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Scattering from Ionic Liquids

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Abstract

Research into the properties and applications of ionic liquids (ILs) has accelerated over the last few decades, driven principally by the advanced reaction kinetics and specificity they offered for synthesis and catalysis. ILs display many highly desirable properties, including high electrical and thermal conductivities and wide electrochemical windows, all of which can be tuned by altering the nature of their constituent ions. The discovery that ILs mediate surfactant self-assembly increased interest further. X-ray and neutron scattering are powerful tools for elucidating structure in both simple and complex, mesostructured liquids that were soon applied to IL-based systems. Early work revealed that many IL solvents are themselves *nanostructured*, and comprise distinct polar and apolar domains produced by the solvophobic segregation of alkyl moieties. Over the last decade scattering techniques have been used to characterise the nanostructure of a diverse range of ILs. Recently, nanostructure changes in ILs produced by the dissolution of salts, polymers, small molecules and amphiphiles have begun to be elucidated. X-ray and neutron scattering have, and will continue to, play a fundamental role in understanding structure-property relationships in IL-based systems.

Introduction

Ionic liquids (ILs) are pure salts with low melting points, generally taken to lie below 100 °C. The high ionic strength of ILs creates a large cohesive energy density through Coulombic forces, but they can also exhibit a range of strong dispersion, π - π , hydrogen bonding, dipole-dipole, magnetic dipole and Lewis acid-base interactions, depending on cation and anion structure. This can establish a unique and effective solvent environment for “difficult” solutes and solute mixtures, which has in turn seen an exponential growth over the past decade or so in their use for organic synthesis and chemical processing application. Many ILs have a number of favourable *and tunable* physical properties ranging from electrical and thermal conductivity and viscosity to a broad electrochemical window. Of particular relevance to this review is the ability of a large number of ILs to support the self-assembly of amphiphiles into micelles, lyotropic mesophases and microemulsions.

Recently, a growing amount of attention has been focussed on understanding the origins of these properties, and this prompted interest of the structure of ILs in their liquid state, and also as solvents or in mixtures. X-ray and neutron scattering are powerful tools for elucidating structure in both simple and complex, mesostructured liquids. Scattering is a primary tool for understanding structure in macromolecular and self-assembled soft-matter systems, and can probe structures ranging from the sub-nanometre to hundreds of nanometres.

ILs can be divided into different sub-genres based on a variety of criteria. Most commonly this is done via their ion structures as either protic (PILs) or aprotic (AILs) organic cation salts, distinguished by proton lability. **Figure 1** gives the structures of ions commonly employed in ILs. An emerging class of interest here are complex or solvate ionic liquids (SILs), in which (usually) the cation is a metal complex, or solvate. In both PILs[1] and SILs,[2] a key question is whether the IL is better-described as a purely ionic species (a ‘strong’ IL) or as a mixture of ionic and molecular species (through acid-base or complexation equilibria – a ‘weak’ IL).

Figure 1. Structures of common ions used in ILs: A) imidazolium (R_1 = alkyl group and R_2 = H or alkyl group); B) ammonium (R_1 = alkyl group and R_2 , R_3 and R_4 = H or alkyl group); C) phosphonium (R_1 , R_2 , R_3 and R_4 = alkyl groups); D) pyrrolidinium (R_1 and R_2 = alkyl groups); E) pyridinium (R = alkyl group); F) halide (Cl, Br, I); G) hexafluorophosphate; H) tetrafluoroborate; I) nitrate; J) acetate; K) trifluoroacetate; L) bis(trifluoromethylsulfonyl)imide.

Micelle formation in ILs was one of the first heralds of their remarkable solvent characteristics. Prior to this, only a handful of molecular solvents apart from water had been demonstrated to support surfactant self-assembly, and all contained a dense, three-dimensional H-bond network.[3] The significance of the H-bond

network of water in generating the hydrophobic effect, so critical in enabling surfactant self-assembly, was reinforced and expanded into a generalised concept of a solvophobic effect.

