Experimental report

03/02/2021

Proposal: 6-02-593 **Council:** 10/2018

Title: Water structure in 'water-in-salt'and 'water-in-bisalt' electrolytes

Research area: Materials

This proposal is a continuation of 6-02-577

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Samples: (CF3SO2NLiSO2CF3)(H2O)2.7
(CF3SO2NLiSO2CF3)(D2O)2.7
(CF3SO2NLiSO2CF3)0.75(CF3SO3Li)0.25(H2O)2
(CF3SO2NLiSO2CF3)0.75(CF3SO3Li)0.25(D2O)2

Instrument	Requested days	Allocated days	From	To
D7	3	2	18/06/2019	20/06/2019
D4	1	1	17/02/2020	19/02/2020

Abstract:

This is a continuation proposal aiming to explore the local structure around water in 'water-in-salt' and 'water-in-bisalt' systems by performing a first difference experiment in samples prepared with H2O and D2O. A first experiment has been performed in D3 (6-02-577), but the data correction procedure is not straightforward and the limitations in the accessible low-Q range and the statistical quality of the data make difficult to obtain accurate information. Therefore, we ask for 3 days of beam time in D7 in order to obtain good data at low Q and 1 day in D4 to obtain the complete S(Q) for the deuterated samples. The new data will serve also as a reference to analyse unambiguously the D3 data, providing a set of reliable S_HX(r) and g_HX(r) functions that will be used to determine the ordering of the ions around water.

We have performed measurements on highly concentrated aqueous solutions of lithiumolecular bis(trifluoromethane sulfonyl)imide (LiTFSI) and LiTFSI + lithium trifluoromethane sulfonate (LiOTf). Solutions were prepared with both light and heavy water, so six samples were measured: $[LiTFSI][H_2O]_{4.0}$, $[LiTFSI][D_2O]_{4.0}$, $[LiTFSI][H_2O]_{2.64}$, $[LiTFSI][D_2O]_{2.64}$, $[LiTFSI]_{0.75}[LiOTf]_{0.25}[H_2O]_{2.0}$, and $[LiTFSI]_{0.75}[LiOTf]_{0.25}[D_2O]_{2.0}$. This structural work complements our recently published QENS results on the same systems.[1]

Polarized neutron diffraction measurements were carried out on D7 over the Q range 0.2 – 3.5 Å^{-1}, and unpolarized neutron measurements on D4 over the range 0.3 – 20 Å^{-1} with somewhat poorer Q resolution. The results were compared with Molecular Dynamics numerical simulations performed by Borodin et al.[1,2] Despite some detailed discrepancies in the Q-dependence, to be discussed in the forthcoming publication, the MD results proved useful in determining the normalization of the data and subtraction of the Q-dependent self-scattering in order to obtain the neutron-averaged structure factors $S(Q)$.

