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Solution structure of propane and propene dissolved in the ionic liquid 1-butyl-3-methylimidazolium *bis*[(trifluoromethyl)sulfonyl]imide from neutron diffraction with H/D substitution and Empirical Potential Structure Refinement modelling

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ABSTRACT

Neutron scattering combined with H/D-isotopic substitution, fitting the experimental data using the Empirical Potential Structure Refinement (EPSR) method has been used to investigate the liquid structure of 1-butyl-3-methylimidazolium *bis*[(trifluoromethyl)sulfonyl]imide ([C₄mim][NTf₂]) and solutions of propane (0.15 mol fraction) and propene (0.3 mol fraction) dissolved in the ionic liquid dissolved after pressurising at 6 bar. Both strong cation-anion and cation-cation correlations are observed in the first coordination shell with anions and cations occupying mutually exclusive positions around the imidazolium cation, consistent with previous models derived from molecular dynamics simulation. No significant changes in the neutron scattering data were observed after dissolution of either propane and propene suggesting that the primary coulombic structure of the ionic liquid is preserved. Modelling the data with EPSR reveals subtle differences in the cation-hydrocarbon correlations, with propene associated with all three imidazolium ring C-H positions whereas propane exhibits less association with the C(2)-H ring position and has a greater level of correlation with the terminal –CH₃ group of the cation butyl-chain.

KEYWORDS

Neutron Scattering, ISIS, Ionic Liquids

Figure 1. Structure of the ionic liquid, $[\text{C}_4\text{mim}][\text{NTf}_2]$

1. Introduction

Ethene and propene are globally the largest-volume organic chemical feedstocks and currently the primary source of monomers for the highest demand polymers, polyethylene and polypropylene. However light olefin/paraffin separations require cryogenic distillation, one of the most costly unit operations in the petrochemical industry [1]. Consequently, liquid (or supported liquid) membranes are of interest as potential low-energy alternatives to [2], and the application of ionic liquids (ILs) [3, 4] to gas separation and purification, exploiting the negligible vapour pressure of the ionic liquids to avoid potential downstream contamination as a major advantage over conventional absorption solvents, has been established [5–9].

The light alkene gases have significantly greater solubility than the corresponding saturated alkanes [10]. Costa Gomes, Padua and co-workers [8] have explained that the differences in ethane/ethene solubility are due to a balance of enthalpic and entropic factors, with entropy playing the greatest influence in ILs with simple, saturated alkyl side-chains such as $[\text{C}_4\text{mim}][\text{NTf}_2]$ (Figure 1). Different preferential solvation sites for the two gases in the IL were identified using MD simulation, with ethene reported to solvate closer to the imidazolium ring than ethane which associates most strongly with the terminal $-\text{CH}_3$ groups of the cation’s butyl chain. However, while the thermochemistry of hydrocarbon gas/IL mixtures has been studied [11] and modelled using regular solution theory [12], the molecular mechanisms for solvation are still not fully understood.

Neutron scattering combined with isotopic substitution has become well established as a tool to study liquid structure at the atomistic scale [13–15]. As systems of interest become increasingly complex (including biomolecules and drugs [16], surfactant solutions [17], electrolytes and solvents [18, 19], and metal-amine liquids [20]) the Empirical Potential Structure Refinement (EPSR) approach to fit models to the experimental scattering data first introduced by Soper in the mid 1990s [21], and advanced since then [22], has made it possible to routinely study structurally complex systems.

ILs are intrinsically complex fluids that contain, in their simplest form at least a pair of ionic components. The bulk structure, and consequently, the properties of ILs are dependent on a complex interplay of variables that affect the ion–ion interactions. The relative importances of different contributions is still a matter for some conjecture [23, 24] and drives efforts to develop force fields for simulation [25] that can reliably reproduce experimental spectroscopic data [26–28]. Neutron scattering, combined with EPSR modelling of the data, has proven invaluable to study the interplay of coulombic, hydrogen-bonding and dispersive interactions that dominate structure and solvation in ILs [29, 30]. Moreover, the experimental data is valuable as a benchmark for validating the quality and reliability of MD simulation models [31]. It is worth noting that efforts to obtain information on the low temperature ILs: 1-ethyl-3-methylimidazolium chloride/HCl ($[\text{C}_2\text{mim}]\text{Cl}/\text{HCl}$) [32] and 1-ethyl-3-methylimidazolium chloride/aluminium chloride ($[\text{C}_2\text{mim}]\text{Cl}/\text{Al}_2\text{Cl}_6$) [33] using neutron scattering experiments prior to the advent of EPSR were only able to yield limited structural insight.

Here we present a total neutron scattering study of the IL $[\text{C}_4\text{mim}][\text{NTf}_2]$ using H/D isotopic substitution and EPSR to fit the experimental data, and the preliminary exploration of solutions of propane and propene dissolved in the IL under 6 bar gas pressure, where propane and propene are miscible in $[\text{C}_4\text{mim}][\text{NTf}_2]$ to $\chi_{\text{propane}} = 0.15$ and $\chi_{\text{propene}} = 0.23$.

Figure 2. Limits of propane and propene miscibility with $[\text{C}_4\text{mim}][\text{NTf}_2]$. Data from Lee and Outcalt [10].

Table 1. Isotopomers of $[\text{C}_4\text{mim}][\text{NTf}_2]$ and the IL-propane and IL-propene mixtures investigated

Sample	Empirical composition
$[\text{C}_4\text{mim}][\text{NTf}_2]$	
IL-H	$[\text{C}_8\text{N}_2\text{H}_{15}][\text{NS}_2\text{O}_4\text{C}_2\text{F}_6]$
IL-D	$[\text{C}_8\text{N}_2\text{D}_{15}][\text{NS}_2\text{O}_4\text{C}_2\text{F}_6]$
IL-H/D^a	$[\text{C}_8\text{N}_2\text{H}_{7.5}\text{D}_{7.5}][\text{NS}_2\text{O}_4\text{C}_2\text{F}_6]$
$[\text{C}_4\text{mim}][\text{NTf}_2] + \text{propane } (\chi_{\text{propane}} = 0.15)$	
IL-H + propane	$[\text{C}_8\text{N}_2\text{H}_{15}][\text{NS}_2\text{O}_4\text{C}_2\text{F}_6] + (\text{C}_3\text{H}_8)_{0.177}$
IL-D + propane	$[\text{C}_8\text{N}_2\text{D}_{15}][\text{NS}_2\text{O}_4\text{C}_2\text{F}_6] + (\text{C}_3\text{H}_8)_{0.177}$
$[\text{C}_4\text{mim}][\text{NTf}_2] + \text{propene } (\chi_{\text{propene}} = 0.23)$	
IL-H + propene	$[\text{C}_8\text{N}_2\text{H}_{15}][\text{NS}_2\text{O}_4\text{C}_2\text{F}_6] + (\text{C}_3\text{H}_6)_{0.3}$
IL-D + propene	$[\text{C}_8\text{N}_2\text{D}_{15}][\text{NS}_2\text{O}_4\text{C}_2\text{F}_6] + (\text{C}_3\text{H}_6)_{0.3}$

^a 1:1 mixture of 1 and 2.