The advent of self-assembly in ILs is widely attributed to Evans *et al.*, who demonstrated micelle formation by several surfactants in ethylammonium nitrate (EAN).[4]**,[5] This was explained by EAN also having the ability to form such an H-bond network through donors and acceptors on -NH_3^+ and NO_3^- . [6] These studies were closely followed by the first small angle X-ray scattering (SAXS) study of lyotropic phases formation via the $L_{\beta'} \rightarrow P_{\beta'}$ (ripple phase) $\rightarrow L_{\alpha}$ phase transitions in the phospholipid, β,γ -distearoylphosphatidylcholine, in EAN.[7] In fact it was shown as early as 1967 that micelles form in molten pyridinium chloride,[8-10] although it was then referred to as a molten or fused salt and, with a melting point near 150 °C, might not fit today's criteria for an IL. Importantly however, pyridinium chloride does not have a dense H-bond network.

After a long lull, there has been an explosion in the use of ILs as amphiphile self-assembly solvents over the last decade. The number of ILs in which micelles or lyotropic phases have been observed now vastly exceeds the number of molecular solvents.[11-19] Only 16 molecular solvents are known to mediate amphiphile self-assembly.[20] In contrast, an estimated 37 protic and 11 aprotic ILs are known to have this ability.[21]* As small-angle X-ray and neutron scattering (SAXS and SANS) are extensively used to study such complex fluids, this has naturally prompted a corresponding surge in scattering studies of ILs themselves.

Undoubtedly the most important recent development in understanding IL structure and function has been the identification of amphiphilic nanostructure within pure ILs themselves.[22] This is a consequence of the anisotropic structure of IL cations and/or anions, and the resulting anisotropy of their intermolecular forces. Strong Coulomb and H-bond interactions between polar moieties generate a solvophobic segregation of non-polar groups. This, in turn, produces a self-assembled nanostructure on lengths scales larger than nearest-neighbour distance in individual ion pairs, but smaller than those typical of surfactant or polymer based complex fluids. Nanostructure can significantly influence physicochemical properties, solvent strength, reaction rates and outcomes, and can template electro-deposited materials.

Self-assembled amphiphile phases formed in nanostructured ILs thus have complex scattering behaviour. Two characteristic sets of length scales, one due to amphiphile assemblies and the other due to solvent nanostructure, may be present and may interact differently with each other as a function of composition. IL nanostructure is thus discussed first, before considering added solutes and amphiphilic self-assembly structures.

Scattering studies of ionic liquid nanostructure

The first scattering study of IL structure was reported in 1986 on AlCl_3 -*n*-butylpyridinium chloride mixtures using X-rays,[23] identifying butylpyridinium AlCl_4^- as the dominant species in the 1:1 ionic liquid. However, most early studies of IL structure were indirect, inferring liquid organisation from crystal structures, as in 1-methyl-imidazolium chloride, 1,3-dimethylimidazolium (Mmim) bis(trifluoromethylsulfonyl)imide (TFSI), 1,2,3-triethylimidazolium TFSI, and 1-ethyl- and 1-butyl-3-methylimidazolium (Emim and Bmim) Cl, I, BF_4 and PF_6 determined using X-ray diffraction (XRD) and SAXS.

Direct investigations of IL liquid organisation using scattering began to be reported from 2003, with Mmim PF_6 [24]* and Cl,[25]** followed by Emim acetate,[26] 1-methyl-4-cyanopyridinium[27] and Mmim TFSI.[28] Emim chloroaluminate,[29] Emim, BmimX (X = Cl, Br, I and BF_4)[30] and PF_6 [31]. Interpretation of the liquid diffraction patterns was primarily done by comparison with molecular dynamics (MD) simulations,[32-34] or using the empirical potential structure refinement (EPSR) Monte Carlo approach[24]* developed by Soper *at al.*[35, 36] High-level simulation techniques at or near atomic resolution are critical to the emerging detailed understanding of structure, especially in ILs with complex cation and anion structures and interactions. Whereas in MD the simulation is usually stand-alone, and the model outputs are directly compared with experimental scattering patterns, the philosophy of EPSR is more experiment oriented: Structure factors calculated from equilibrated simulations are converged to the experimental scattering by applying an additional, constrained, empirical, intermolecular potential that minimises the difference between theory and experiment, and thus alters the real-space atomic arrangements.

