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Solvation of inorganic nitrate salts in protic ionic liquids

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Abstract-

The bulk nanostructure of several inorganic salt solutions in protic ionic liquids is elucidated using neutron diffraction and empirical potential structure refinement (EPSR) modelling. The protic ionic liquids studied are ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN), which are mixed with either LiNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, or $\text{Al}(\text{NO}_3)_3$, at 1:10 or 1:30 solute:solvent mol:mol ratios. The models show inorganic metal ions are solvated within the polar domains of the nanostructure, and can induce significant differences in bulk solvent nanostructure from that of the pure ionic liquids. For EtAN, the uncharged groups aggregate and form an apolar domain in spite of the cation's reduced amphiphilicity because the TRANS rotamer is favoured when an inorganic salt is added.

Keywords: solute, electrolyte, self-assembly, neutron diffraction, bicontinuous phase, amphiphilicity

Introduction-

Ionic liquids (ILs) are low melting point salts. Computer simulations and scattering experiments have shown that pure ILs are nanostructured liquids have ordered polar and apolar domains in the bulk.^[1-26] This solvent nanostructure forms because the IL ions self-assemble, often into bicontinuous morphologies. For protic ILs, cation alkyl chains as small as an ethyl (C₂) group, can produce nanostructures reminiscent of *L*₃-sponge phases.^[10,19] Aprotic ILs with alkyl chains longer than propyl (C₃) form bicontinuous structures,^[4,23] while aprotics with longer alkyl groups (C₁₂-C₁₈) form liquid crystal smectic phases.^[27] Other more complicated ‘clustered’^[5,10,14] or tricontinuous^[28,29] IL nanostructures have been reported. Notably, next to an interface (solid-liquid,^[30-36] air-liquid^[37-39] or liquid-liquid^[40,41]), nanostructure closely related to, but more ordered than, the bulk phase is formed. This is because the second surface orients and aligns the pre-existing ion arrangement.^[31,42]

ILs can dissolve a broad spectrum of polar and apolar compounds,^[43-48] often simultaneously. This is widely thought to be related to their solvent nanostructure. However, solvation structures in ILs are poorly understood. To date, researchers have largely focused on the (nano)structure of ILs mixed with *uncharged* compounds including water,^[15,49-51] alcohols,^[28,52] simple alkanes,^[52] glycerol,^[53] brønsted acid/bases^[15] non-ionic dodecyl poly(ethylene oxide) surfactants,^[54,55] C₆₀,^[56] aromatics,^[57,58] glucose,^[59,60] or cellulose,^[61] usually examining only one (low) solute concentration. In general, the solute is found to be accommodated in either the polar or apolar domains depending on its size and polarity. In this way, the IL solvent resists changes in its self-assembled organization by creating a different, but related nanostructure,^[49] a population of nano-scale objects^[28] or a clathrate-type arrangement^[58] in the bulk. At high solute concentrations, contact ion pairs, solvent-separated ion pairs and then molecularly dispersed IL ions are detected,^[51] similar to well-understood behaviour of ions in molecular liquids.^[62-65]

The solubility of inorganic salts in ILs is reasonably high, but difficult to predict.^[44] Recently, several papers have emerged that show differences in macroscopic IL properties when combined with inorganic salts,^[66-68] similar to molten salt mixtures.^[69,70] Whilst some papers have reported differences in IL interfacial structure with dissolved ions,^[71,72] an understanding of how IL bulk structure changes with addition of inorganic solutes is only beginning to emerge. To date, researchers have largely focused on Li^+ salts mixed in aprotic ILs,^[73-77] spurred by interest in Li-batteries.^[78] Only two papers have characterized structure in protic IL mixture with inorganic salts. In 2011, D'Angelo *et al.* used X-ray absorption spectroscopy to investigate the speciation and solvation structure of ZnCl_2 in ethylammonium nitrate (EAN).^[79] Unlike corresponding aqueous solution, ZnCl_2 was solubilised in EAN without dissociation. It was suggested that there is almost no reorganization of the pre-existing EAN solvent structure. This was confirmed in a recent molecular dynamics (MD) simulation of lithium nitrate (LiNO_3) + EAN mixtures, where the inorganic ions were found to be embedded in the polar domains of the IL nanostructure.^[80]

