# Experimental report

16/05/2022

**Proposal:** **6-07-83** **Council:** 10/2020

**Title:** Study of the uniaxial water dynamics in electrolyte solutions confined in oriented silica nanochannels

**Research area:** Materials

**This proposal is a new proposal**

**Main proposer:** **Diane REBISCOUL**

**Experimental team:** David KHODER
Diane REBISCOUL

**Local contacts:** Jacques OLLIVIER

**Samples:** Al2O3/SiO2

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN5 | 3 | 2 | 22/06/2021 | 25/06/2021 |

## Abstract:

The macrospic behavior of nanoporous materials in aqueous solution is driven by processes and chemical reactions occurring in the porosity. Since water molecules take part in most of these processes and chemical reactions, the understanding of water molecules behavior in confined media is essential to be able to predict the behavior of nanoporous materials in aqueous solution. In this study, we propose to characterize by QENS on IN5, the unilateral diffusion of confined water using highly ordered nanoporous silica based materials having oriented nanopores of 2.6 , 3 and 5 nm and filled of electrolytes solutions XCl2 at 1M (X= Ba, Ca, Mg) having ions presenting various komostropic properties. These results will be related to the ions distribution inside the nanopores characterized by SAXS/SANS (proposal to D16) and simulated by atomistic modelling (ICSM).

In this project, we proposed to use confining model systems made of highly ordered nanoporous silica based materials having oriented pores with 5 nm diameter and deposited in macroporous alumina membrane. The unilateral diffusion of confined protons in these materials has been characterized by Quasi-Elastic Neutron Scattering. A manuscript untitled “Anisotropy of water dynamics confined in model silica material” based on the obtained QENS results, will be submitted soon to the *journal of physical chemistry C.*

The water dynamics at the picosecond scale was studied in the membrane with oriented mesoporous silica. QENS spectra were collected for dried and hydrated hybrid alumina-silica membranes. The QENS signal was treated with QENSH software provided by LLB.

The filling of the silica mesopores with water were performed at 25 °C by placing the membranes in a desiccator in the presence of a beaker containing a saturated solution of KCl (fixing a relative humidity (RH) of 82 % at 25 °C) for 1 week before characterization to insure a complete filling of the silica mesopores. At this humidity, water fills the mesopores and does not adsorb around the silica fibers [1].

The instrumental resolution was determined using a vanadium foil as a reference. The scattering intensity was collected in two orientations in order to obtain the mean dynamics of water molecules in both, parallel and perpendicular orientations. The sample orientations, 45 and 135°, were chosen such that the scattering vector Q obtained for $\overrightarrow{k_f} \perp \overrightarrow{k_i}$, was either parallel or perpendicular to the membrane normal respectively.

Figure 1 shows the sum over Q of QENS spectra of the hybrid alumina membrane with oriented silica microfibers filled with water. The spectra of the membranes include several contributions: the sample cell, the hydroxyl groups of the pore surface, the silica and alumina matrix, and the confined water. Empty membrane measured in a dried state (200°C during 4 days) consists of the three first contributions. Since the incoherent scattering cross section of hydrogen is very high, it can be assumed that the main contribution to the scattering intensity comes from hydrogen. Consequently, the spectra are proportional to the probability at which neutrons are scattered by the protons in the sample.

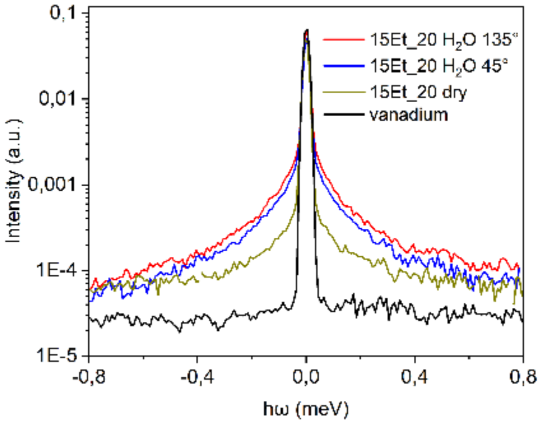

**Figure 1.** (A) Sum over Q of QENS spectra of the dried and hydrated oriented silica microfibers collected at parallel and perpendicular orientations. QENS spectra of vanadium is also shown as reference for instrument resolution. λ = 8 Å.