The complexity and broad peaks in the total structure factor, $S(Q)$, complicates extraction of structural information from a single diffraction pattern. A single peak may result from multiple correlations in partial structure factors for a sample, in which the phase may contribute positive and negative amplitudes. The use of neutrons with isotopic labelling of various components or groups can largely overcome this problem, and has been used for both protic[37-39] and aprotic[24]*,[28]*,[40].[41]**,[42] ILs. It is particularly useful in organic systems where electron density variation, and hence X-ray contrast, is small, but where H/D isotopic substitution can effectively highlight one component or other. In this approach a single liquid structural model or simulation must successfully describe the measured total structure factor of multiple neutron and/or X-ray, diffraction patterns.[43, 44]

Three key peaks are generally reported in IL scattering patterns,[45]*,[46]*,[47]* and extensive simulation and isotopic substitution analysis has allowed their structural origin to be identified. At the lowest angle a “**pre-peak**” occurs at $0.3 < Q \text{ (\AA}^{-1}) < 0.5$, then a **low Q peak** may be observed at $0.8 < Q \text{ (\AA}^{-1}) < 0.9$, followed by a **main peak** at $1.3 < Q \text{ (\AA}^{-1}) < 1.5$. At $Q > 2.5 - 3 \text{ \AA}^{-1}$, $S(Q)$ features arise from purely

intramolecular correlations and can reveal the presence of different conformers. The **main peak** is produced by a combination of intermolecular and intramolecular correlations involving neighbouring ions,[45]*,[46]*,[47]* and is particularly sensitive to ion structure. For example, C2 methylation of an imidazolium cation eliminates hydrogen bonding, altering cation-anion packing and the atom-atom correlations the diffraction peak.

The **low Q peak** is produced by cation-cation and anion-anion correlations, representing charge ordering. This peak can be present only as a shoulder to the main peak, or can even be absent under certain contrast conditions due to the superposition of positive and negative contributions of partial $S(Q)$ functions for different atom-atom correlations.[41]**,[45]*,[48, 49] Increasing alkyl chain length also reduces its intensity due to the effective dilution of scattering centres and increased negative contributions from alkyl chain-anion cross correlations.[45]*,[48, 49]

The **pre-peak** occurs at characteristic distances much larger than nearest-neighbour ion spacings, and identifies a supramolecular organisation or nanostructure within the bulk liquid. It is identified with a solvophobic association of non-polar (alkyl or fluoroalkyl) chains into domains. Like the low Q peak, the pre-peak is the sum of positive and negative contributions[45]*,[46]*,[50]* due to anion-anion, cation head-cation head and cation head-anion correlations across the intervening alkyl chain domains. The prominence of the pre-peak is a function of the scattering power of the anion and cation charged groups under different contrast conditions.[51]* In short-chained primary ammonium ILs like EAN, correlation lengths between polar groups across intervening apolar domains are on the same length scale as the charge-charge correlations which generate the low Q peak, so that only two peaks are typically discerned.