In this manuscript, we test this hypothesis for several of inorganic salts [LiNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$] dissolved in two protic ILs, EAN and ethanolammonium nitrate (EtAN). Both these ILs have well-described solvent structure. EAN forms a bicontinuous sponge-like nanostructure due to self-assembly of ions into polar and apolar domains.^[10,19] A clustered morphology is present in pure EtAN because the $-\text{OH}$ moiety interferes with solvophobic association between cation alkyl chains.^[10] Herein, neutron diffraction and computer simulation^[81] is employed to examine the effect of dissolved inorganic nitrate salt, species and concentration (1:10 or 1:30 solute:solvent mol:mol) on protic IL nanostructure, and the way that metal ions are solvated in both ILs, using multiple H/D isotopic solvent contrasts. These experiments allow us to test concepts of “structure-making” / “structure-

breaking” ions dissolved in pure ionic solvents that are similar to Hofmeister effects in water.^[82,83]

Experimental Section-

Several chemically identical, but isotopically different contrasts were prepared for neutron scattering experiments: hydrogenous (*H*-), headgroup deuterated (*D*₃-, *D*₄-), tail (alkyl chain) group deuterated (*D*₅-, *D*_{4t}-) and fully deuterated (*D*₈-) (c.f Figure 1).

Figure 1- Chemical identical, but isotopically different contrasts for the two ILs, ethylammonium nitrate (top row) and ethanolammonium nitrate (bottom row). From left to right, hydrogenous, headgroup deuterated, tail (alkyl chain) group deuterated and fully deuterated contrasts are shown. ¹H is white, ²H is green, C is grey, N is blue, O is red.

H-EAN and *H*-EtAN were synthesized via acid-base neutralization from concentrated hydrogenous reagents as described previously.^[10] The *D*₃- and *D*₄- contrasts were prepared by H/D isotopic substitution of exchangeable ammonium group protons. This was achieved by mixing volumes of the corresponding *H*- contrast several times in excess fresh deuterium oxide (99% Sigma Aldrich) (where mol:mol of D₂O:PIL >3:1), and removing excess aqueous solvent after each wash. The *D*₃- and *D*₄- were washed at least three times in excess D₂O.

This is because previous ^1H -NMR experiments reveal that, on average, 2.5 out of 3 amino hydrogens are replaced with deuterium per wash in D_2O .^[84]

The deuterated amines 1,1,1,2,2- D_5 -ethylamine ($\text{CD}_3\text{CD}_2\text{NH}_2$, gas at STP) and 1,1,2,2- D_4 -ethanolamine ($\text{HOCD}_2\text{CD}_2\text{NH}_2$, liquid at STP) was used to synthesize deuterated analogues D_5 - and D_4 - respectively. NMR and GC analysis by the manufacturer (CDN Isotopes) showed >99% isotopic exchange and >99.5% chemical purity (respectively) of the amines. The $\text{CD}_3\text{CD}_2\text{NH}_2$ gas was used as received by trapping it in H_2O on a Schenk line with liquid nitrogen. After SANDALS measurement, D_5 - and D_4 - samples were used to prepare D_8 - contrasts by D_2O wash as per preparation of D_3 - and D_4 - contrasts from H -PILs.

Analytical grade (99.99%) LiNO_3 , $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were purchased from Sigma Aldrich. To remove waters of hydration, small volumes of these salts were dried over several months in a vacuum oven between 110-150°C, periodically grinding the salt crystals in a mortar and pestle. Pure white crystals of the anhydrous salts were isolated, with measured m.p. $\pm 1.5^\circ\text{C}$ of literature values using capillary melting point apparatus.^[85]

1:10 or 1:30 mol:mol solute:solvent solutions were prepared on an analytical balance, with the resultant solution heated at $\sim 65^\circ\text{C}$ and sonicated for upwards of 5 hours in a sealed glass vial. Karl Fischer titration showed that the water contents in the mixtures were no higher than 40 ppm, and often undetectable (< 10 ppm). A concentration of 1:30 was chosen as it is the highest solute concentration that all inorganic salts are soluble in both ILs. 1:10 solute:solvent ratio of IL+ LiNO_3 mixtures was also prepared to test the effect of metal ion concentration.

Neutron diffraction data were collected on the SANDALS diffractometer (Rutherford Appleton Laboratories, UK). Empirical Potential Structure Refinement (EPSR)^[81] was used

to develop model the diffraction data for a simulation box of protic IL and inorganic salt ions. For all models, 1000 IL ion pairs were added to the box, and the number of inorganic salt ions varied accordingly. EPSR elucidates the solvent+solute arrangement via an iterative process governed by the standard rules for Monte Carlo simulation, but also by comparison of the measured and predicted $S(q)$ data, as well as physical constraints (chemical composition, atomic overlaps, liquid density). Table 1 the Lennard-Jones and Coulombic parameters used to define the reference potential used in EPSR.

