Experimental report

21/12/2021

Proposal:	**9-10-1720**	**Council:**	4/2021

Title: Investigating self-organisation inionic liquid mixtures containing fluorous and aliphatic cations

Research area: Chemistry

This proposal is a new proposal

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Samples:
[C8MIM-D23]1-x[C8MIM-F13]x[Tf2N]
[C8MIM-D6]1-x[C8MIM-F13D6]x[Tf2N]
[C2MIM]1-x[C8MIM-F13]x[Tf2N]
[C2MIM-D11]1-x[C8MIM-F13]x[Tf2N]
[C10MIM-D6]1-x[C10MIM-F17D6]x[Tf2N]
[C10MIM-D27]1-x[C10MIM-F17]x[Tf2N]
[C12MIM]1-x[C12MIM-F21]x[Tf2N]
[C12MIM-D6]1-x[C12MIM-F21D6]x[Tf2N]

Instrument	Requested days	Allocated days	From	To
D16	3	3	28/09/2021	01/10/2021

Abstract:

We are investigating ionic liquid (IL) mixtures prepared from cations with both fluorocarbon and hydrocarbon chains for use in supported IL-phase (SILP) catalysis to improve catalyst performance and stability. In SILPs, a thin IL film containing a homogeneous catalyst is deposited on a porous support to produce a pseudo-heterogeneous catalyst. The bulk liquid structure of the IL is important for SILP catalysis, as it strongly affects the microenvironment of catalyst molecules dissolved in the IL. As fluorous and aliphatic chains have different natures, their self-organisation in a range of selected IL mixtures will lead to interesting bulk structure and properties and these can be used to promote the ideal conditions for different catalytic reactions. Small-angle scattering, combined with contrast variation through selective deuteriation, will allow us to understand the relationships between structure and composition in these systems. This will form the basis for a more rational design of ILs for applications in SILPs.

9-10-1720: Investigating self-organisation ionic liquid mixtures containing fluorous and aliphatic cations

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Ionic liquids, ILs, which are salts with melting points below 100 °C, are of great interest, due to their interesting characteristics such as low volatility and tunability, and range of applications e.g. in catalysis.[1] Traditionally, ILs have been tuned by varying the structure of the cation or anion, but the huge number of potential structures means that making and testing large numbers of ILs to find the perfect liquid for the desired application is extremely time consuming and costly.[2] To address this, research into IL mixtures is being carried out. Here the advantage is that a small number of ILs can be made and then used to quickly and simply generate a large range of mixtures in which the physical properties (e.g. conductivity and viscosity) and the interfacial and bulk structures may be tuned by varying the composition.

Experimental

The experiments were carried out on a range of mixtures of perfluorinated and hydrocarbon ILs, general structure shown in Fig. 1, in 1mm Hellma cells exploring a *Q* range of approximately 0.08-1.6 Å^{-1} to allow the polar/ non-polar peak, PNPP, and contact peak, CP, to be resolved. The PNPP is caused by the segregation of polar and non-polar regions and while CP relates to the ions of different charge in close contact.

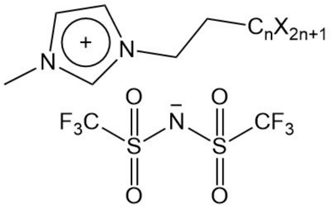

Figure 1: The general structure of $[C_{n+2}MIM]$ $[Tf_2N]$ where X is H or F

Measurements were carried out at 20 °C; as previous measurements carried out at the ISIS neutron scattering facility found that the effect of temperature on the bulk structure of similar systems was negligible. However, for some of the samples studied, it was found that higher temperature measurements may be required in the future to avoid precipitation of the longer-chained perfluorinated ILs from the mixtures. Samples with different degrees of deuteration were used where possible to vary the contrast in the mixtures to best characterise the bulk structure. For samples with the same chain length measurements were carried out at 95:5, 80:20, 65:35, 50:50, 35:65, 80:20 and 5:95 molar ratios to allow for direct comparison with previous measurements, as reported in the proposal, and shown in Fig. 2.

