Experimental report

16/09/2018

Proposal: 6-02-577 **Council:** 4/2017

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

Research area: Materials

This proposal is a new proposal

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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
D3	10	10	02/03/2018	09/03/2018
			09/03/2018	19/03/2018

Abstract:

We propose to measure the structure factor of two promising electrolytes, based on the 'water-in-salt' (LiTFSI + H2O/D2O) and 'water-in-bisalt' (LiTFSI + LiOTf + H2O/D2O) concepts. MD simulations of both systems suggest that the high concentrations prevent a complete solvation of the Li cations by water. In order to verify this picture and get additional details about the structure around the water hydrogens, we propose to use D3 to measure the structure on mixtures using H2O and D2O. Using polarized neutrons we can extract the coherent structure factor for the mixtures with H2O and D2O and use the first difference method to determine the partial r.d.f. H-X.

We have performed measurements in D3 of highly concentrated aqueous solutions of lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) and LiTFSI + lithium trifluoromethane sulfonate (LiOTf). In both cases solutions were prepared using light and heavy water, so 4 samples were measured: $[LiTFSI][H_2O]_{2.67}$, $[LiTFSI][D_2O]_{2.67}$, $[LiTFSI]_{0.75}[LiOTf]_{0.25}[H_2O]_{2.0}$, and $[LiTFSI]_{0.75}[LiOTf]_{0.25}[D_2O]_{2.0}$.

The polarized neutron data have been used to determine the coherent and incoherent contributions, which are shown in Figs. 1 and 2.

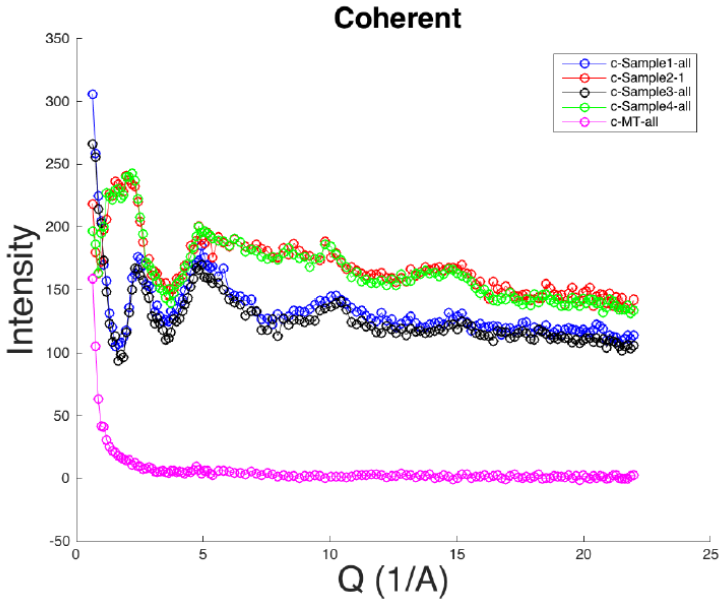

Figure 1

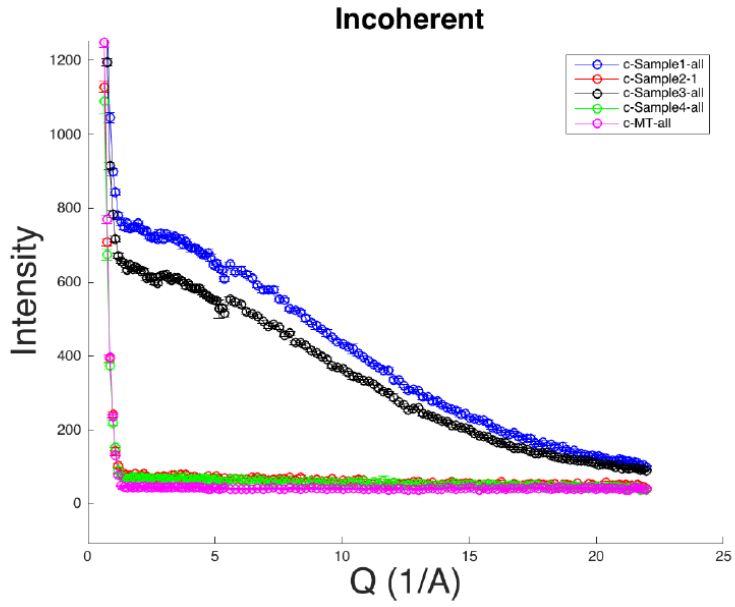

Figure 2

The data are still under analysis, but a few problems are already evident: 1) The minimum Q reachable in the experiment is ≈ 1.4 $Å^{-1}$, so the low-Q region where the differences between MD simulations