Liquid density measurements on the pure ILs, and IL+salt mixtures were obtained on Anton Paar Densitometer DMA5000. Further details regarding the instrument, data normalization and fitting procedure have been described elsewhere.^[10,11]

Table 1- Lennard-Jones and Coulombic charge parameters for EPSR modelling. Atom point charges were determined from Spartan 08 modelling at the 3-21G* basis set and Hartree–Fock (HF) theory level. ϵ is in kJ.mol^{-1} , σ is in Å and q is elemental charge.

Nitrate Anion				Metal Ions				Ethylammonium Cation				Ethanolammonium Cation			
Atom	ϵ	σ	q	Atom	ϵ	σ	Q	Atom	ϵ	σ	q	Atom	ϵ	σ	q
N _O	0.711	3.25	+0.845	Li	0.690	1.50	+1.00	C ₁	0.276	3.50	+0.263	C ₁	0.276	3.50	+0.091
O ₁	0.879	2.96	-0.615	Mg	0.366	1.06	+2.00	C ₂	0.276	3.50	-0.411	C ₂	0.276	3.50	+0.315
O ₂	0.879	2.96	-0.615	Ca	0.522	3.02	+2.00	N	0.711	3.25	-0.529	N	0.711	3.25	-0.589
O ₃	0.879	2.96	-0.615	Al	0.907	1.45	+3.00	H ₁	0.126	2.50	+0.069	O ₁	0.879	2.96	-0.753
								H ₂	0.126	2.50	+0.147	H ₁	0.126	2.50	+0.124
								H _N	0.126	2.50	+0.366	H ₂	0.126	2.50	+0.020
												H _N	0.126	2.50	+0.382
												H _O	0.126	2.50	+0.502

Results & Discussion-

The neutron diffraction data for four solvent contrasts of 1:10 solvent:solute mixtures for EtAN+LiNO₃ and EAN+LiNO₃ is presented in Figure 2A and Figure 2B respectively. Data for the more dilute 1:30 concentration, and other IL+salt mixtures [with Mg(NO₃)₂, Ca(NO₃)₂, or Al(NO₃)₃] are presented in the Supporting Information.

Figure 2 shows good agreement between the SANDALS data (diamonds) and EPSR fits (solid lines). This indicates EPSR can account for the distribution of spacings in the bulk, which appear in the data as a non-trivial sum of (positive and negative) scattering for all the ion-ion and atom-atom correlations.^[17,18] Notably, the EPSR fits all the different isotopic substitutions (contrasts) simultaneously, and a model for each IL+salt system is developed upon convergence of the simulated and experimental data; the models are thus consistent with the constraints of the diffraction data and Monte Carlo simulation.

Figure 2- SANDALS data (dots) and EPSR fits (solid lines) as a function of Q ($\text{\AA}^{-1}$) for different isotopomers of the 1:10 solute:solvent mol:mol mixtures of (A) EtAN+LiNO₃ and (B) EAN+LiNO₃; fully hydrogenous (H -EAN, H -EtAN) is shown in red, head deuterated (D_3 -EAN, D_4 -EtAN) is purple, tail deuterated (D_5 -EAN, D_{4r} -EtAN) in green and fully deuterated (D_8 -EAN, D_8 -EtAN) is blue. The intensities are offset to +0.25, +0.75, +1.25, & +1.75.

A recent MD simulation showed that the addition of LiNO_3 did not appreciably affect the bulk structure of the protic IL, even beyond saturation concentration.^[80] This is consistent with the scattering data in Figure 3, with the form of the data (peak positions / intensities) for IL+salt mixtures is similar to published neutron diffraction data for the pure ILs.^[10,11] In fact, data for the pure ILs and 1:30 solute:solvent mixtures of LiNO_3 or $\text{Mg}(\text{NO}_3)_2$ or $\text{Ca}(\text{NO}_3)_2$ or $\text{Al}(\text{NO}_3)_3$ overlay between 0.0–20.0 $\text{\AA}^{-1}$ (c.f. Supporting Information). This suggests that either the IL nanostructure is effectively unchanged upon dissolution of a small amount of inorganic salt or that any differences present are beyond the resolution of the SANDALS instrument.

In some respects, this null result is surprising as a 1:30 inorganic salt:IL concentration equates to ~2 wt% solution of inorganic salt in the solvent, which is high enough to alter the diffraction spectra of molecular liquids, leading to changes in solvent structure.^[86-88] However, the IL bulk is governed by different solvent-solvent interactions. Unlike molecular solvents, the electrostatic charges are well-screened in the IL, leading to Debye lengths smaller than 0.1 nm. This means that dissolution of inorganic salt ions does not change solvent ordering across multiple solvation shells, as it will in molecular solvents.^[86-88] Instead, at low inorganic salt concentrations the IL nanostructure would only be slightly perturbed by the because their ions are well-solvated in the pre-existing polar domains of the solvent.^[80] Here, dissolved Li^+ cations interacted with multiple anions in the polar domain, suggesting that the dissolution of salt primarily has a packing effect on IL nanostructure.