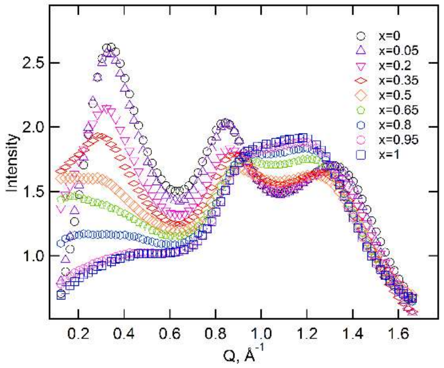

Figure 2: SAXS data for $[C_8MIM]_{1-x}[C_8MIM\text{-}F_{13}]_x$ $[Tf_2N]$ mixtures carried out at room temperature

Preliminary Results

As previous X-ray measurements were carried out on the $[C_8MIM]_{1-x}[C_8MIM\text{-}F_{13}]_x[Tf_2N]$ system data were utilised in combination with the data collected on D17 to provide additional contrast and allow full characterisation of the bulk structure present in these mixtures.

The SAXS measurements, shown in Fig. 2, indicate that the peaks assigned to be the charge ordering peak, COP, caused by the characteristic distance between ions of the same charge appear to be shortening as the mole fraction of the perfluorinated cation increases while the CP appears to be lengthening, although the positions of these peaks cannot be well resolved from the X-ray data alone. The neutron contrasts have a single well-resolved peak at high *Q*, the CP, as can be seen from the example data in Fig. 3, the COP on the other hand is either not seen in the neutron scattering data or is present only at low intensity. This quirk of contrast allows the CP and COP to be better resolved, which is helpful here.

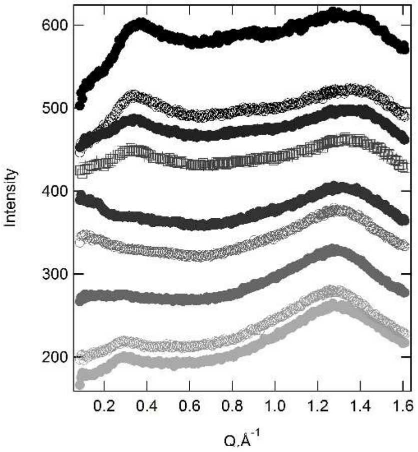

Figure 3: Neutron scattering data for [C_8MIM-H]$_{1-x}$[C_8MIM-F_{13}]$_x$[Tf_2N] mixtures carried out on D17, top data are for [C_8MIM] [Tf_2N] with the mol fraction of the fluorinated component increasing down the graph

From the combination of the two data sets we can confidently assert that the spacing associated with the CP increases reasonably linearly as the proportion of the fluorinated IL increases, from a peak position of ~4.7 Å to ~5.0 Å indicating that the ions become more separated. The behaviour of the COP is the opposite, moving to shorter distances as the concentration of the fluorinated cation increases, Fig. 4. The cause for these shifts requires some further consideration as while the increase in the CP can be rationalised by the greater chain diameter of the perfluorinated component causing the cation-anion distance to increase by a small amount, the decrease in the cation-anion-cation distance is more difficult to rationalise. The PNPP, peak at low *Q*, which is attributed to the characteristic separations caused by the segregation of polar and nonpolar domains within the IL, shifts to lower *Q* as the concentration of the perfluorinated IL increases, the cause of this also requires further consideration, as the chain lengths of the molecules should be similar.

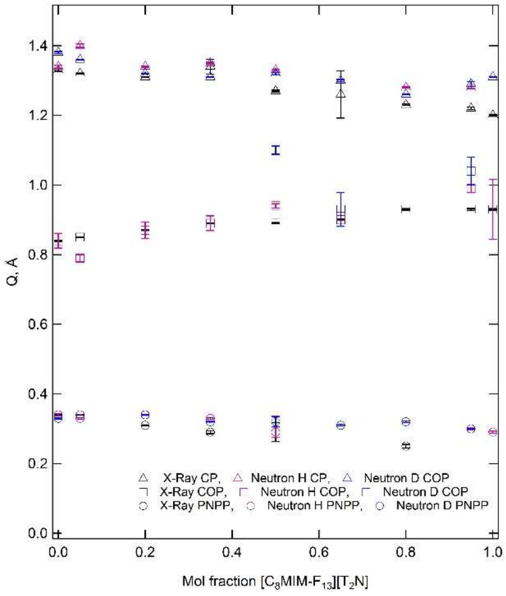

Figure 5: Peak positions for the PNPP, COP and CP from neutron and X-ray scattering data