2. Experimental

Three H/D-isotopologues of $[\text{C}_4\text{mim}][\text{NTf}_2]$ were studied (fully-protiated, fully-deuteriated, and a 1:1 H/D mixture). $[\text{C}_4\text{mim}][\text{NTf}_2]$ and the perdeuterated analogue, $[\text{C}_4\text{mim-d}_{15}][\text{NTf}_2]$, were prepared by metathesis of $[\text{C}_4\text{mim}]\text{Br}$ (and perdeuterated $[\text{C}_4\text{mim-d}_{15}]\text{Br}$) with LiNTf_2 in water (or D_2O respectively) followed by drying *in vacuo*. $[\text{C}_4\text{mim-d}_{15}]\text{Br}$ was prepared by N-alkylation of 1-methylimidazole-d₆ with bromobutane-d₉ [34]. The density of $[\text{C}_4\text{mim}][\text{NTf}_2]$ prepared, measured using an Anton Paar DMA 4500 densitometer at 25 °C, was 1.430 g cm³, consistent with the literature [35].

Neutron scattering data was collected from the seven samples shown in Table 1 of the neat $[\text{C}_4\text{mim}][\text{NTf}_2]$ IL (protiated (IL-H), deuteriated (IL-D) and a 1:1 mix (IL-H/D) of the two isotopomers) and IL-H and IL-D under 6 bar pressure of propane and propene respectively. Data was collected using ‘null scattering’ $\text{Ti}_{0.68}\text{Zr}_{0.32}$ flat plate cells with internal geometries of $1 \times 35 \times 35$ mm and wall thicknesses of either 1 mm (IL and IL-D + gas) or 3.5 mm (for IL-H + gas measurements) equipped with a Swagelock tap to minimise headspace. To ensure that the ILs achieved equilibrium saturation with the two gases ($\chi_{\text{propane}} = 0.15$ and $\chi_{\text{propene}} = 0.23$ in $[\text{C}_4\text{mim}][\text{NTf}_2]$ at 6 bar as reported by Lee and Outcalt [10]), the sample cans loaded with IL were pressurised with gas for 3 days off-line and then sealed by closing the Swagelock taps before data collection using the SANDALS spectrometer at the ISIS pulsed neutron and muon source, Rutherford Appleton Laboratory, UK. The instrument has a wavelength range of 0.05–4.5 Å, and data were collected over a Q range from 0.05–50 Å^{−1} at 298 K.

Table 2. Comparison of experimental averaged scattering levels from samples with predicted compositions and densities, calculated based on the neat $[\text{C}_4\text{mim}][\text{NTf}_2]$ atomic density of $0.08214 \text{ atoms } \text{\AA}^{-3}$, corresponding to the measured density of IL-H

Sample	Average merged dcs /barns $\text{sr}^{-1} \text{ atom}^{-1}$	% Difference in dcs from predicted (from neat IL)	Calc. Density /g cm^3
IL-D	0.726	+1	1.476
IL-H	2.652	-2	1.430 ^a
IL-H/D	1.671	0	1.454
IL-D + propane	1.024	12 (+43)	1.433
IL-H + propane	2.770	-1 (+2)	1.389
IL-D + propene	1.062	+17 (+50)	1.436
IL-H + propene	2.841	+3 (+7)	1.394

^a measured density.

3. Results and Discussion

3.1. Experimental considerations and raw scattering data

Data reduction was performed using GUDRUN [36] to produce a differential scattering cross-section for each experimental sample after calibration and background subtraction for single atom scattering. For the pure IL samples (IL-H, IL-D and IL-H/D), the experimental sample densities and scattering levels were consistent with the isotopic compositions of the samples, based on the measured density of IL-H (Table 2).

It was not possible to measure the experimental density of the gas saturated samples at pressure. for the IL + gas samples, densities were estimated by comparison of experimental scattering differential cross sections obtained with expected atomic composition derived from the literature solubility data for the two gases [10]. Comparison of the experimental scattering levels from the different samples (Table 2) reveals that the total scattering from protiated $[\text{C}_4\text{mim}][\text{NTf}_2]$ (IL-H) is insensitive to addition of propane or propene due to the large hydrogenous scattering component of the IL. In contrast, the neutron scattering differential cross sections obtained using the deuterated $[\text{C}_4\text{mim-d}_{15}][\text{NTf}_2]$ (IL-D), which scatters significantly less than IL-H, showed much greater sensitivity to the addition of the hydrogenous gases with neutron scattering levels that were *ca.* 40-50 % higher than those from the pure IL-D. The scattering levels obtained from both IL-D + propane and IL-D + propene were consistent with those predicted based on the reported gas solubility [10] assuming no volumetric change. Indirect confirmation of gas solubility was obtained by the by the observation on opening the sample cans to atmospheric pressure after completion of the experiments of gas evolution from the ILs.

Scattering data for the IL and IL + gas mixtures are shown in Figure 3 for the protiated and deuterated isotopologues. Above $Q = 10 \text{ \AA}^{-1}$ the total structure factor, $F(Q)$, is dominated by the intramolecular structure of the IL and no significant differences were anticipated, or observed, between the data for the IL and IL-H + gas mixtures. In contrast, intermolecular interactions contribute to the Q -range of $1\text{-}6 \text{ \AA}^{-1}$ and over this region some small differences in the scattering the neat IL and the IL-H + gas mixtures are observable. Residual differences, calculated between the structure factors of the IL and IL + gas mixtures and plotted in Figure 3, show the magnitude of these differences. For the protiated IL, the two IL + gas samples show small variations between $1.5\text{-}3 \text{ \AA}^{-1}$ compared to the neat IL. In contrast, both IL + gas structure factors for the IL-D samples are almost identical at values of $Q > 1$ with a small ‘peak’ in the difference plots at $1.5 \text{ \AA}^{-1}$ corresponding to the difference in intensity of scattering compared to the neat IL. Notably, there are no changes in the peak positions for the remaining features in the data between the IL and IL + gas systems showing that dissolution of the hydrocarbons has only a minimal impact on the most significant coulombic cation-anion correlations that dominate the scattering data, and that ion-ion correlation distances across the three systems, *i.e.* that the dissolved gas occupies ‘free volume’ within the liquids and does not disrupt the ionic liquid lattice structure.

Below $Q = 1 \text{ \AA}^{-1}$, all IL + gas samples show higher scattering levels than the corresponding neat IL. These low- Q variations could be due to differences in the degree of correction applied in GUDRUN to account for inelastic scattering by hydrogen in the systems, and these data corrections could also propagate into the intensities of scattering up to $Q = 2$ in the protiated samples.

Figure 3. Experimental $F(Q)$ scattering data from experiments using protiated (blue) and deuteriated (red) $[C_4mim][NTf_2]$, for neat ionic liquid (solid lines), IL + propane (dotted lines) and IL + propene (dashed lines). The corresponding residual differences between the IL and IL + gas structure factors are shown in black. Only minor differences in the $F(Q)$ profiles are observed with small variations in the intensity levels in the low- Q region that may be a consequence of increased inelastic scattering from the IL + gas samples that contain greater hydrogenous content of dissolved hydrocarbon gases than the neat ILs. Notably, the position of the highest intensity peak at $1.4 \text{ \AA}^{-1}$ is unchanged.