In light of the 1:30 results, a lower solute:solvent ratio of 1:10 was measured for LiNO_3 dissolved in EAN and EtAN. This tested the effect of solute concentration on bulk nanostructure and corresponds to ~6 wt% solution LiNO_3 in EAN and ~5.2 wt% solution in

EtAN. At a 1:10 concentration, differences in the measured spectra are evident (*c.f.* Figure 3). In the subsequent sections, we focus on the key results for the 1:10 EtAN+LiNO₃ and EAN+LiNO₃ mixtures, where differences in scattering data were detected.

Figure 3- Effect of LiNO₃ dissolution on IL SANDALS data. Comparison of pure IL (solid lines) and 1:10 IL:LiNO₃ mixtures (dots) as a function of Q ($\text{\AA}^{-1}$) for different isotopomers of (A) ethanlammonium nitrate (EtAN) and (B) ethylammonium nitrate (EAN); fully hydrogenous (H -EAN, H -EtAN) is red, head deuterated (D_3 -EAN, D_4 -EtAN) is purple, and fully deuterated (D_8 -EAN, D_8 -EtAN) is blue. D_5 -EAN & D_{4t} -EtAN is shown in green, but the corresponding contrasts in pure solvent were not obtained. Intensities are offset to +0.25, +0.75, +1.25, +1.75.

For EtAN (Figure 3A), the changes in scattering data are prominent. This indicates the solvent nanostructure of EtAN+LiNO₃ is markedly different from pure EtAN. Not only is the feature $\sim 1.7 \text{ \AA}^{-1}$ much sharper and more intense in the EtAN+LiNO₃ data, but a well-defined bulk structure peak emerges at $0.70 \text{ \AA}^{-1}$; this peak is weakly-defined in pure D_4 -EtAN. The peak at $0.70 \text{ \AA}^{-1}$ equates to a repeat distance of $9.0 \text{ \AA}$ in the mixture, which confirms a longer-range structure is present compared to the pure IL ($8.2 \text{ \AA}$), which suggests that the Li⁺ ions change the liquid nanostructure. The analysis below explores the nature of this change.

Differences between scattering data for pure EAN and 1:10 EAN:LiNO₃ (Figure 3B) are more marked than for EtAN. The first peak in the *D*₃-EAN+LiNO₃ contrast is slightly sharper, and has shifted to higher *Q* (0.65 Å⁻¹) compared to the pure *D*₃-EAN (0.625 Å⁻¹). This corresponds to a reduction in the bulk correlation length from 10.1 Å (pure *D*₃-EAN) to 9.66 Å (*D*₃-EAN+LiNO₃). Likewise, the second feature at ~1.7 Å⁻¹ is fractionally more intense in *H*- and *D*₃- and less intense in *D*₈- compared to the pure IL data. Both these results suggest subtle changes in EAN's nanostructure with dissolved LiNO₃.

Representative snapshots of the bulk ion arrangements in the 1:10 EtAN+LiNO₃ and EAN+LiNO₃ mixtures developed from converged EPSR simulations are shown in Figure 4 and Figure 5 respectively. Figures 4A-C and Figures 5A-C show the same face of the cubic simulation box; (A) shows all atoms in the EPSR models, whilst in (B) and (C) some atoms are deliberately hidden to highlight different areas of structure in the bulk. In this way, the black voids are revealing as they highlight space available for other atoms.

In the absence of added salt, pure EAN has a sponge-like nanostructure while pure EtAN has a clustered morphology.^[10] On addition of LiNO₃, the structure of EAN remains sponge-like, but *EtAN's structure has changed from clustered to sponge-like*. Evidence for this is seen in the simulation boxes. In Figures 4 and 5, apolar domains are identified from the grouping of white (hydrogen) and grey (carbon) atoms of the aggregated cation alkyl chains. Conversely, the coloured regions of blue (nitrogen), red (oxygen) and white (hydrogen) atoms from the -NH₃ groups, NO₃⁻ anions, and (for EtAN) -OH moieties make up the polar domains. As both domains can be physically connected across the dimensions of the boxes, the nanostructure in EAN+LiNO₃ and EtAN+LiNO₃ is bicontinuous. Thus, the correlation between successive

polar (or apolar) domains is the origin of the peak at low Q in the diffraction data, as we have explained previously.^[10,11,19]

Figure 4- Snapshot of fitted ethanolammonium nitrate (EtAN) + LiNO_3 mixture (1:10) bulk structure at thermal equilibrium (298 K). From left to right, the front face of the 3D simulation box of (A) all atoms: 1000 EtA^+ , 1100 NO_3^- & 100 Li^+ (B) lithium ion solvation: 1100 NO_3^- & 100 Li^+ (EtA^+ omitted) (C) Apolar $-\text{C}-\text{C}-$ domains: ($-\text{NH}_3$, $-\text{OH}$, NO_3^- , Li^+ omitted). Atoms colours: C (grey), H (white), N (blue), O (red), Li^+ (yellow).