Long-range nanostructure was first predicted for 1-alkyl-3-methylimidazolium ILs with moderate chain lengths by MD simulation,[52] and measured by wide angle X-ray scattering (WAXS) and diffraction,[32]* then later by SANS.[41]** At about the same time, nanostructure was detected in PILs using SANS[53]** and WAXS.[54]**

Additionally, in 2008, asymmetric correlation functions for the C2-H and C4 and 5-H atoms of BmimPF₆ derived from neutron scattering were suggested to be consistent with, but not proof of, the self-assembled structures predicted by the preceding MD studies.[40] Demonstrations of nanostructure in a suite of protic and aprotic ILs soon followed. Note that the peaks diagnostic of nanostructure are often absent from neutron scattering patterns of perdeuterated and perhydrogenous ILs, due to a lack of contrast between polar and apolar domains. However, deuteration of polar groups (e.g. cation –CH₃ protons for 1-alkyl-3-methylimidazolium or ammonium protons for alkylammonium ILs) introduces contrast, producing peaks at low Q characterising polarity alternation in the IL.[41]**

Micelle-like structure was inferred from XRD studies of C_nmim PF₆ ILs based on a linear alkyl chain length-Bragg repeat spacing relationship[32]*,[55]* (c.f. **Figure 2**) and from the SAXS patterns of many

protic ILs and their aqueous mixtures.[56]** More recent and detailed scattering studies, coupled with simulations, have shown instead that both protic[38]* and aprotic[57]** ILs with single alkyl chains commonly form a bicontinuous network (c.f. **Figure 3**) of interpenetrating polar and apolar domains composed of polar anion and cation groups solvophobically segregated from (usually) cation alkyl chains, which is consistent with predictions of MD simulations for C_n mim PF₆.[33]

Figure 2. X-ray diffraction patterns for $[C_n\text{mim}]\text{Cl}$, $n = 3, 4, 6, 8, 10$, at 25 °C. In the inset the spatial correlation $L = 2\pi/Q_{\text{MAX}}$, Q_{MAX} being the interference peak position, is plotted (circles) as a function of n , the alkyl chain length, for $n \geq 4$. The corresponding data are also reported for the cases $n = 6$ and 8 for $[C_n\text{mim}][\text{BF}_4]$ (squares). Figure reproduced with permission from reference [32]*.

Figure 3. Snapshot of propylammonium nitrate (PAN) bulk structure (298 K) by EPSR simulation converged to multiple-contrast neutron diffraction. From left to right, the front face of the 3D simulation box of (A) 500 propylammonium (PA^+) & 500 nitrate (NO_3^-) (B) Apolar -ethyl- domains only ($-\text{NH}_3$ and NO_3^- omitted) and (C) Anionic 500 NO_3^- only (500 PA^+ omitted) is presented. Atom colourings are: C (grey), H (white), N (blue), O (red). (D) Shows the spatial density function for the arrangement of cation terminal methyl carbon atoms around the terminal methyl carbon of a central PA^+ cation as they pack in a locally lamellar bilayer structure with cation alkyl chains aggregated together. Figures (A-C) were reproduced with permission from reference [38] and figure (D) from reference [39].

It is now known that solvophobic nanostructure is generated in common aprotic ILs with alkyl chains with $C \geq 4$,[57]** while $C \geq 2$ is sufficient for protic, primary ammonium ILs.[37]** In addition to the bicontinuous

sponge, a range of other bulk nanostructures have also been described. Discrete clusters are produced when the cation amphiphilicity is disrupted by incorporation of polar moieties like hydroxyl[37]** (as in ethanolammonium nitrate, EtAN rather than EAN) or ether[50]*,[58]* (in ethoxy- rather than alkyl-quaternary ammonium or phosphonium salts, c.f. **Figure 4**), and more complex, tricontinuous structures can be produced in ILs containing immiscible hydrocarbon and fluorocarbon non-polar groups.[59],[60]*