Figure 4. Atomic labels for unique atom positions of $[C_4mim][NTf_2]$ and propane and propene sites defined for the EPSR fitting.

3.2. EPSR modelling of $[C_4mim][NTf_2]$ and $[C_4mim][NTf_2]$ + propane/propene liquid structures

Data from the neutron diffraction experiments was analysed using EPSR [21, 22] fitting a three dimensional simulation model self-consistently against the experimental structure factors. The neat IL was modelled using a cubic simulation box of sides $62.4 \text{ \AA}$ containing 500 ion pairs with three data sets (from IL-H, IL-D and IL-H/D), the IL + propane mixture contained 250 ion pairs and 44 propane molecules ($\chi_{propane} = 0.15$) in a box with sides $50.3 \text{ \AA}$, and the IL + propene mixture was modelled using 500 ion pairs and 150 propene molecules ($\chi_{propene} = 0.23$) in a box of sides $63.8 \text{ \AA}$. Both IL + gas systems were fitted against two experimental data sets collected using protiated gasses (propane and propene) dissolved in both protiated and deuteriated ILs.

All three EPSR models were refined against the experimental data over the full data range ($Q = 0.1\text{--}50 \text{ \AA}^{-1}$). Initial potentials for the EPSR fitting were taken from the non-bonded terms in the OPLS-AA forcefields for ionic liquids [37] and hydrocarbons [38], with interatomic distance constraints defining basic molecular geometries obtained using MOPAC with the AM1 model. Atom types in each system were defined based on their unique positions in the molecular skeletons, as shown in Figure 4, and full rotational flexibility was enabled in the model. The full parameters of the reference potential and the interatomic distance and angular constraints used to define the basic molecular geometries are shown in Tables 3 and 4.

In each case, the EPSR models obtained after refinement fitted well to the experimental data sets

Table 3. Lennard-Jones well depth (ϵ), range (σ), and charge (q) parameters used for the reference potential of the Empirical Potential Structure Refinement model.

Atom label	ϵ /kJ mol ⁻¹	σ /Å	q /e
Cation			
N1	0.71100	3.25	-0.83850
C1	0.29300	3.55	-0.94150
C2	0.29300	3.55	0.12500
C3	0.29300	3.55	-0.10340
C4	0.29300	3.55	-0.45800
H1	0.12500	2.50	0.13652
H2	0.12500	2.50	0.13652
H3	0.12500	2.50	0.13652
H4	0.12500	2.50	0.13652
H5	0.12500	2.50	0.13652
H6	0.12500	2.50	0.13652
C5	0.29300	3.55	-0.16965
C6	0.29300	3.55	-0.21580
Anion			
NA	0.71128	3.25	-0.66000
SA	1.04600	3.55	1.0200
CA	0.27614	3.50	0.35000
FA	0.22175	2.95	-0.16000
OA	0.87864	2.96	-0.53000
Propane			
CP1	0.27614	3.50	-0.21060
CP2	0.27614	3.50	-0.15990
HP1	0.12552	2.50	0.07266
HP2	0.11000	2.50	0.07266
Propene			
CP3	0.31798	3.55	-0.22800
CP4	0.31798	3.55	-0.16040
CP5	0.27614	3.50	-0.19000
HP3	0.12552	2.42	0.09640
HP4	0.12552	2.50	0.09640

(Figure 5). The scattering data from the neat $[\text{C}_4\text{mim}][\text{NTf}_2]$ IL shows a large rise in the scattering at low- Q for the 1:1 H/D-mixture that is absent from the solely protiated or deuteriated samples and can be interpreted as a consequence of longer-range H/D correlations between cation sites within the disordered and slowly diffusing coulombic lattice of the IL. This is well reproduced in the fitted model. In most IL systems previously examined with neutron scattering, this 1:1 H/D-contrast has not been included in data sets, and is likely to provide useful information when attempting to understand the extent of longer range correlation structure beyond the first shell.

Centre of mass radial distribution functions (COM RDFs) were calculated between the anion and imidazolium ring of the cation for each of the three systems under investigation (IL, IL + propane, and IL + propene) and are shown in Figure 6. The general solvation and structure trends that have been previously shown for 1,3-dimethylimidazolium and 1-ethyl-3-methylimidazolium ILs [30] are also evident here with a strongly ordered liquid containing alternating cation–anion correlations.

The most notable difference in the COM RDFs compared to the corresponding 1,3-dimethylimidazolium and 1-ethyl-3-methylimidazolium ILs [30] is the clear presence of cation–cation correlation in the first coordination shell of the imidazolium rings as a large ‘shoulder’ in the RDF at $r < 6$ Å. This is examined and discussed below.

Residual differences between the RDFs of the neat IL and IL+gas systems are also plotted in Fig. 6 and show the magnitudes of the differences between the respective pairs of RDFs. These are rather small, especially considering the sizes of the ions and molecules in these liquids; the $[\text{C}_4\text{mim}]^+$ cation has a planar cross-section of approximately 9×5 Å. This similarity in the ion–ion RDFs in each system indicates that dissolution of both propane and propene produce only minor perturbation of the ionic structure of the liquids, even when 0.23 mole fraction of propene is dissolved. This supports the conclusions drawn from direct observation of the scattering data in Fig. 3, that there are no significant changes in the dominant ion–ion interactions. The changes in the ion–ion RDFs between the IL and

Table 4. Intramolecular bond distance ($\text{\AA}$) and non-hydrogen bond-angle ($^\circ$) constraints used to define the basic geometries of the $[\text{C}_4\text{mim}]^+$ cation, $[\text{NTf}_2]^-$ anion, and propane and propene molecules in the initial EPSR simulation model.

Bond Distance / Å		Bond Angle / °		Bond Angle / °	
Cation					
N1-C1	1.40	C1-N1-C2	108.3	C5-C4-H4	109.5
N1-C2	1.38	C1-N1-C3	125.8	N1-C4-H4	107.4
N1-C3	1.44	C1-N1-C4	125.9	H4-C4-H4	108.5
N1-C4	1.45	C2-N1-C4	125.8	C4-C5-C5	109.2
C1-C1	1.40	C2-N1-C3	126.0	C4-C5-H5	110.4
C1-H1	1.10	C1-C1-N1	107.3	C5-C5-C6	110.8
C2-H2	1.10	C1-C1-H1	130.1	C5-C5-H5	109.6
C3-H3	1.12	N1-C1-H1	122.5	C6-C5-H5	109.7
C4-C5	1.53	N1-C2-N1	108.8	H5-C5-H5	107.6
C4-H4	1.13	N1-C2-H2	125.6	C5-C6-H6	110.5
C5-C5	1.52	N1-C3-H3	109.5	H6-C6-H6	108.3
C5-H5	1.12	N1-C3-H3	109.4		
C5-C6	1.51	H3-C3-H3	109.5		
C6-H6	1.12	C5-C4-N1	114.2		
Anion					
NA-SA	1.570	FA-CA-FA	104.08		
SA-CA	1.818	SA-CA-FA	114.25		
SA-OA	1.442	SA-NA-SA	125.82		
CA-FA	1.323	CA-SA-OA	101.02		
		NA-SA-CA	102.31		
		NA-SA-OA	116.97		
		OA-SA-OA	114.49		
Propane					
CP2-HP2	1.122	CP1-CP2-CP1	111.79		
CP2-HP2	1.122	HP2-CP2-CP1	109.43		
CP2-CP1	1.507	HP2-CP2-HP2	107.08		
HP1-CP1	1.117	CP2-CP1-HP1	110.56		
		HP1-CP1-HP1	108.26		
Propene					
CP3-CP4	1.332	CP4-CP3-HP3	122.51		
CP3-HP3	1.098	HP3-CP3-HP3	114.99		
CP3-HP3	1.098	CP3-CP4-CP5	123.72		
CP4-CP5	1.478	CP3-CP4-HP3	120.77		
CP4-HP3	1.103	CP5-CP4-HP3	115.51		
CP5-HP4	1.118	CP4-CP5-HP4	110.79		
		HP4-CP5-HP4	108.22