Figure 5- Snapshot of fitted ethylammonium nitrate (EAN) + LiNO_3 mixture (1:10) bulk structure at thermal equilibrium (298 K). From left to right, the front face of the 3D simulation box of (A) all atoms: 1000 EA^+ , 1100 NO_3^- & 100 Li^+ (B) lithium ion solvation: 1100 NO_3^- & 100 Li^+ (EA^+ omitted) (C) Apolar $-\text{C}-\text{C}-$ domains only: ($-\text{NH}_3$, NO_3^- , Li^+ omitted). Atoms colours: C (grey), H (white), N (blue), O (red), Li^+ (yellow).

Such a structure is surprising in $\text{EtAN}+\text{LiNO}_3$ (Figure 4). This is because the EtA^+ cation is not neatly amphiphilic; for all protic ILs examined to date, sponge-like nanostructures have only been observed for with primary alkylammonium cations, which possess well-defined segregation of their charged and uncharged moieties.^[18] In pure EtAN, the alkyl chains in the simulation box showed polydisperse clusters, because the $-\text{OH}$ group impeded solvophobic attraction.^[10] Figure 4C confirms the association between EtA^+ alkyl groups for 1:10 $\text{EtAN}+\text{LiNO}_3$ now at least as well-defined as in pure EAN, or 1:10 $\text{EAN}+\text{LiNO}_3$ (Figure 5C).

In both systems, Li^+ ions are evenly dispersed throughout the boxes, and solvated exclusively in the polar domains of the nanostructures, as predicted by MD simulations.^[80] For every yellow Li^+ cation, multiple coloured nitrate anions are located immediately around it (*c.f.* Figure 4A,B & Figure 5A,B). This shows that LiNO_3 dissolves into ILs via the charged regions of the bulk. This is almost certainly the common mechanism for dissolution of inorganic salts into the ILs; simulations of the other IL+nitrate salt mixtures showed that the metal ions (Mg^{2+} , Ca^{2+} & Al^{3+}) reside in polar domains (*c.f.* Supporting Information).

Partial radial distributions [$g(r)$], angular probability distributions (P_θ), coordination numbers and spatial density function (sdf) plots are determined from the averaging ~5000 of the equilibrated box configurations. This reveals short-range ion-ion structures. Results for the 1:10 EtAN+ LiNO_3 and EAN+ LiNO_3 mixtures, that are representative of how dissolved inorganic salt ions affects IL nanostructure, are presented in Figures 6, 7, & 8 with data compared to that in the pure solvents.

Figure 6A and 6B compare $g(r)$ functions of the IL+salt mixtures (dots) to the pure solvents (black dashes) for key atom-atom correlations along the cation backbone. This shows the pronounced effect of LiNO_3 on structure in the apolar domains of the ILs.

The structure in the apolar domain is quite different in EtAN+ LiNO_3 than in pure EtAN (Figure 6A). Changes are observed across all the $g(r)$ functions, and is more noticeable for atoms furthest away from the ammonium nitrogen. Prominent peaks are seen for EtAN+ LiNO_3 in the $\text{O}_1\cdots\text{O}_1$ (3.48 Å), $\text{C}_2\cdots\text{C}_2$ (3.99 Å), and $\text{C}_1\cdots\text{C}_1$ (3.87 Å) $g(r)$ data, all of which are at slightly larger separations than the pure solvent. Whilst the $\text{N}\cdots\text{N}$ $g(r)$ has a peak at 5.6 Å, fractionally smaller than in pure EtAN (5.7 Å), its shape is appreciably different and

the correlation at ~ 3.3 Å is absent. Moreover, unlike pure EtAN (where there was no simple order), the intensity of $g(r)$ peaks follows the order of connection for atoms on the alkyl chain i.e. $O_1 \cdots O_1 > C_2 \cdots C_2 > C_1 \cdots C_1 > N \cdots N$. This is important as it suggests solvophobic interactions between the uncharged groups, that are absent in pure EtAN, have been turned on EtAN+LiNO₃.