Noting that the signal broadening observed between the samples and the vanadium is related to the energy transfer between incoming neutrons and the diffusing water molecules. Thus, the broadening observed for the dry membrane suggests the presence of residual water at the silica pore surface after the drying process.

A slight broadening is observed when rotating the sample from 45 to 135°, showing that the water dynamics are more pronounced in the perpendicular direction where the interfacial layer is the main driver of the dynamics. This means that water dynamics anisotropy has been detected.

The model described by Malikova et al.[2] was used in this study in order to fit the experimental scattered intensities. The obtained results for both, parallel and perpendicular orientations are shown in Figure 2.

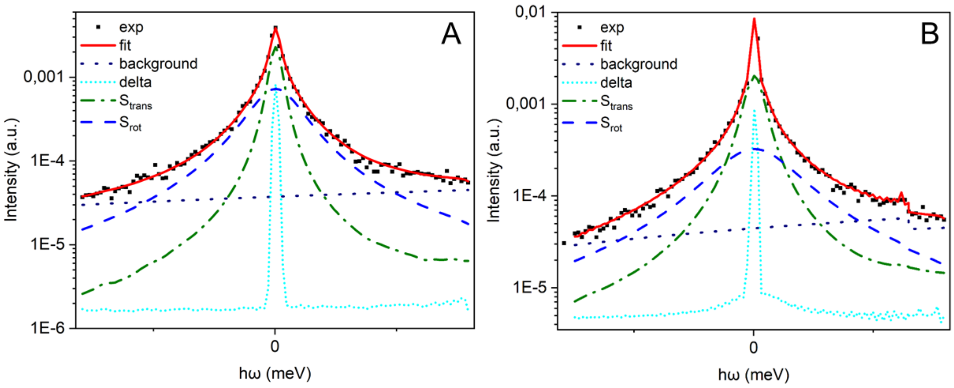

**Figure 2**. Experimental and fitted curves S (Q, ω) using one elastic and two Lorentzian functions at A: 135° orientation (perpendicular) and B: 45° orientation (parallel).

The analysis of these results reveal that the anisotropy of water dynamics was detected and it shows a perpendicular diffusion coefficient of $0.61*10^{-9}$ $m^2/s$ higher than the parallel one, $0.35*10^{-9}$ $m^2/s$. This finding raises the question whether the water dynamics is governed by the interaction of the interfacial layer with the pore surface or/and by the confinement. However, it has been shown that the dynamical properties of the interfacial and the centered pore water are differents[3]. Moreover, we have shown recently by a Monte Carlo simulation study[4] that the interfacial pore water presents a strong distortion of the tetrahedral hydrogen bonds network comparing to the intermediate and the centered pore water. We have shown also by DSC analysis and low-field NMR relaxometry that the thermal and dynamical properties of the interfacial pore water are different from those of centered pore water [5]. These findings may explain the difference between the parallel and perpendicular water dynamics. In the perpendicular direction, the water dynamics is governed by the hydrogen bonding between the interfacial pore water and the silica pore surface. Whereas, in the parallel direction the main contribution comes from the dynamics of the centered pore water.

In addition, the dynamics of water confined in mesoporous MCM41 materials of 2.6 nm diameter has been studied in presence of ions, XCl at [1M] (X= Cs, Li, Na), having different kosmotropic and chaotropic properties. An abstract untitled “How the behavior of cations within interfacial layer can influence the water dynamics in confined media”, based on the obtained data, has been accepted in the conference QENS/WINS that will be held at San Sebastian - Spain on 23 - 27 May 2022. Figures 3, 4 and table 1 show the results obtained from the QENS data performed on the MCM41 samples filled with water and electrolytes solutions.