Figure 5. Comparison of experimental scattering data (blue, solid) and fit from epsr model (red, dashed) for $[\text{C}_4\text{mim}][\text{NTf}_2]$ (H, H/D, and D) and the protiated and deuteriated ionic liquids containing propane (middle) and propene (top).

Figure 6. Centre of mass RDFs and residual differences ($\Delta g(r)$ between the IL and IL + gas RDFs) between cations and anions (cation-anion, red; cation-cation, blue; and anion-anion, green) in the three ionic liquid systems under investigation: Neat $[C_4mim][NTf_2]$ (solid lines), IL + propane (dotted lines) and IL + propene (dashed lines).

IL + gas mixtures that are evident from Fig. 6 are: (i) a shortening of the cation–cation correlation distance in the presence of both gases (shown by the small peak at ca. 4.5 Å in the cation–cation residual trace) and (ii) a small reduction in anion–anion correlation in the IL + gas mixtures below 7 Å (indicated by the negative peak at 6 Å in the anion–anion residual) which is presumed to be a result of increased anion–gas correlation on dissolution.

3.3. $[C_4mim][NTf_2]$

Examining first the liquid structure of the neat $[C_4mim][NTf_2]$, the COM RDFs show the expected primary cation–anion first shell correlation as a broad peak (r_{max} ca. 6.0 Å). The first shell cation–anion correlation is a common feature of all ionic liquid materials and, as Hardacre and co-workers [29] have previously shown for 1,3-dimethylimidazolium ILs, the cation–anion correlation peak becomes broader and r_{max} moves to longer distances on changing the anion from Cl^- to $[PF_6]^-$ to $[NTf_2]^-$ as a consequence of increased size and charge diffusivity in the anions.

The RDFs (Figure 6) also reveal cation–cation association in the first coordination first shell through the presence of the peak (or leading shoulder) at 6.0 Å. While the most dominant features in the local environment of the IL are the cation–anion interactions, the presence of cation–cation contacts can lead to additional structure [30]. Cation–cation association through ring-stacking $\pi - \pi$ aggregation was first suggested on the basis of NMR spectroscopy [39, 40], and has also been seen more recently in *N*-methylpyridinium ILs where the rigid planar cations appear to promote greater π - π association [41]. However, examination of centre-of-ring and terminal methyl RDF correlations in $[C_4mim]Cl$ by Hunt *et al.* [42] suggested that non-specific chain–chain aggregation (driven by Van der Waals interactions) was more dominant in the liquid and only weak ring–ring correlations were present.

Site-site partial RDFs, derived from the EPSR model, provide more detail on the specific associations of the ions. Selected correlations between $[NTf_2]^-$ anion oxygen (OA) atoms and C1, C2, and C6 sites in the cation are shown in Figure 7, and the corresponding coordination numbers are shown in Table 5.

For the neat IL, the largest correlation to the anion OA site is from the terminal-methyl group of the cation butyl-chain (site C6) with a peak at $r_{max} = 3.5$ Å (coordination number 2.82 ± 1.23). This reflects the mobility and proximal position of this terminal methyl-group in the cation. Strong cation–anion correlation also evident to the C(2)-H (site C2) and C(4/5)-H (site C1) positions of the imidazolium ring (peak maximum at 3.4 Å). The correlation to the C(2)-H position is greater than that to the C(4/5)-H positions (site C1), with coordination numbers of 2.08 ± 1.08 and 1.67 ± 1.08 respectively, indicating

Figure 7. Site-site cation-cation and cation-anion radial distribution functions derived from the EPSR model of neat $[\text{C}_4\text{mim}][\text{NTf}_2]$ showing correlations from the C1 and C2 ring atom types, C6 (terminal methyl group of cation butyl chain) and anion OA positions to C1 (red), C2 (blue), and C6 (green)

Table 5. $[\text{C}_4\text{mim}][\text{NTf}_2]$ and $[\text{C}_4\text{mim}][\text{NTf}_2] + \text{propane/propene}$ site-site coordination numbers calculated to the minimum after the first peak ($r_{\min}$) in the cation-anion (4.25 Å), cation-cation (5.0 Å), and cation-hydrocarbon (7.0 Å) correlations. For cation-hydrocarbon correlations, coordination numbers to the first peak maximum, $r_{\max}$ are also given in parentheses.

	$[\text{C}_4\text{mim}][\text{NTf}_2]$	IL + propane	IL + propene
C1-C1	1.96 ± 1.13	2.19 ± 1.23	2.09 ± 1.25
C1-C2	1.32 ± 0.51	1.42 ± 0.56	1.37 ± 0.55
C1-C6	0.89 ± 0.81	0.62 ± 0.72	0.59 ± 0.68
C1-OA	1.67 ± 1.08	1.53 ± 1.07	1.49 ± 1.03
C2-C2	0.18 ± 0.40	0.23 ± 0.45	0.26 ± 0.47
C2-C6	1.03 ± 0.74	0.55 ± 0.67	0.56 ± 0.68
C2-OA	2.08 ± 1.08	1.83 ± 1.05	1.90 ± 1.13
C6-C6	0.57 ± 0.69	0.46 ± 0.63	0.39 ± 0.57
C6-OA	2.82 ± 1.23	2.72 ± 1.30	2.68 ± 1.31
C1-hydrocarbon		0.82 ± 1.08 (0.12 ± 0.37)	0.78 ± 0.84 (0.10 ± 0.30)
C2-hydrocarbon		0.87 ± 1.09 (0.07 ± 0.27)	0.82 ± 0.88 (0.09 ± 0.29)
C6-hydrocarbon		1.04 ± 1.14 (0.15 ± 0.38)	0.75 ± 0.87 (0.13 ± 0.36)

Figure 8. SHARM spatial probability maps of anions (red, 2.0–9.0 Å, top 20 % probability) and cations (blue, 2.0–7.4 Å, top 20 % probability) around a central $[\text{C}_4\text{mim}]^+$ ring showing the marked preference for $[\text{NTf}_2]^-$ association with the C(2)-H position out of the plane of the imidazolium ring, and with anion–cation correlations on the opposing side of the imidazolium ring bridging the ring C(4/5)-H and N-methylene/methyl hydrogens in the plane of the ring. Cation–cation association in the first coordination shell are evident above/below the ring.

that cation–ring to anion correlations occur prominently through the C(2)-H site.