A structural change is also evident by comparing the coordination numbers from the O₁ oxygen, which sample the local packing environment around the –OH group of the cation, from the average number of atoms. In pure EtAN, the –OH group has near equal preference for either end of the cation; between $0 < r < 4.0$, coordination numbers to the charged ammonium ($0.97 O_1 \cdots N$) or uncharged hydroxyl are the same ($0.98 O_1 \cdots O_1$). When LiNO₃ salt is added, these values become 0.42 and 3.33 respectively. This indicates that –OH groups are principally associated with each other in the bulk, because they have been expelled from the polar regions so that alkyl chains can now interact solvophobically. This arrangement is likely supported by enhanced H-bonding between aggregated –OH groups, given similar changes in the H_O-O₁ (cation-cation) and H_O-O (cation-anion) $g(r)$ functions (Supporting Information).

Effect of LiNO₃ on EtAN: Apolar

Effect of LiNO₃ on EAN: Apolar domain

Figure 6- Local structure in the apolar domains for 1:10 IL+LiNO₃. $g(r)$ data for (A) EtAN+LiNO₃ and (B) EAN+LiNO₃ is compared to pure ILs (dashed line). $g(r)$ functions are offset for clarity. (C-F) are sdf plots of C1 carbon atom distribution as a function of distance & angular position from a central cation C1 atom for (C) pure EtAN, (D) EtAN+LiNO₃, (E) pure EAN and (F) EAN+LiNO₃. 20% probability surfaces are shown between the radial limits.

Together, these results suggest a structural change has been induced in the apolar domain of EtAN by the addition of LiNO₃. This is confirmed from the comparison of the sdf plots in Figure 6C (pure EtAN) and Figure 6D (EtAN+LiNO₃). The preferred sites for adjacent C₁ carbons has switched from around the ammonium group (pure EtAN) to the underside of the cation. Contrary to pure EtAN, the sdf plot in Figure 6D for EtAN+LiNO₃ is consistent with solvophobic interaction between alkyl groups, similar to the sdf distribution of pure EAN (Figure 6E) or EAN+LiNO₃ (Figure 6F). This highlights the origin of the structural change in the bulk from polydisperse ion clusters (pure EtAN) to bicontinuous nanostructure (EtAN+LiNO₃). Hence, LiNO₃ incorporation into the polar domain of the fluid results in

stronger segregation of alkyl groups into apolar domains. Thus for EtAN, LiNO₃ appears to be a “structure making” solute.

In EAN (Figure 6B), the shape and peak positions in the presence and absence of LiNO₃ are similar. Further, Figure 6E (pure EAN) and Figure 6F (EAN+LiNO₃) reveal near identical 3D distribution of C₁ (methylene) carbons around a central C₁ carbon. This means that solvophobic segregation of alkyl chains is retained with dissolution of LiNO₃ in EAN, as the two yellow lobes are located away from the charged regions of the EA⁺ cation. The only notable difference between data sets is that the intensity of the first peak in C₂...C₂ g(r) is lower in EAN+LiNO₃ than the pure liquid. This indicates ethyl-ethyl correlations are weaker between adjacent cations in the apolar domain. Integration of the C₂...C₂ peak between 0.0 < r < 5.0 Å reveals that on average 2.84 methyl carbons surround each other in the apolar domain, corresponding to a ~10% decrease compared to the same coordination number for pure EAN (3.16). This is likely related to a decrease in the fraction of linearly aligned alkyl chains (Supporting Information) as we have explained previously.^[19] Both these results imply that the presence of Li⁺ and extra NO₃⁻ ions in the polar domain disrupts packing in the apolar domain, producing a weak structure breaking effect. A similar, yet less pronounced effect was noted for H₂O in EAN.^[49]

Figure 7- Local structure in the polar domains for 1:10 IL+LiNO₃ mixtures compared to pure ILs. (A) and (B) show key atom-atom pair correlations $g(r)$ data for EtAN and EAN respectively. (C) and (D) are normalized angle distributions plot of N- $H_N \cdots O$ triplet for all H-bond lengths up to the first local minimum in the $g(r)$ data in (A) and (B). Pure IL data is shown as a black dashed line.

For both ILs, the structure in polar domains appears less affected by dissolution of inorganic salt ions than the apolar domains (c.f. Figure 7). Good agreement between the pure and IL+LiNO₃ $g(r)$ data corresponding to polar groups is obtained across the radial range. The exception for this is the $N_O \cdots N_O$ $g(r)$ functions, which denote anion-anion correlations. However, in 3D space, the anions are shown to be stacked along the z-axis, same as previously observed for the pure liquids (c.f. Supporting Information). This suggests that the net arrangement of nitrate anions in the polar domains is retained, and forms a locally layered anion-anion organization. Thus, the changes in the shape and peak positions of the $N_O \cdots N_O$

$g(r)$ are related to the additional nitrate ions packing into the polar domains, which are also solvating Li^+ cations. Thus, although LiNO_3 is solvated in the polar domain of the solvent, interactions between IL ions are largely unaffected, leading to minimal change in polar region local structure.