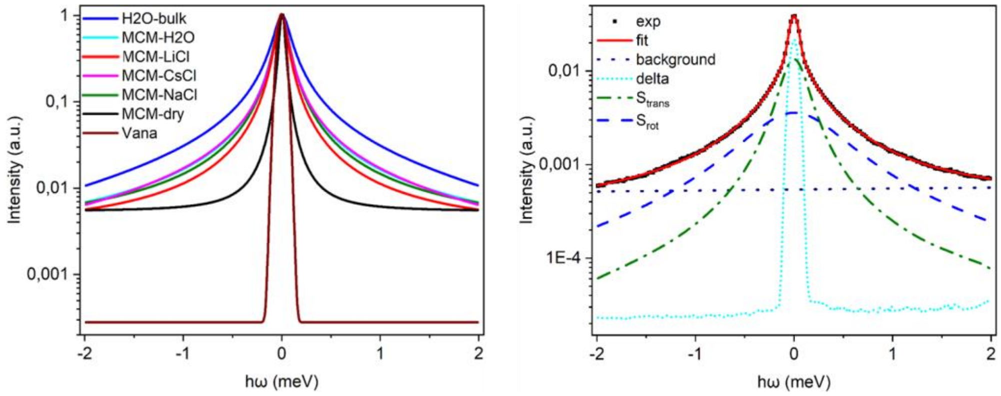

**Figure 3.** Left: sum over Q of QENS spectra of bulk, dry MCM-41 and MCM-41 filled with water and the various electrolytes at room temperature. Right: example of experimental and fitted curves S (Q, ω) using two Lorentzian functions.

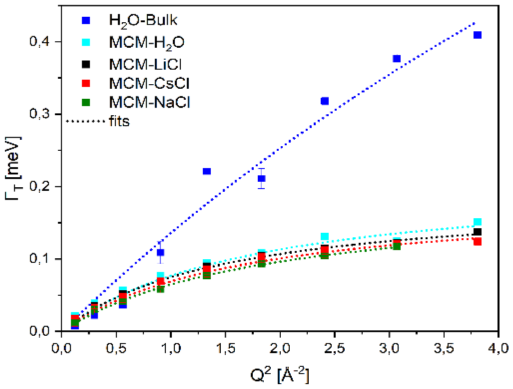

**Figure 4.** Evolutions of the half width at half -maximum $\Gamma_T$ of the first Lorentzian as a function of $Q^2$ obtained from the fitting of QENS spectra for bulk water and water confined in MCM-41 in presence of the different ions.

**Table 1.** Fitting parameters $D_T$ and $\tau_T$ obtained by fitting of $\Gamma_T(Q)$ using the jump diffusion model.

| **Samples** | **$D_T$ [m²/s] *10⁻⁹** | **$\tau_T$ [ps]** |
|---|---|---|
| $H_2O$-bulk | 2.23 | 1 |
| MCM-$H_2O$ | 1.82 | 4.7 |
| MCM-CsCl | 1.89 | 5.4 |
| MCM-NaCl | 1.67 | 5.4 |
| MCM-LiCl | 1.49 | 5.3 |

## References.

(1) Briman, I. M.; Rébiscoul, D.; Diat, O.; Zanotti, J.-M.; Jollivet, P.; Barboux, P.; Gin, S. Impact of Pore Size and Pore Surface Composition on the Dynamics of Confined Water in Highly Ordered Porous Silica. *J. Phys. Chem. C* **2012**, *116* (12), 7021–7028. https://doi.org/10.1021/jp3001898.

(2) Malikova, N.; Longeville, S.; Zanotti, J.-M.; Dubois, E.; Marry, V.; Turq, P.; Ollivier, J. Signature of Low-Dimensional Diffusion in Complex Systems. *Phys. Rev. Lett.* **2008**, *101* (26), 265901. https://doi.org/10.1103/PhysRevLett.101.265901.

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(4) Khoder, H.; Schaniel, D.; Pillet, S.; Bendeif, E.-E. X-Ray Scattering Study of Water Confined in Bioactive Glasses: Experimental and Simulated Pair Distribution Function. *Acta Crystallogr. Sect. Found. Adv.* **2020**, *76* (5), 589–599. https://doi.org/10.1107/S2053273320007834.

(5) Rjiba, A.; Khoder, H.; Jelassi, J.; Bouguet-Bonnet, S.; Gardiennet, C.; Bendeif, E.-E.; Gansmüller, A.; Dorbez-Sridi, R. Differential Scanning Calorimetry and NMR Study of Water Confined in a Mesoporous Bioactive Glass. *Microporous Mesoporous Mater.* **2021**, *316*, 110922. https://doi.org/10.1016/j.micromeso.2021.110922.