The cation–cation site-site RDF correlations in Figure 7 also show a similar picture of preferred directionality. The C(2)-H position (C2 site) participates in much less association with cations (C1/C2/C6 sites) with only small peaks present between C2–C1 (ring–ring) or C1–C6 (ring–chain terminal- CH_3) sites at the contact separation distance (*ca.* 4 Å). Notably, the C2–C2 coordination number is significantly lower (0.18 ± 0.40) than those for correlations of the C2 site to other cation carbons. In contrast, C1–C1, C1–C6, and C6–C6 correlations are evident with peaks in their respective RDFs at $r_{\text{max}} = 4.2$ Å. The coordination numbers for these correlations (Table 5) are double those observed to the C1 position and indicate that directional ring–ring correlations between C1–C1 sites and ring–chain correlations occur with approximately equal probability.

Spatial distribution functions (SDFs), which show the locations of cations and anions relative to one another, were calculated for the cation–anion and cation–cation association in the first shell around $[\text{C}_4\text{mim}]^+$ cations using the SHARM routines in EPSR and are shown in Figure 8. The SDFs show both cation–anion and cation–cation distributions that are consistent with the site-site RDF analysis. The positions of highest anion association around the $[\text{C}_4\text{mim}]^+$ cation are associated with the ring C(2)-position as a broad arc encompassing space above and below the plane of the imidazolium ring. The two smaller lobes of high correlation probability represent anions associated with both the ring C1 and N– CH_2/CH_3 positions on the cation. Compared with a simple model of linear hydrogen-bonded association of small, point-charge anions equally with the three hydrogen-bond donor C-H sites on the imidazolium ring in a planar trigonal network, the anion–cation correlation present in $[\text{C}_4\text{mim}][\text{NTf}_2]$ is more localised at the imidazolium ring C(2)-H position and is accompanied by considerable ‘out of plane’ anion–cation association ‘above/below’ the imidazolium ring in a broad arc.

Cation–cation correlation in the first coordination shell is associated with locations above and below the central imidazolium ring and offset from the ring centre of mass towards the C1 positions. That is, the cation–cation correlations occur through positions that are not occupied by anions. This cation–cation correlation, evident in both the SDF (Figure 8) and COM RDF (Figure 6) plots, appears consistent with increased association induced as an indirect consequence of the changes in relative anion–cation correlations with the imidazolium ring C(2)-, C(4)- and C(5)-sites.

This is likely to be driven by steric factors due to the free volume required for the butyl-chain on the cation, the associated reduction in anion association with the C1 sites as the N-alkyl chain is increased [31], and changes in the anion–cation spatial correlation from trigonal towards tetrahedral, *water-like*,

local anisotropy. It is notable that the absence of C1–C2 and C2–C2 correlations over these distances ($<4\text{--}5\text{ \AA}$) also suggests that cation–cation interactions are not co-planar π - π stacking correlations, but are likely to be edge-to-edge or Y-oriented angular correlations as have been shown to be predominant in liquid aromatics such as benzene [43].

This experimental data is consistent with previous SANS [44] and SWAXS [45] data, and the analysis is consistent with MD simulation [46] where analogous cation–anion and terminal carbon–carbon RDF correlations were found and, for the longer-chain $[\text{C}_8\text{mim}][\text{NTf}_2]$, cation–cation correlations with evidence for a ‘close contact’ shoulder was interpreted as cation–cation pairing. Similarly, Marekha *et al.* [47] concluded, summarising previous simulation studies [23, 48–53], that $[\text{NTf}_2]^-$ anions occupy positions above/below the plane of the $[\text{C}_4\text{mim}]^+$ ring and are much more strongly associated with the C(2)-H site than that with the C(4/5)-H positions.

These changes in ion–ion radial and spatial correlation, particularly the increased degree of cation–cation association, evident in $[\text{C}_4\text{mim}][\text{NTf}_2]$ compared to the symmetric, methyl-substituted $[\text{C}_1\text{mim}][\text{NTf}_2]$ [29], and that become increasingly prevalent as the alkyl-chain is extended [46] are a consequence of the need to accommodate bulky alkyl-groups within the alternating-charge liquid lattice present in molten salts and ionic liquids containing small, freely rotating cations [30]. This leads to local distortion and disruption of the coulombic charge ordering, producing low- Q signals in the structure factors associated with the length scales of the ions, and because of conformational restrictions placed on the cations within the ionic lattice due to the appended alkyl-chains, an inevitable increase in cation–cation contacts.

In summary, experimental neutron scattering data was collected from H, D, and H/D-isotopomers of $[\text{C}_4\text{mim}][\text{NTf}_2]$ and a self-consistent model fitted using EPSR that reveals liquid structure consistent with that derived from MD simulation, with a tetrahedral distribution of anions around cation (broad arc, predominantly above/below ring plan around C2 position) and within the plane of the ring associated with C1 sites, and with cation-cation first shell correlation through non-specific C1-C1 ring–ring and C1-C6 chain contacts.

3.4. $[\text{C}_4\text{mim}][\text{NTf}_2] + \text{propane/propene}$

As discussed above, the scattering data obtained from the IL + propane and IL + propene systems did not show significant differences from those of the parent ILs (IL-H or IL-D in Figure 3), however the dissolution of the gases at high concentrations ($\chi_{\text{propane}} = 0.15$ and $\chi_{\text{propene}} = 0.23$ in $[\text{C}_4\text{mim}][\text{NTf}_2]$ [10]) was confirmed by examination of the dcs levels from the neutron experiments with deuteriated IL samples. It can be concluded then, that cation–anion correlations that dominate the structure of ILs are not impacted by the dissolution of the hydrocarbon gases. This appears reasonable since (i) insertion of a non-polar hydrocarbon is unlikely to significantly disrupt coulombic attractive interactions and it has been shown that $[\text{C}_4\text{mim}][\text{PF}_6]$ undergoes aggregation even in polyaromatic solvents such as naphthalene [54] and (ii) the general understanding of alkane solubility in ionic liquids is that it is entropically driven through favourable interactions with the alkyl chain and dispersed anions of ILs [8].

The higher solubility of ethene over ethane has been ascribed to an increase in the entropy of solvation due to the participation of a larger number of solvation sites in the IL [8] with both ethene and ethane locating in regions associated with the large, charge-delocalised anions and with cation N-alkyl substituents (where dispersive interactions are maximised and disruption of associative coulombic interactions between charges components are minimised). However, ethene, when compared to ethane and to butanes [55] tended to be preferentially solvated closer to the imidazolium ring. This was identified through reduction in the relative size of the ethene-C(T) RDF, and a small increase in ethene-C(ring) correlations, particularly at the C(4/5) positions compared to the ethane case.