Figure 4. Left: Isodensity spatial distribution functions for all atoms in the bis(trifluoromethylsulfonyl)imide anions (green) surrounding representative (a) triethyloctylammonium (N_{2228}^+), (b) (2-ethoxyethoxy)ethyltriethylammonium ($N_{222(2O2O2)}^+$), (c) triethyloctylphosphonium (P_{2228}^+), and (d) (2-ethoxyethoxy)ethyltriethylphosphonium ($P_{222(2O2O2)}^+$) cations. In each case, isovalues reflect the first solvation shell. Anions are present only near the cation headgroup in the case of the alkyl-substituted ILs, but this is not the case for diether substituted systems where anions also cap the tails. Tail configurations have distinctly different geometries in both types of systems. It is common for tails to curl back toward the head in the case of the diether substituted systems. Right: spatial density functions for the C_1 atom, bonded directly to the N atom of the cation, surrounding the C_1 atom of a central cation for (e) Ethanolammonium nitrate (EtAN) and (f) Ethylammonium nitrate (EAN). In each case, isovalues reflect the first solvation shell for the respective ILs. Note that in the case of EAN (f) C_1 atom density is only located around the alkyl tail of neighbouring cations while cation density is located adjacent to the alkyl chain and the ammonium group in the case of EtAN (e). Figures A-D reproduced with permission from reference [50]* and Figure E reproduced from reference [61].

Simulation techniques for interpreting neutron and X-ray scattering on a wide range of ILs have also yielded a wealth of short-range structural details. Local ion-ion arrangements are significantly influenced by the anion. In imidazolium ILs, for example, larger, less coordinating anions such as PF_6 [24]* or TFSI[28]* are found to sit above and below the ring, which disrupts π - π stacking of the cations, while strongly coordinating, H-bonding anions, such as chloride[25]** or acetate,[26] sit in-plane with the ring due to strong interactions with the C2 hydrogen, and this facilitates π - π stacking. Overall, the local packing of ions in the liquid state is not vastly different from the respective crystal lattices. However, thermal motion and

conformational isomerism generates a degree of disorder absent in the crystal state.[28]* Notably, crystal polymorphs of imidazolium[30],[62]* and TFSI[28]* ILs have been discovered that correspond to coexisting rotamers found in the liquid by scattering and simulation studies, underscoring the importance of intramolecular rotational isomerism in destabilising crystal lattices and producing low melting temperatures.

H-bonding network structure in protic ILs has also been found by scattering techniques to depend strongly on anion type.[39] By systematically varying anion structure and cation alkyl chain length, solvophobic nanostructure in primary ammonium ILs was deduced to be primarily driven by Coulomb rather than H-bonding interactions. Very recently, EPSR analysis of neutron scattering has been extended to include acid-base equilibria through a free proton model in a weak, putative protic IL system, pyridine + acetic acid.[63]** This system was found to be better described as a molecular mixture containing novel non-amphiphilic nanostructure in the form of extended H-bonded strings of acetic acid.

SILs first emerged from examinations of inorganic hydrate melts,[64] with interest growing out of investigations of Li-salt:PEO rubbery electrolytes,[65] especially with the discovery of “crystallinity gaps” for certain salt:PEO ratios and PEO lengths which produce highly conductive low melting point amorphous phases.[66] In certain equimolar mixtures of lithium salts and oligo-ethers (glymes), strong complexation between the metal cation and the glyme produces stable $[\text{Li}(\text{glyme})]^+$ complex cations yielding solvate ionic liquids.[2] As with conventional ILs, scattering was first used to investigate SIL crystal structures, characterising crystals formed in different regions of salt-glyme phase diagrams.[67, 68] Liquid behaviour has since been investigated using Raman spectroscopy, NMR and thermal and electrochemical methods[2] as well as computational approaches,[69] revealing that glymes containing four or 5 O atoms effectively solvate Li^+ when paired with a weakly coordinating anion (such as TFSI), leading to the glyme and Li^+ diffusing as a single species and producing higher thermal and electrochemically stable mixtures. Only recently has scattering been combined with MD simulations to characterise bulk structure directly.[70]* It is shown that the presence of stable Li-glyme complexes (such as formed in $[\text{Li}(\text{tetraglyme})][\text{TFSI}]$) result in low Q peaks in WAXS and HEXRD spectra while these are absent where stable solvates are absent (for example, in a LiNO_3 :tetraglyme mixture). The MD simulations corroborate the importance of competition between the glyme molecules and anions for coordination sites around Li^+ , [2] and predict the existence of complicated glyme-complex distributions; involving 1:1 $[\text{Li}(\text{glyme})]^+$ complexes, glyme molecules bridging between Li^+ cations and uncoordinated glyme molecules, with fewer Li^+ -anion interactions in the presence of longer glymes.