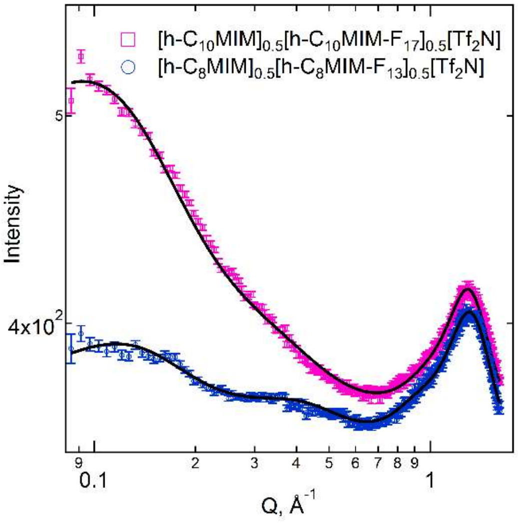

Figure 5: Neutron scattering data for [C_{10}MIM]$_{0.5}$ [C_{10}MIM-F_{17}]$_{0.5}$ [Tf_2N] and [C_8MIM-H]$_{0.5}$[C_{10}MIM-F_{17}]$_{0.5}$ [Tf_2N] samples

We then investigated samples with longer chains attached to the imidazolium ring, mixtures of $[C_{10}MIM]_x[C_{10}MIM\text{-}F_{17}]_{1-x}[Tf_2N]$ were fully characterised over the same range of compositions, with two contrasts measured. The pure fluorinated IL was not measured, due to its melting point being above room temperature. To fully characterise these samples the complementary SAXS measurements need to be carried out, however, from the SANS data we see that while the CP position is similar to that seen for the C8/C8F mixtures, Fig. 5, the data at low *Q* are considerably different. For these longer chain materials, we see the evolution of scattering at very low *Q*, which requires further studies to understand fully. These low-*Q* data are not observed in all $C_{10}/C_{10}F$ mixtures, are not seen when a large excess of either component is present (>80 mol%). In order to determine the nature of this scattering further beamtime has been applied for at SANS2d at the ISIS neutron and Muon source to explore the scattering at lower *Q*.

We also carried out measurements on samples with unequal chain lengths. $C_8/C_{10}F$ mixtures also show some interesting behaviour at low *Q*, although peak intensities are lower, and shifted to even lower *Q* than the data for the $C_{10}/C_{10}F$ mixtures, and so also requires further investigation.

Conclusions:

Using a combination of the neutron data collected during the beamtime and previously collected SAXS data, the liquid structure of mixtures prepared from mixtures of $[C_8MIM]_x[C_8MIM\text{-}F_{13}]_{1-x}[Tf_2N]$ can be fully characterised as bicontinuous, as seen previously for long chained ILs using similar methodology. The nature of the structure of these systems indicates that the perfluorinated and hydrogenated components seem to be miscible at room temperature.

The measurements made with longer-chained ILs indicate that some additional structure is present for these samples, so in order to fully characterise the bulk liquid structure of these samples we plan to use the data measured during this experiment in combination with further SAXS and lower *Q* SANS measurements.

Future work:

Further beamtime has been applied for at ISIS on SANS2d to determine the nature of the structure observed at low *Q* in the mixed systems, which is particularly clear for the mixtures containing $[C_{10}MIM\text{-}F_{17}][Tf_2N]$. Further SAXS measurements will also be carried out to better refine the positions of the COP and CP peaks observed for these mixtures.

References

1 H. P. Steinrück and P. Wasserscheid, *Catal. Let.*, 2015, **145**, 380–397.

2 H. Niedermeyer, J. P. Hallett, I. J. Villar-Garcia, P. A. Hunt and T. Welton, *Chem. Soc. Rev.*, 2012, **41**, 7780–7802.