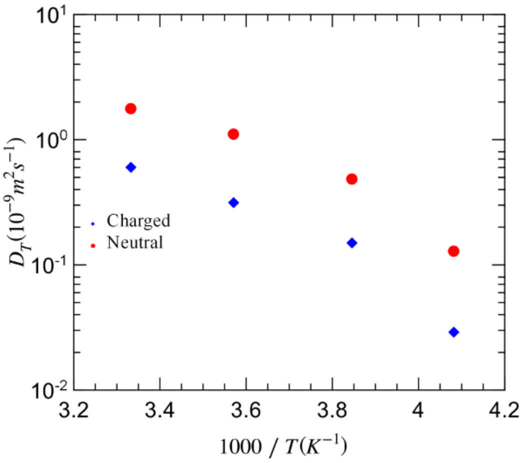

Fig. 3 Arrhenius plot of the diffusion coefficient of water confined in charged (red) and neutral (blue) Pyr-PMO.