With X-rays, contrast variation is not possible. Two main approaches have been employed to deconvolute the $S(Q)$: (1) an approximate *intramolecular*, $S_{\text{intra}}(Q)$, is calculated from crystal or *ab initio* structures and subtracted from the measured $S(Q)$ to give an approximate $S_{\text{inter}}(Q)$, [49] (2) correlations responsible for the measured $S(Q)$ can be extracted from MD simulations which accurately replicate the scattering spectra.[71]*

Scattering studies have recently been extended from alkylammonium, imidazolium and pyrrolidinium ILs to explore the effects of systematic structure variation such as dialkylimidazolium,[72, 73] phosphonium[50, 74, 75] and quaternary ammonium[50],[51]⁺ cations. Liquid nanostructure has also been shown to persist in alkylsulfate ILs, with alkyl chains attached the anion rather than the cation.[76]⁺ Cyclic or branched alkyl chains[77]⁺ as well as ‘bolaform’ dicationic[78],[79]⁺ ILs, with charge carriers separated by alkyl chain linkers, have also been shown to exhibit solvophobic nanostructure. It is unsurprising that short-range structure, contributing to $S(Q)$ through nearest-neighbour ion-ion correlations are nearly unaffected by such modifications, but longer-range features produced by polarity alternation are more complex. Here solvophobic nanostructure depends on the physical dimensions of the alkyl groups rather than simply the total number of carbons. In dicationic ILs for example, alkyl group segregation appears to be sterically frustrated compared to equivalent monocationic counterparts (with alkyl chains half the linker length in the dication), but micellar-type aggregates are still proposed to form.[78]

Scattering from ILs as solvents

The intermolecular forces that produce IL nanostructure can also promote good solvency, enhance reaction rates or produce desirable physicochemical properties. However, solute addition can also dramatically affect IL properties, even when the dissolved species is present as only a trace contaminant. Most practical applications of ILs also necessitate the presence of solutes, whether deliberate or adventitious. Understanding the interplay between solute type and concentration and solution nanostructure and properties is critical as it influences reaction outcomes, rheological properties, thermal and electrical conductivity, tribological properties, among other things. IL-based solutions examined using scattering include LiTFSI, dimethylsulfoxide,[80] acetonitrile,[81] hexane,[82] water,[56, 81, 83] n-alkanols,[81, 82, 84-86] glycerol,[87] benzene,[81],[88]⁺,[89] inorganic nitrate salts,[61] glucose[90]⁺,[91] and poly(ethylene oxide) (PEO)[92]⁺,[93]⁺,[94],[95] in addition to a wide range of amphiphiles (discussed below). As with pure ILs, the measured $S(Q)$ functions are often interpreted through the aid of computational approaches. Here solutes are discussed under three broad categories; (1) salts (2) small molecules and (3) polymers.

Salts in ILs

Wide composition ranges and electrochemical windows are available in IL:salt mixtures.[96] ILs are ideal candidates to replace the volatile and flammable organic electrolytes presently used in electrochemical cells, stimulating the investigation of IL-based electrolytes using both X-ray and neutron scattering. In 2011, HEXRD and MD simulations of lithium TFSI in N-methyl-N-propyl-pyrrolidinium TFSI (PmpyTFSI) and EmimTFSI,[97] demonstrated $[\text{Li}(\text{TFSI})_x]^{(x-1)-}$ clusters (where x predominantly = 2) that induce conformational changes in the anion, reducing peak intensities in anion-anion correlations and eliminate their contributions to the low Q peak. Similar charge ordering changes have been demonstrated in separate