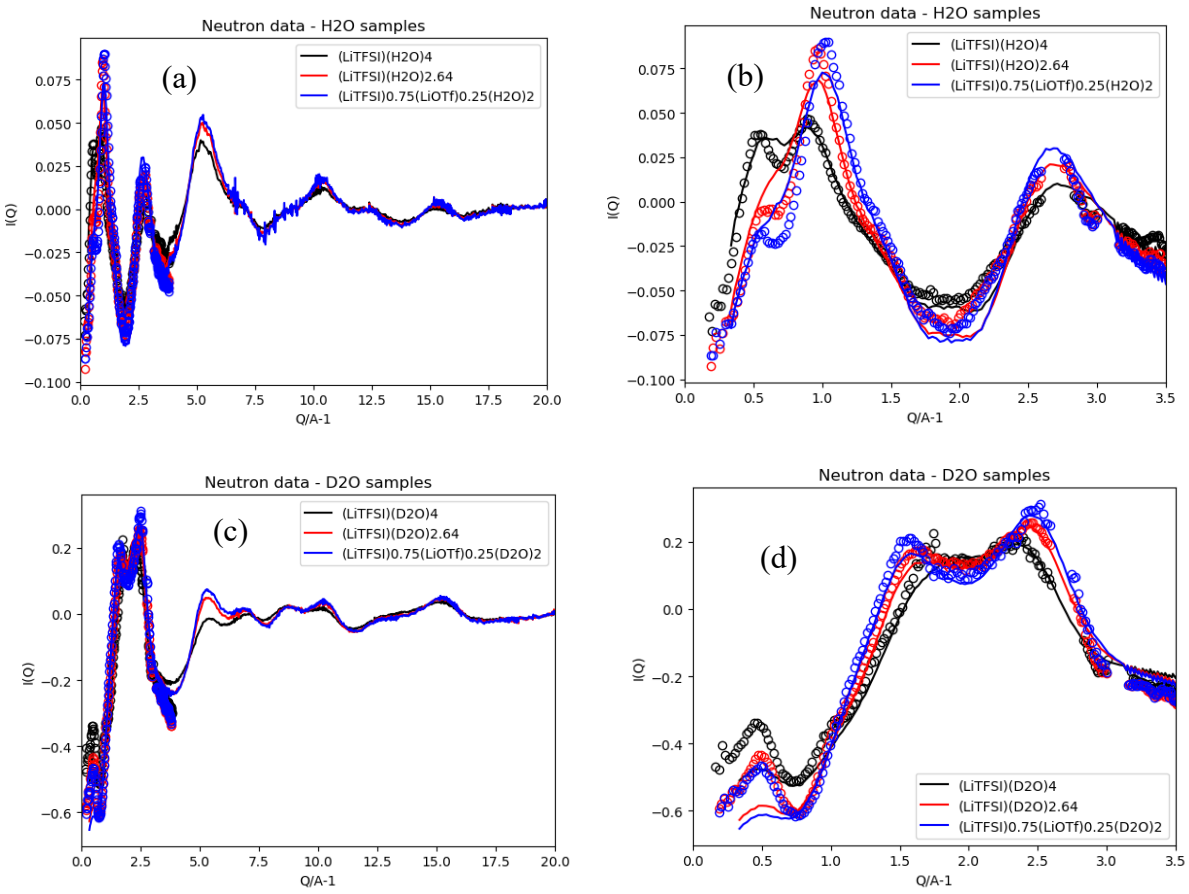

Fig. 1. Neutron-weighted average structure factors for (a, b) $[LiTFSI][H_2O]_{4.0}$, $[LiTFSI][H_2O]_{2.64}$ and $[LiTFSI]_{0.75}[LiOTf]_{0.25}[H_2O]_{2.0}$, and (c, d) $[LiTFSI][D_2O]_{4.0}$, $[LiTFSI][D_2O]_{2.64}$ and $[LiTFSI]_{0.75}[LiOTf]_{0.25}[D_2O]_{2.0}$. Panels (a, c) show the entire Q range of the measurements and (b, d) blow-ups of the low-Q region. The D7 results are denoted by circles and those from D4 by continuous curves.

With the use of polarized neutrons at D7 it was possible to separate the coherent and incoherent contributions. It was found that for the samples with H_2O the levels of both were in reasonable agreement with the theoretical prediction, but for those with D_2O the incoherent levels were about twice as large, which could be explained by a small H_2O contamination of a few %.

The results for *S(Q)* from D7 and D4 are shown in Fig. 1. Overall, the D7-D4 agreement is reasonably good, even for the samples with H_2O, in spite of the large incoherent scattering contribution. Marked discrepancies are found for all samples at low Q, 0.3 – 0.7 $Å^{-1}$. For the samples with H_2O the MD results in this region differ from both data sets, while for the samples with D_2O they agree somewhat better with the D7 data. Since the incoherent scattering is an order of magnitude larger than the coherent at low Q for the samples with H_2O and, as noted above, larger than predicted for the samples with D_2O, discrepancies between the D4 and D7 results due to difficulties in subtracting the self-scattering are not unexpected.

These results along with synchrotron x-ray data from SPring-8 in Japan will be compared with those predicted by the MD simulations in a forthcoming publication.

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[1] M. A. González *et al.,* J. Phys. Chem. Lett. **2020**, 11, 7279−7284.
[2] O. Borodin *et al., ACS Nano* **2017**, 11, 10462-10471.