From the EPSR models of IL + propane and IL + propene, partial RDFs were calculated between propane or propene with the cation butyl-chain and imidazolium rings (Figure 9). Both gases show similar correlation with the imidazolium ring, with a first correlation peak at *ca.* $5.0\text{ \AA}$, although the propene–ring correlation distances is approximately $0.4\text{ \AA}$ shorter than that with propane. In contrast, the correlation between the two gases and the butyl-chain of the IL shows substantial differences. The propane–chain correlation peak has a first maximum at *ca.* $5.2\text{ \AA}$ compared to $4.8\text{ \AA}$ for the correspond-

Figure 9. RDFs showing the association of the two gasses propane (solid lines) and propene (dashed lines) with the $[\text{C}_4\text{mim}][\text{NTf}_2]$ butyl chain (green), imidazolium ring (red) and $[\text{NTf}_2]^-$ anion (blue). The most significant difference observable is the greater size of the first peak in the propane–butyl chain correlation at *ca.* 5.6 Å compared with the corresponding propene–butyl chain correlation at *ca.* 5.0 Å.

Figure 10. Site–site, solute–cation radial distribution functions of propane (left) and propene (right) in the ionic liquid, $[\text{C}_4\text{mim}][\text{NTf}_2]$, showing correlations with the hydrocarbon- CH_3 (solid line), propane central- CH_2 (dotted line), and propene terminal- CH_2 (dotted line) groups. The reduction in intensity and broadening of the propene–terminal- CH_3 and increase in propene- NCH_3 correlations compared to those with propane is evident.

Figure 11. SHARM spatial probability maps of propane (left) and propene (right) around a central $[\text{C}_4\text{mim}]^+$ cation, plotted to show the top 25 % probability of association between 2.0–10 Å from the centres of mass of the gas probes and the imidazolium ring.

ing propene–chain correlation, and the first peak in the propane–chain correlation is also significantly larger. These observations appear remarkably consistent with previous MD simulation [8] where ethene was found to associate more closely to the imidazolium ring of $[\text{C}_4\text{mim}][\text{NTf}_2]$ than ethane which correlated more strongly with the terminal $-\text{CH}_3$ groups of the cation butyl chain.

Hydrocarbon–cation site-site RDFs (Figure 10) provide greater detail of the propane and propene association with the IL cation. For both IL + propane and IL + propene, the largest correlation peak ($r_{\text{max}} = 4.1$ Å) is between the gas molecules and the terminal- CH_3 group of the imidazolium cation (C6 site) consistent with simulation and with expectations for solvation of non-polar gases in the IL. Propane also exhibits correlations with the cation C3 ($\text{N}-\text{CH}_3$) and C1 sites ($r_{\text{max}} = 4.0 - 4.1$ Å), but notably much less correlation with the C2 site. This pattern resembles that of the cation–cation correlations in the neat IL, with propane–ring interactions at sites not occupied by the anions.

In contrast, propene exhibits association with both the C1 and C2 ring sites at the 4.0 Å contact distance. Correlation between propene and the C3 ($\text{N}-\text{CH}_3$) site in the IL is also enhanced relative to that observed in the IL + propane system, and the corresponding correlation with the C6 site decreases. Overall, propene is found more closely associated with the cation ring, correlating with both the C1 and C2 ring-sites, whereas propane only shows association with the ring-C1 sites. Propane shows greater correlation with the cations terminal- CH_3 site whereas in the IL + propene system, this correlation is reduced due to the increased propene–ring association. It appears evident that this greater degree of propene–imidazolium ring interaction, compared to that with propane, is a consequence of the presence of the unsaturated double-bond in propene and is likely to be associated with greater ability to form hydrogen-bonds from the electron-rich π -bond to the δ^+ C-H sites on the imidazolium ring competing with cation–anion associations present in the neat ionic liquid.

Coordination numbers for site-site correlations corresponding to the RDFs in Figure 10 are shown in Table 5. Compared with the structure of the neat IL, the IL + gas mixtures show similar cation–anion ($\text{Cn}-\text{OA}$) coordination numbers, and a reduction in cation–cation correlation through the C1– and C2–C6 contacts of *ca.* 30 and 45 % respectively. There are no differences in the averaged cation–gas coordination numbers calculated over the entire first correlation peaks to 7.0 Å for the correlations to the cation ring. In contrast, the propane–C6 coordination number is 25 % greater than that for propene–C6. However, only limited information can be gained considering the entire population of correlations in this first shell due to its broadness. Comparing just the strongest, shortest correlations at distances up to 4.25 Å that encompass to the first maxima (r_{max}) in the site-site RDFs in Figure 10 provides greater information of preferred association sites. For the IL + propane system, the C2–hydrocarbon coordination number to r_{max} is significantly reduced compared to that from the C1 site (0.07 ± 0.27 compared to 0.12 ± 0.37) whereas the corresponding correlations in the IL + propene systems have coordination numbers that are almost identical (0.09 ± 0.29 and 0.10 ± 0.30) responding to the increased association of propene with all three sites on the imidazolium ring.

These small changes in the gas-cation association can be seen in the SDFs (Figure 11) of propane and propene calculated around a central $[\text{C}_4\text{mim}]^+$ cation, and plotted to encompass the top 25 % probability of association calculated to a separation distance of 10 Å from the cation centre of mass. This distance allows the principle correlations of the C3 hydrocarbons with both the imidazolium ring, N-CH₃ and N-butyl functions to be captured in the pictures. For propane dissolved in the IL, the SDF shows the strong correlations with the cation N-CH₃, terminal-CH₃, and ring C(4/5) positions and the reduced correlation at the ring C(2)-site, consistent with the interpretations of the RDFs from Figure 10. In comparison, the SDF for propene around the IL cation shows a much more homogeneous dispersion with an even, relatively featureless average correlation to all the fixed positions on the imidazolium ring, and a comparatively lesser proportion of association with the butyl-chain terminal position.

4. Conclusions

Using EPSR, the liquid structure of $[\text{C}_4\text{mim}][\text{NTf}_2]$ was determined from experimental neutron scattering data, fitting the model self-consistently to data from protiated, deuterated and 1:1 H/D mixed samples, producing a model of the IL with spatial correlations that are consistent with previous MD simulation and shows showing that the first correlation shell around the $[\text{C}_4\text{mim}]^+$ cation consists predominantly of anions (through charge-associated coulombic packing) with the greatest probability of association occurring with the C(2)-H position of the imidazolium ring in a large arc encompassing significant space above/below the plane of the ring, and with off-set association with the C(4/5)-H positions of the ring. Cation-cation association is also observed within the cation-first coordination shell, with interactions that are complementary to the cation-anion association showing non-specific chain-chain and chain-ring correlations and ring-ring correlation through the C(4/5)-H sites, and with cation-cation spatial distribution above/below and between the C(4)-H and C(5)-H positions on the imidazolium ring.

