



	Experiment title: Structural analysis of electrolyte solutions confined in mesoporous silica	Experiment number: MA5201
Beamline: ID15A	Date of experiment: from:03/04/2022 to: 04/04/2022	Date of report:
Shifts: 3	Local contact(s): Gavin Vaughan	<i>Received at ESRF:</i>
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The results presented in this experimental report correspond to the experiments performed in april 2022 (MA5201).

The goal of these experiments was to study the effect of cations, presenting various size and solubility, on the structural properties of water confined in nanoporous MCM-41. The samples were prepared by immersing the silica powder in 1M concentration solutions of LiCl, NaCl, and CsCl for 24 hours.

In this report, we will present the main results obtained so far. Figures 1-a, 1-b and 1-c, show the total scattering intensities, the structure factor $S(Q)$, and the pair distribution function respectively for the dry MCM sample, and the ones filled with water and aqueous solutions. The pair correlation functions for all samples show the Si-O at 1.6 Å and the O-O pair correlations at 2.6 Å, typical of amorphous silica. However, we need to subtract the signal coming from silica to access the difference in the structural properties of water.

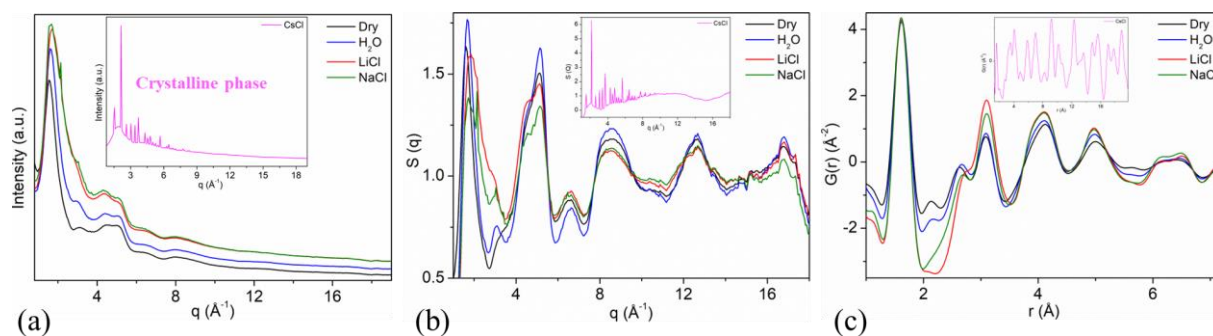


Figure 1. (a) Raw scattering intensities $I(q)$, (b) total structure factors $S(q)$, and (c) pair distribution functions, for dry MCM41 and MCM41 filled with water, LiCl and NaCl. The insets show the data of CsCl.

Before presenting the results of the confined water, figure 2 (a) shows the PDF of the bulk solutions. The PDF of bulk water shows two main peaks at 2.8 and 4.5 Å corresponding to the distances of the first and second neighbors of the tetrahedral arrangement of

water molecules. Adding cations resulted in a clear impact on the water structure, particularly in the CsCl solution, where the first neighbors between water molecules were completely distorted and shifted to a higher distance. In contrast, the tetrahedral arrangement of water molecules was not distorted in the case of LiCl, where a high peak intensity remained present at 2.8 Å, and a correlation at 4.5 Å was at the same distance as for bulk water. The NaCl solution presents a PDF with intermediate distortion between LiCl and CsCl. We suggest that the first neighbors water distance was elongated in the presence of ions because the major contribution to peak intensity comes from the correlation between water molecules.

We will proceed our investigations to study the structural properties of confined water by calculating the differential pair distribution function that has been calculated by subtracting the signal of the dry sample from the signal of the sample filled with an aqueous solution. This allows for the calculation of the PDF of the confined solution with the contribution of the liquid surface interaction. The obtained results are shown in figure 2 (b), with the PDF of bulk water also shown for comparison.

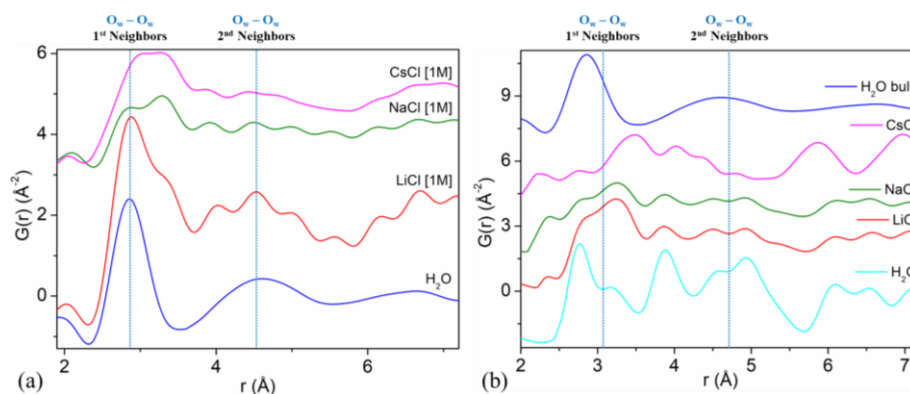


Figure 2. (a) Total pair distribution functions of bulk solutions of LiCl, NaCl, and CsCl at 1M concentration, as well as bulk water. (b) Differential pair distribution functions of confined solutions of H₂O, LiCl, NaCl, and CsCl at 1M concentration, as well as bulk water.

As can be seen, the structure of confined water exhibits significant differences with respect to the bulk structure. The first neighbors are localized at 2.8 Å, as in bulk water, but the second neighbors are distributed on different sites between 3.7 and 5 Å. In addition, a small peak appears in the vicinity of the first neighbors. This peak has already been observed in the literature and was attributed to the distortion of the first neighbors of the interfacial confined water^{1,2}. These findings suggest that the tetrahedral hydrogen-bonded network is altered under confinement, potentially as a result of either the modified geometry of the water molecules in the confined space or their interaction with the silica.

The data obtained for confined water in the presence of ions indicate that the water distortion follows the same order as in bulk solutions. The PDF obtained for LiCl and NaCl solutions exhibits correlation at the same distances as confined water, with a difference in peak intensities around the first neighbors. However, for the CsCl solution, a clear distortion of the water structure is observed. These findings suggest that both confinement and ion properties influence the water structure. The signals obtained from these experiments contain contributions from both water and ions. To investigate the interfacial water structure in the vicinity of the pore surface and separate these signals, we performed atomistic simulations.

This study is part of a larger project that also aims to investigate the dynamics properties of water confined in MCM41 samples, in the presence of the same electrolyte solutions, i.e., LiCl, NaCl, and CsCl. To analyze the dynamics properties, quasi-elastic neutron scattering measurements were conducted at the IN5 time-of-flight spectrometer at ILL. The obtained results, both structural and dynamics, will be correlated and discussed in a scientific paper that is currently being written.

References

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