MD simulations of LiTFSI:BmimTFSI and Li pyrrolide:Bmpy pyrrolide solutions, where cation-anion-cation ordering is replaced by cation-anion-Li-anion-cation ordering in salt-doped ILs.[98] SILs also show great promise in electrochemical applications. SILs display enhanced electrochemical stabilities and transport properties over many competing Li^+ electrolytes.[99, 100] Moreover SILs promote enhanced battery cycling performance, as the solubility of active electrode materials are lower in some SILs than currently employed electrolytes.[99, 100] The practical application of SILs in electrochemical devices could be greatly enhanced by the structural insights scattering techniques can provide.

A remarkable difference in the effect of LiNO_3 on the liquid structure of ethanolammonium nitrate (EtAN) and EAN was recently observed by neutron diffraction.[61] Li^+ had a “structure-breaking” effect in EAN, caused by competition with the ammonium cation for nitrate ions, frustrating packing of adjacent cation ethyl chains. But in EtAN, interactions between Li^+ and the EtA^+ ammonium and hydroxyl groups result in the *anti* conformer being favoured, facilitating association of the $-\text{CH}_2\text{CH}_2-$ groups and enhancing long range order in the solvent.

Small molecules in ILs (and vice versa)

If there is a single feature that distinguishes ILs from molecular solvents, it is structure. This is true at the nearest-neighbour level of ion pairing, and also at the larger scale nanostructure level. There is virtually nowhere that ILs and their solutions can be understood via a continuum model. Addition of a molecular solute or dilution by a co-solvent might be expected to initially produce contact ion pairs, then solvent separated ion pairs, and ultimately a dilute electrolyte solution (by which point the fact that the salt was dissolved above its melting point scarcely matters). However, although the study of such IL mixtures is in its infancy, findings have so far indicated that IL nanostructure is surprisingly persistent at quite high dilutions.

IL-water miscibility is itself a subject with some open questions,[101] but clear evidence of nanostructure has been documented in numerous water-miscible ILs. Drummond *et al.*[56]** have contrasted the retention of a nanostructure peak in SWAXS patterns of water-rich mixtures with pentylammonium nitrate (PeAN, see **Figure 4**) and other PILs, with the unstructured mixtures formed with precursor amines and acids.

Figure 5. SWAXS patterns for PeAN–water mixtures at 50 °C, showing retention of nanostructure through the persistence of Peak 1 down to IL mole fractions near 0.1. SWAXS patterns have been offset to aid in viewing. Figure reproduced from reference [56].**

The relative insensitivity of the peak position to the IL:water ratio is interpreted as being due to the water is preferentially being taken up by the IL polar domains where it does not influence correlation lengths across apolar domains. Neutron scattering with EPSR modeling of a 6:1 mole ratio (approx. 50:50 v/v) water:EAN mixture,[102]** confirms the persistence of solvophobic nanostructure and the incorporation of water into the $\text{-NH}_3^+\cdots\text{NO}_3^-$ H-bond network, but also reveals that the bicontinuous nanostructure of the pure IL is transformed from a locally lamellar, sponge-like morphology into a branched cylindrical structure. Within the polar domains, water retains atom-atom correlations closely resembling those in pure water. A similar transformation in nanostructure is found in a 50:50 v/v mixture of ethylammonium formate (EAF) and glycerol.[87]* Glycerol of relevance here, as it is one of very few solvents that enables amphiphile self-assembly. In this mixture the distribution of glycerol conformers is also drastically changed from the bulk liquid, as it accommodates the EAF nanostructure.