Secondly, the first experimental study of gas dissolution in ILs using neutron scattering has been reported, with results that show dissolution of propane and propene in the ILs at 6 bar gas pressure, generating saturated solutions containing respectively $\chi_{\text{propane}} = 0.15$ and $\chi_{\text{propene}} = 0.23$ in $[\text{C}_4\text{mim}][\text{NTf}_2]$, does not cause significant disruption or change in the experimental $F(Q)$ scattering data, and hence minimal perturbation of the dominant ion-ion structure controlling correlations present in the liquids. The IL + propane and IL + propene liquids were modelled with EPSR, with good self-consistent fits to the data in each case that reproduce the ion-ion structure in the scattering data and also show subtly different distributions of propane and propene gases within the IL. The results show subtly different distributions of the two hydrocarbons in the IL, with propene exhibiting greater association with the $[\text{C}_4\text{mim}]^+$ cation imidazolium ring through both the C(4/5)- and C(2)-sites whereas propane only exhibited association with the C(4/5)-position on the imidazolium ring and had a significantly greater correlation with the terminal-CH₃ group of the butyl chain. These results are remarkably consistent with, and support conclusions from, previous MD simulation [11] of ethane and ethene dissolved in $[\text{C}_4\text{mim}][\text{NTf}_2]$ where greater ethene/ $[\text{C}_4\text{mim}]^+$ -ring association was observed compared to preferred ethane-alkyl chain association driven by differences in the polarisation and charge distribution between ethane and ethene.

Data availability statement

Raw data were collected on the SANDALS instrument at The ISIS Neutron and Muon Source, Rutherford Appleton Laboratory and will be publicly available at <https://doi.org/10.5286/ISIS.E.84424468> from 29 February 2020 in accordance with ISIS data management policy. Derived data supporting the findings of this study are available from the corresponding author (JDH) on request.

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References

- [1] Materials for Separation Technologies. Energy and Emission Reduction Opportunities, , Oak Ridge National Lab. (ORNL), Oak Ridge, TN (United States) 2005 .
- [2] V. Mokrushin, D. Assenbaum, N. Paape, D. Gerhard, L. Mokrushina, P. Wasserscheid, W. Arlt, H. Kistenmacher, S. Neuendorf and V. Goeke, *Chem. Eng. Technol.* **33**, 63–73 (2010).
- [3] J.P. Hallett and T. Welton, *Chem. Rev.* **111**, 3508–3576 (2011).
- [4] J. Estager, J.D. Holbrey and M. Swadźba-Kwaśny, *Chem. Soc. Rev.* **43**, 847–886 (2014).
- [5] L.A. Blanchard, D. Hancu, E.J. Beckman and J.F. Brennecke, *Nature* **399**, 28–29 (1999).
- [6] A.M. Scurto, S.N.V.K. Aki and J.F. Brennecke, *J. Amer. Chem. Soc.* **124**, 10276–10277 (2002).
- [7] P. Scovazzo, J. Kieft, D.A. Finan, C. Koval, D. DuBois and R. Noble, *J. Membrane Sci.* **238**, 57–63 (2004).
- [8] L. Moura, M. Mishra, V. Bernalles, P. Fuentealba, A.A.H. Padua, C.C. Santini and M.F.C. Gomes, *J. Phys. Chem. B* **117**, 7416–7425 (2013).
- [9] M. Abai, M.P. Atkins, A. Hassan, J.D. Holbrey, Y. Kuah, P. Nockemann, A.A. Oliferenko, N.V. Plechkova, S. Rafeen, A.A. Rahman, R. Ramli, S.M. Shariff, K.R. Seddon, G. Srinivasan and Y. Zou, *Dalton Trans.* **44**, 8617–8624 (2015).
- [10] B.C. Lee and S.L. Outcalt, *J. Chem. Eng. Data* **51**, 892–897 (2006).
- [11] L. Moura, C.C. Santini and M.F.C. Gomes, *Oil Gas Sci. Tech.* **71**, 23 (2016).
- [12] D. Camper, C. Becker, C. Koval and R. Noble, *Ind. Eng. Chem. Res.* **44**, 1928–1933 (2005).
- [13] F.G. Edwards, J.E. Enderby, R.A. Howe and D. Page, *J. Phys. C* **8**, 3483–3490 (1975).
- [14] J.L. Finney and A.K. Soper, *Chem. Soc. Rev.* **23**, 1–10 (1994).
- [15] S. Lenton, N.H. Rhys, J.J. Towey, A.K. Soper and L. Dougan, *Nature Commun.* **8**, 919 (2017).
- [16] N. Steinke, R.J. Gillams, L. Carlos Pardo, C.D. Lorenz and S.E. McLain, *Phys. Chem. Chem. Phys.* **18**, 3862–3870 (2016).
N.H. Rhys, A.K. Soper and L. Dougan, *J. Phys. Chem. B* **116**, 13308–13319 (2012).
S.E. McLain, A.K. Soper and A. Watts, *J. Phys. Chem. B* **110**, 21251–21258 (2006).
- [17] D.T. Bowron and K.J. Edler, *Langmuir* **33**, 262–271 (2017).
- [18] T. Murphy, S.K. Callear, N. Yepuri, K. Shimizu, M. Watanabe, J.N.C. Lopes, T. Darwish, G.G. Warr and R. Atkin, *Phys. Chem. Chem. Phys.* **18**, 17224–17236 (2016).
- [19] Y.M. Delavoux, M. Gilmore, M.P. Atkins, M. Swadźba-Kwaśny and J.D. Holbrey, *Phys. Chem. Chem. Phys.* **19**, 2867–2876 (2017).
- [20] A.G. Seel, H. Swan, D.T. Bowron, J.C. Wasse, T. Weller, P.P. Edwards, C.A. Howard and N.T. Skipper, *Angew. Chem. Int. Ed.* **56**, 1561–1565 (2017).
- [21] A.K. Soper, *Chem. Phys.* **202**, 295–306 (1996).
- [22] A.K. Soper, *Mol. Phys.* **99**, 1503–1516 (2001).
A.K. Soper, *Phys. Rev. B* **72**, 104204 (2005).
S.E. McLain, S. Imberti, A.K. Soper, A. Botti, F. Bruni and M.A. Ricci, *Phys. Rev. B* **74** (2006).
- [23] P.A. Hunt, C.R. Ashworth and R.P. Matthews, *Chem. Soc. Rev.* **44**, 1257–1288 (2015).
- [24] T. Köddermann, D. Reith and R. Ludwig, *ChemPhysChem* **14**, 3368–3374 (2013).
K. Fumino, T. Peppel, M. Geppert-Rybczyńska, D.H. Zaitsau, J.K. Lehmann, S.P. Verevkin, M. Köckerling and R. Ludwig, *Phys. Chem. Chem. Phys.* **13**, 14064–14075 (2011).
S. Zahn, G. Bruns, J. Thar and B. Kirchner, *Phys. Chem. Chem. Phys.* **10**, 6921–6924 (2008).
- [25] J.G. McDaniel, C.Y. Son and A. Yethiraj, *J. Phys. Chem. B* **122**, 4101–4114 (2018).
- [26] O. Borodin, W. Gorecki, G.D. Smith and M. Armand, *J. Phys. Chem. B* **114**, 6786–6798 (2010).
- [27] M. Herstedt, M. Smirnov, P. Johansson, M. Chami, J. Grondin, L. Servant and J.C. Lassgès, *J. Raman Spectrosc.* **36**, 762–770 (2005).
- [28] K. Fujii, T. Fujimori, T. Takamuku, R. Kanzaki, Y. Umebayashi and S.I. Ishiguro, *J. Phys. Chem. B* **110**, 8179–8183 (2006).
- [29] C. Hardacre, J. Holbrey, S. McMath, D. Bowron and A.K. Soper, *J. Chem. Phys.* **118**, 273–278 (2003).
C. Hardacre, S.E.J. McMath, M. Nieuwenhuyzen, D.T. Bowron and A.K. Soper, *J. Phys.: Condens. Matter* **15**, S159–S166 (2003).
M. Deetlefs, C. Hardacre, M. Nieuwenhuyzen, A.A.H. Padua, O. Sheppard and A.K. Soper, *J. Phys. Chem. B* **110**, 12055–12061 (2006).
- [30] C. Hardacre, J.D. Holbrey, M. Nieuwenhuyzen and T.G.A. Youngs, *Acc. Chem. Res.* **40**, 1146–1155 (2007).

