Experimental Report

15/10/2013

Proposal:	**8-03-779**	**Council:**	4/2012

Title: Ion-Ion pairing in aqueous solutions of imidazolium chloride

This proposal is a new proposal

Researh Area: Biology

Main proposer: **JUNGWIRTH Pavel**

Experimental Team: MASON Philip
PATEROVA Jana

Local Contact: FISCHER Henry

Samples: C3N2H5Cl and C3N2H4 (H/D) in D2O

Instrument	Req. Days	All. Days	From	To
D4	4	4	23/11/2012	28/11/2012

Abstract:

The structure factors of aqueous (D2O) solutions of 3m d-5 imidazolium chloride, 3m imidazolium chloride (natural abundance) and an equimolar mixture of the previous two solutions will be measured. Similar sets of three measurements will be performed on a 3m imidazole solution and a mixture of 1.5m imidazole and 1.5m imidazolium chloride. From these measurements the function SHnonHnon(Q) and gHnonHnon(r) (where Hnon are the non-exchangeable hydrogens) containing information on the ion-ion structure will be determined. This will provide the first structural data on the imidazolium-imidazolium ion pairing, and how this varies with the protonation state of this species. Given the importance of the imidazole motif in the side-chain of the amino-acid histidine, and its common occurance in the active sites of enzymes, this study will be of significant importance.

Report for Proposal Number 8-03-779: Ion-Ion pairing in aqueous solutions of imidazolium chloride

The imidazole motif is biologically relevant as it is the side chain of the amino acid histidine, and is found in the active sites of many enzymes. In part this is due to its ability to pick up a proton and become cationic. Imidazolium salts are also the largest class of molten salts.

This experiment was designed to examine the ion-ion and hydration structure of imidazole and the imidazolium ion. In the current case, both sulfate and chloride were used as the anions for the imidizolium salts. This experiment used the method of first order neutron diffraction with isotopic substitution (NDIS) using H/D substitution on the non-exchangeable hydrogens of imidazole/ imidazolium. 3 molal solutions of imidazole, imidazolium chloride and imidazolium sulfate were prepared using both H_3-imidazole/ imidazolium and d_3-imidazole/ imidazolium in D_2O. Raw total neutron scattering patterns were acquired on all of these solutions at the D4C diffractometer. The acquired data sets were subject to multiple scattering and absorbtion corrections and were normalized versus a standard vanadium rod in order to obtain corrected total neutron scattering patterns F(Q). From this data the first order NDIS functions ($\Delta S_{HX}(Q)$ where X is any atom in the system) were calculated for all three sets of solutions. The constitution of the three first order difference functions ($\Delta S_{HX}(Q)$) were as follows for the imidazole, imidazolium chloride and imidazolium sulfate solutions respectively.

$${}^{imidazole}\Delta S_{HX}(Q) = 3.0\ S_{HC}(Q) + 2.8\ S_{HN}(Q) + 16.1\ S_{HO}(Q) + 38.7\ S_{HH}(Q)$$

$${}^{imidazoliumchloride}\Delta S_{HX}(Q) = 2.8\ S_{HC}(Q) + 2.6\ S_{HN}(Q) + 15.1\ S_{HO}(Q) + 37.4\ S_{HH}(Q) + 1.4\ S_{HCl}(Q)$$

$${}^{imidazoliumchloride}\Delta S_{HX}(Q) = 2.7\ S_{HC}(Q) + 2.5\ S_{HN}(Q) + 16.1\ S_{HO}(Q) + 35.7\ S_{HH}(Q) + 0.19\ S_{HS}(Q)$$

The functions ${}^{imidazole}\Delta S_{HX}(Q)$ and ${}^{imidazoliumchloride}\Delta S_{HX}(Q)$ are shown in Figure 1.

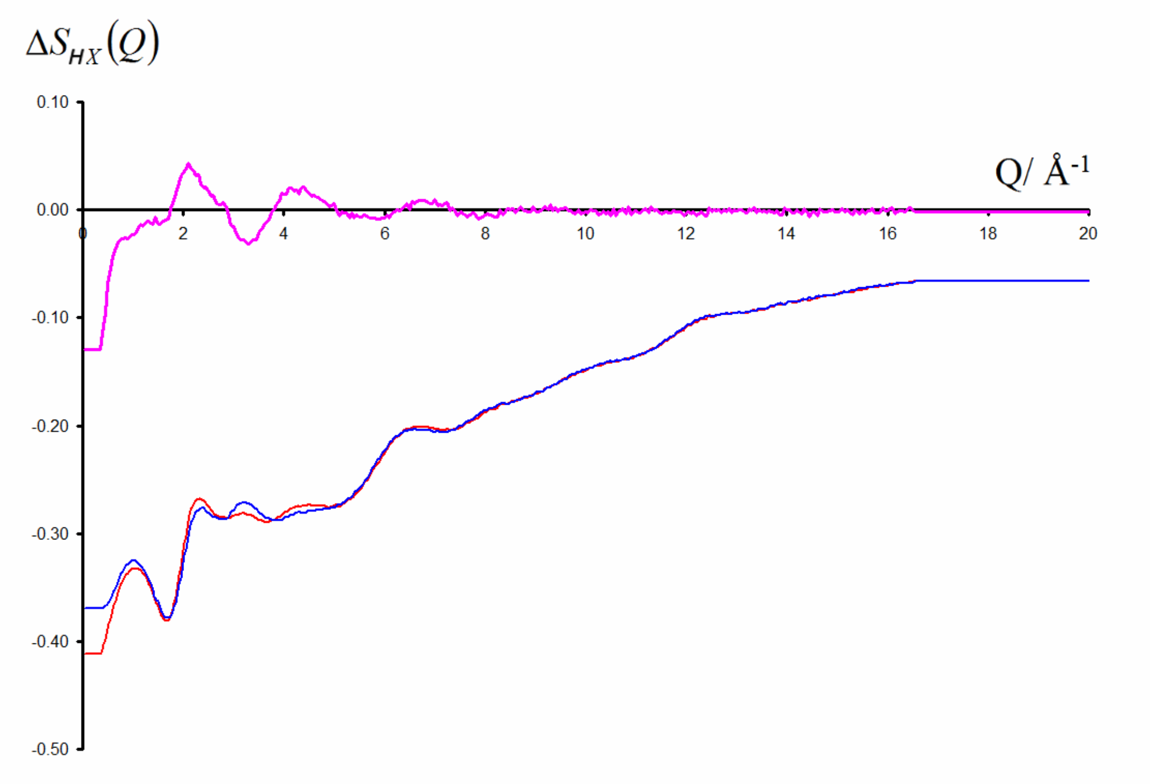

Figure 1, the functions ${}^{imidazole}\Delta S_{HX}(Q)$ (red) and ${}^{imidazoliumchloride}\Delta S_{HX}(Q)$ (blue). Shown in purple (scaled by a factor of 3) is the difference between these two functions, highlighting the difference in the solvation structure between the neutral imidazole and cationic imidazolium ion.

The H/D NDIS functions successfully measured here are a direct measure of the solvation structure around imidazole or the imidazolium ion. Not only do these results give an insight into the changes of the solvation structure that occur when the imidazole motif becomes cationic, they also give an insight into how the solvation of this ion changes with the counter-ion (chloride versus sulfate). This experiment not only fulfils the original goals of the proposal, it also demonstrates what can be achieved with a stable, reliable diffractometer such as D4C and well prepared samples.

Currently we are running molecular dynamics studies on systems mirroring those in these experiments in order to better interpret the experimental results.