Figure 7C and Figure 7D show the probability distribution (P_θ) of $\text{N-H}_\text{N}\cdots\text{O}$ H-bond angles in the IL nanostructure. For both EAN and EtAN the probability of a linear H-bond ($165^\circ \leq \theta \leq 180^\circ$)^[89] is lower in the presence of added salt. The probability of bent H-bonds is consequently higher, particularly for $\theta < 150^\circ$ in EtAN or $\theta < 140^\circ$ in EAN. Non-linear H-bonds in pure protic ILs were identified as a consequence of solvent nanostructure,^[12] as the formation of a polar domain leads to multiple acceptor atoms interacting with each ammonium hydrogen donor. In EAN (and EtAN) this leads to a population of bifurcated H-bonds.^[12] Dissolving LiNO_3 in the ILs has a similar effect, as it increases the average proportion of nitrate oxygen atoms in the polar domain, and so greater population of bent H-bonds is reasonable.

The solvation of Li^+ cations is examined in Figure 8. In both liquids, the arrangement is broadly similar and shows that Li^+ is close to the polar groups and is strongly associated with nitrate anions. Analysis of the coordination numbers in reveals every Li^+ cation is solvated by approximately four nitrates (3.91 in EtAN and 4.21 in EAN). Notably, the $\text{Li}^+\cdots\text{O}$ $g(r)$ peaks occur at very short separations (1.95 Å for EtAN, 1.92 Å for EAN) and the correlations are much more intense than any other atom-atom $g(r)$ we have previously reported. Similar, but less-intense bimodal distributions are observed for $\text{Li}^+\cdots\text{N}_\text{O}$ $g(r)$ s, consistent with a population of both monodentate and bidentate geometries, as reported in MD simulations of EAN+ LiNO_3 mixtures.^[80]

Figure 8- Local solvation of Li^+ cations in (A) EtAN and (B) EAN for the 1:10 mixtures. (A) and (B) show key atom-atom pair correlations $g(r)$ data for EtAN and EAN respectively.

A question naturally arises: why does LiNO_3 have a structure making effect in EtAN but a weak structure-breaking effect in EAN when the mechanism of solvation is so similar? Because a 3-D H-bond network is maintained in both neat and IL- LiNO_3 mixtures, the results cannot be explained by Li^+ simply changing solvent H-bonding as per Hofmeister effects in water.^[63,82,83] This is because H-bonds are not the most important interaction for producing structure in PILs^[12] and that the majority of H-bonds formed in the PILs (between $-\text{NH}_3^+$ NO_3^-) are minimally affected by dissolved LiNO_3 .

In EAN, a bicontinuous sponge-like nanostructure is formed with a periodicity of ~ 1 nm. Such a lamellar-like, near-zero preferred curvature structure forms because the cation is amphiphilic^[10] and the ratio of non-polar and polar fragments areas ($a_{\text{alkyl}}/a_{\text{polar}}$) is near unity.^[19] Added LiNO_3 does not appreciably change the EAN's net ion arrangements because (1) the small, charged Li^+ and NO_3^- ions can be accommodated in the polar domains with negligible variation in $a_{\text{alkyl}}/a_{\text{polar}}$ ^[19] and (2) solvophobic segregation of charged/uncharged PIL groups is maintained. Instead, the inorganic ions induce small differences in local

packing of both domains. Within the polar regions, Li^+ and $-\text{NH}_3^+$ compete for NO_3^- anions. As Li^+ concentration is ten times smaller than EA^+ cation, in most cases the $-\text{NH}_3^+$ groups wins. Thus, polar domain structure is only slightly decreased compared to the pure IL. A slightly larger change is noted for apolar domain because solvophobic interactions are weaker than the electrostatic interactions; ethyl groups expelled from the polar domain are less likely to be linearly aligned across the bilayer.