and X-ray diffraction data are larger (Fig. 3) is not accessible; 2) the statistical quality of the data is such that first difference curves (needed to determine the H-X correlations) are quite noisy and difficult to interpret; and 3) the data correction procedure is not straightforward. This is due to at least two different problems: It was found after the experiments that the sample changer was not perfectly centred, making that at different detector positions a given sample is not in exactly the same position that it was during the previous measurement, so part of the intensity is lost and very fine angle dependent corrections have to be applied to correct the data. The high concentration of the samples makes that at ambient conditions we are very close to a phase separation. To avoid this happening during the experiment, we used a heat gun to heat slightly the samples during the measurement. But it seems that each time that the samples were removed to measure the polarisation and then put back into the beam, the first measurement was obtained before the sample had re-equilibrated completely, giving some strange artefacts in the total signal (Fig. 4).

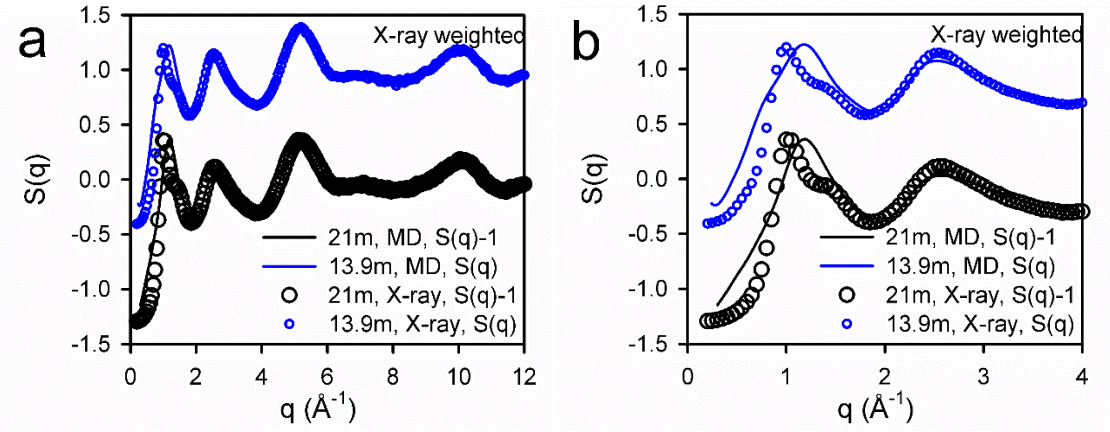

Figure 3

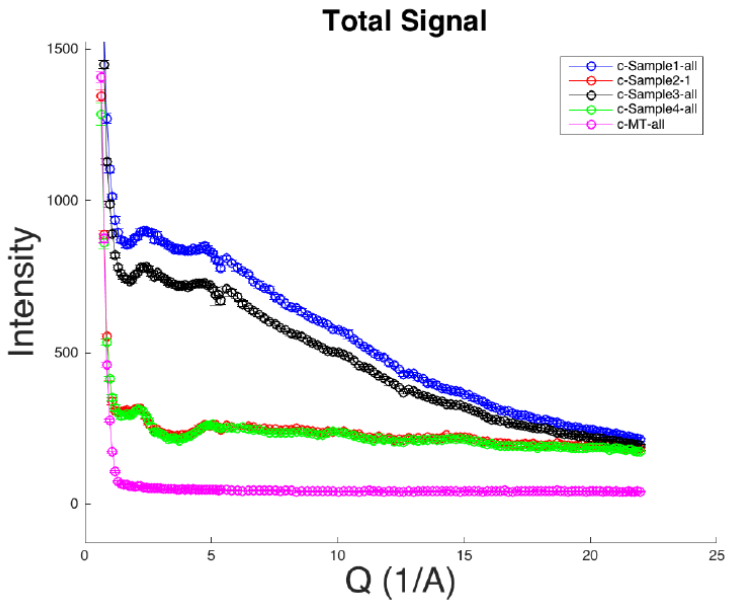

Figure 4