- D.T. Bowron, C. D'Agostino, L.F. Gladden, C. Hardacre, J.D. Holbrey, M.C. Lagunas, J. McGregor, M.D. Mantle, C.L. Mullan and T.G.A. Youngs, *J. Phys. Chem. B* **114**, 7760–7768 (2010).
- T.G.A. Youngs, J.D. Holbrey, C.L. Mullan, S.E. Norman, M.C. Lagunas, C. D'Agostino, M.D. Mantle, L.F. Gladden, D.T. Bowron and C. Hardacre, *Chem. Sci.* **2**, 1594–1605 (2011).
- R. Hayes, S. Imberti, G.G. Warr and R. Atkin, *Angew. Chem. Int. Ed.* **52**, 4623–4627 (2013).
- O.S. Hammond, D.T. Bowron and K.J. Edler, *Angew. Chem. Int. Ed.* **56**, 9782–9785 (2017).
- [31] C. Hardacre, J.D. Holbrey, C.L. Mullan, T.G.A. Youngs and D.T. Bowron, *J. Chem. Phys.* **133**, 074510 (2010).
- [32] P.C. Truelove, D. Haworth, R.T. Carlin, A.K. Soper, A.J.G. Ellison and D.L. Price, in *Proc. 9th Int. Symp. Molten Salts*, edited by C. L. Hussey, D. S. Newman, G. Mamantov and Y. Ito, Vol. 13 (Electrochem. Soc., San Francisco, CA, 1994), pp. 50–57.
- [33] S. Takahashi, K. Suzuya, S. Kohara, N. Koura, L.A. Curtiss and M.L. Saboungi, *Z. Phys. Chem.* **209**, 209–221 (1999).
- [34] C. Hardacre, J.D. Holbrey and S.E.J. McMath, *Chem. Commun.* pp. 367–368 (2001).
- [35] H.F.D. Almeida, J.N. Canongia Lopes, L.P.N. Rebelo, J.A.P. Coutinho, M.G. Freire and I.M. Marrucho, *J. Chem. Eng. Data* **61** (8), 2828–2843 (2016).
- [36] A.K. Soper, *Mol. Phys.* **107**, 1667–1684 (2009).
- A.K. Soper, GudrunN and GudrunX: Programs for correcting raw neutron and X-ray diffraction data to differential scattering cross section, RAL-TR-2011-013, , Rutherford Appleton Laboratory 2011 .
- [37] J.N. Canongia Lopes and A.A.H. Pádua, *J. Phys. Chem. B* **108**, 16893–16898 (2004).
- J.N. Canongia Lopes and A.A.H. Pádua, *J. Phys. Chem. B* **110**, 19586–19592 (2006).
- [38] S.W.I. Siu, K. Pluhackova and R.A. Böckmann, *J. Chem. Theory Comput.* **8**, 1459–1470 (2012).
- [39] A.G. Avent, P.A. Chaloner, M.P. Day, K.R. Seddon and T. Welton, *J. Chem. Soc., Dalton Trans.* pp. 3405–3413 (1994).
- [40] A. Mele, C.D. Tran and S.H. De Paoli Lacerda, *Angew. Chem. Int. Ed.* **42**, 4364–4366 (2003).
- [41] A.H. Turner and J.D. Holbrey, *J. Solution. Chem.* **44**, 621–633 (2015).
- [42] P.A. Hunt and I.R. Gould, *J. Phys. Chem. A* **110**, 2269–2282 (2006).
- [43] T.F. Headen, C.A. Howard, N.T. Skipper, M.A. Wilkinson, D.T. Bowron and A.K. Soper, *J. Am. Chem. Soc.* **132**, 5735–5742 (2010).
- [44] K. Fujii, R. Kanzaki, T. Takamuku, Y. Kameda, S. Kohara, M. Kanakubo, M. Shibayama, S.i. Ishiguro and Y. Umebayashi, *J. Chem. Phys.* **135** (24), 244502 (2011).
- [45] O. Russina, A. Triolo, L. Gontrani, R. Caminiti, D. Xiao, L.G.H. Jr, R.A. Bartsch, E.L. Quitevis, N. Pleckhova and K.R. Seddon, *J. Phys.: Condens. Mat.* **21**, 424121 (2009).
- [46] E. Androulaki, N. Vergadou, J. Ramos and I.G. Economou, *Mol. Phys.* **110**, 1139–1152 (2012).
- E. Androulaki, N. Vergadou and I.G. Economou, *Mol. Phys.* **112**, 2694–2706 (2014).
- [47] B.A. Marekha, V.A. Koverga, E. Chesneau, O.N. Kalugin, T. Takamuku, P. Jedlovszky and A. Idrissi, *J. Phys. Chem. B* **120**, 5029–5041 (2016).
- [48] S. Tsuzuki, H. Tokuda, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B* **109** (2005).
- S. Tsuzuki, H. Tokuda and M. Mikami, *Phys. Chem. Chem. Phys.* **9**, 4780–4784 (2007).
- [49] M. Kohagen, M. Brehm, J. Thar, W. Zhao, F. Müller-Plathe and B. Kirchner, *J. Phys. Chem. B* **115**, 693–702 (2011).
- [50] H. Weber, O. Hollóczki, A.S. Pensado and B. Kirchner, *J. Chem. Phys.* **139**, 084502 (2013).
- [51] A. Mondal and S. Balasubramanian, *J. Phys. Chem. B* **118**, 3409–3422 (2014).
- [52] B.A. Marekha, O.N. Kalugin, M. Bria and A. Idrissi, *Phys. Chem. Chem. Phys.* **17**, 23183–23194 (2015).
- [53] R.P. Matthews, I.J. Villar-Garcia, C.C. Weber, J. Griffith, F. Cameron, J.P. Hallett, P.A. Hunt and T. Welton, *Phys. Chem. Chem. Phys.* **18**, 8608–8624 (2016).
- [54] M.G. Del Pópolo, C.L. Mullan, J.D. Holbrey, C. Hardacre and P. Ballone, *J. Am. Chem. Soc.* **130**, 7032–7041 (2008).
- [55] M.F.C. Gomes, L. Pison, A.S. Pensado and A.A.H. Padua, *Faraday Disc.* **154**, 41–52 (2012).
- L. Pison, V. Bernalles, P. Fuentealba, A.A.H. Padua and M.F.C. Gomes, *J. Chem. Thermodynamics* **89**, 98–103 (2015).
- L. Pison, K. Shimizu, G. Tamas, J.N. Canongia Lopes, E.L. Quitevis and M.F.C. Gomes, *Phys. Chem. Chem. Phys.* **17**, 30328–30342 (2015).