While the effect of dissolved LiNO_3 on ion-ion interactions is similar, a new structure is induced in EtAN because the starting point is a clustered nanostructure rather than a bicontinuous sponge. In pure EtAN, both polar and apolar domains are present, yet they are not networked as in EAN or EAN+ LiNO_3 . This is because long-range solvophobic segregation of alkyl groups is absent. Locally, such a structure is possible because the EtA^+ cation has rotational freedom around its $\text{C}_1\text{-C}_2$ covalent bond and so cation chains associate with each other (*TRANS* conformer) or the charged groups (*CIS* conformer). Figure 9 shows that a broad population of rotamers are present based on the dihedral angle σ . In pure EtAN neither orientation is preferred, with σ broadly distributed across the angular range. Conversely, for the EtAN+ LiNO_3 mixture, the *TRANS* conformers are now favoured, and the probability of obtaining a *CIS* ($165^\circ \leq \sigma \leq 195^\circ$) or near *CIS* and *GAUCHE* ($120^\circ < \sigma < 240^\circ$) dihedral angle is lower than pure EtAN. This indicates that the $\text{HOCH}_2\text{CH}_2\text{-}$ tails of the EtA^+ cations are now expelled by charged groups and stretch out. The change in *CIS* / *TRANS* populations is also the origin of the increase in bulk correlation length from 8.21 Å to 9.0 Å from the neutron diffraction data.

Figure 9- Normalised probability distribution of the dihedral angle (σ) for ethanolammonium (EtA^+) cations in pure EtAN ($\diamond$) compared to EtAN+LiNO₃ ($\diamond$). As shown in the inset, the σ is defined as the angle between the planes containing the bonds N–C₁–C₂ and C₁–C₂–O₁. As per convention, we have defined *CIS* conformer to be $165^\circ \leq \sigma \leq 195^\circ$ whereas *TRANS* conformer for $0^\circ \leq \sigma \leq 15^\circ$ or $345^\circ \leq \sigma \leq 360^\circ$.

Hence, dissolved Li⁺ and NO₃[−] ions are attracted to the charged groups in EtAN at the expense of uncharged groups. Similar to EAN, this leads to some rearrangement among charged groups on PIL ions, leading to an initial change in polar domain structure. The key structural effect of LiNO₃ on EtAN is to favour a *TRANS* cation conformation in the bulk. In doing so, this forces the HOCH₂CH₂− moieties to aggregate and form an apolar domain *in spite of* the EtA⁺ cation’s reduced amphiphilicity. This is favoured energetically as it better segregates the charged and uncharged groups in the bulk. Moreover, these results suggest EtAN is well-poised to change its solvent nanostructure in response to solutes that dissolve in the polar regions of the clusters by changing the *CIS/TRANS* conformer ratio.

Conclusions-

The concept of “structure making” and “structure breaking” ions is well-established in chemistry literature of dilute aqueous electrolytes. Solvated inorganic ions induce a different local structure of water molecules in the first, and even the second or third solvation shells, to accommodate the dissolved species. These effects are usually framed in terms of the

Hofmeister series that orders ions according to their ability to salt-out proteins.^[82,83] In this manuscript, we have demonstrated that similar ideas can be applied to protic ILs. However, this is distinct from classical Hofmeister effects in water as IL structure is an order of magnitude larger, with well-defined polar and apolar domains in the bulk.

LiNO₃ is ‘structure breaking’ in EAN. It incorporated into the polar domain of the sponge nanostructure and this reduces structure by disrupting neat alignment of ethyl chains in the apolar domain. LiNO₃ also serves to weaken anion-cation H-bonding interactions, resulting in fewer linear N-H_N...O H-bonds and a higher proportion of bifurcated H-bonds.

Conversely, in EtAN, dissolved LiNO₃ is ‘structure making’. Whilst the inorganic salt is also dissolved into the polar domains in the bulk, it induces a longer-range solvent rearrangement, such that a bicontinuous rather than a clustered nanostructure is formed. This is because the TRANS cation conformation is favoured. As consequence, strong correlations between the uncharged ethyl chains in EtAN+LiNO₃ mixture emerge which were negligible in the pure IL.

While we cannot make unequivocal conclusions about the structural effect of Mg(NO₃)₂, Ca(NO₃)₂, or Al(NO₃)₃ on these ILs, it is likely that similar changes will be induced. This is because the metal ions are larger than Li⁺ and multivalent, and multiple nitrate anions are dissolved for every mole of inorganic salt. At minimum, the data for LiNO₃ strongly suggest that inorganic salt ions will be solvated in the polar domains of the bulk on account of IL amphiphilicity and the drive to segregate charged and uncharged species in the bulk. Further investigations of the solutes on protic IL nanostructure are ongoing.

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Notes

The authors declare no competing financial interest

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ASSOCIATED CONTENT

Supporting Information

SANDALS data for several EAN+nitrate salt and EtAN+ nitrate salt mixtures at different concentrations is presented. This information is available free of charge via the Internet at <http://pubs.acs.org>

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