The solvophobic nanostructure observed in pure C_nmim ($n \geq 4$) ILs is similarly robust to dilution with water. Because of the relatively long alkyl chains, SANS has been used to extensively characterise micellar aggregates of such ILs behaving as cationic surfactants in aqueous solution, beginning with the landmark work of Bowers *et al.* in 2004,[83] which then spawned an entire sub-field of ionic liquid surfactants. Dilution of BmimBF_4 , C_8mimCl and C_8mimI with water yields compact globular (or slightly eccentric) micelles at concentrations below about 1M. These are well-described by standard SANS fitting techniques involving decomposition of the small-angle scattering intensity into form and structure factors, although this approach failed at low water content. SANS was also used to show that Bmim ILs with strongly hydrated anions form homogenous aqueous solutions, while less-coordinating anions, such as trifluoromethanesulfonate (CF_3SO_3), form clusters,[103] consistent with the roles of anions in both bulk IL

structure and in cationic surfactant assembly. In fact, similar structuring had been reported by SANS as early as 1990 for a quaternary ammonium IL masquerading as a surfactant, dodecyltributylammonium bromide ($\text{N}_{4,4,4,12}\text{Br}$, m.p. = 30°C), [104] which also forms compact micelles in dilute aqueous solution. In hindsight, scattering patterns observed in IL-rich mixtures of these and similar systems correspond to the nanostructure or pre-peak of the IL, which is shifted into the SANS-accessible region by the long alkyl tails and consequently large apolar domains.

Water is hardly a typical additive, but many molecular species with differing intermolecular forces have been found to affect structure and nanostructure in various ILs. The earliest detailed neutron diffraction study (in 2005) found that benzene was molecularly dispersed throughout MmimPF_6 at 1:2 and 2:1 mol:mol [88]* in a highly ordered arrangement. Benzene was found to intercalate between cations and displace the anions, leading to a superstructure of alternating layers of cation and anion rings, similar to the crystal structure of $\text{MmimPF}_6 \cdot 0.5\text{C}_6\text{H}_6$. In both the pure IL and in benzene, methyl-methyl association between cations is evident. Longer cation alkyl chains induce IL nanostructure and partial miscibility with benzene; Here SANS has been used to show pronounced clustering of dodecyl chains of $\text{C}_{12}\text{mimTFSI}$ in dilute benzene solution. [89] Similar effects have been reported by SANS and NMR for $\text{C}_n\text{mimTFSI}$:methanol mixtures, including heterogeneous nanostructures that increase with IL alkyl chain length at $x_{\text{MeOH}} = 0.8 - 0.995$. [83]

The importance of cation amphiphilicity and anion H-bonding is underscored by the contrasting behaviour of EmimTFSI and Cl mixtures. SANS, in conjunction with NMR, [81] has shown that EmimCl forms homogeneous solutions in water and methanol, as does water-immiscible EmimTFSI in acetonitrile and benzene, while EmimCl and EmimTFSI aggregate in acetonitrile and methanol, respectively. Neutron and X-ray scattering have shown that EAN and DMSO are homogeneously mixed at all compositions, but form a 2:1 DMSO:EAN H-bonded cluster. [80]

Alkanes are typically sparingly soluble in ILs, but this can be improved by a single functional group such as hydroxyl, with quite dramatic effects on IL nanostructure. This is a result of the preferential uptake of long alkyl moieties by non-polar domains, which can be swollen, causing the nanostructure scattering peak to shift to lower Q . [82] . A recent systematic SAXS investigation of n -alkanols ($2 \leq n \leq 12$) in 6 protic ILs [85]* demonstrated that alkanol chains that exceeded twice the cation alkyl chain length modified the underlying IL nanostructure and formed new self-assemblies with larger non-polar domains. These could be fit by either conventional, form-factor/structure-factor or bicontinuous (Teubner–Strey) [105] models, with dimensions consistent with self-assembled nanostructure, but preventing their unambiguous characterisation. Neutron scattering with EPSR has subsequently revealed the structural evolution with composition in PAN-octanol mixtures. [86] At low concentrations, octanol is molecularly dispersed, but in the vicinity of 10 v/v% it forms polydisperse aggregates, and then (≥ 30 v.v%) the aggregates percolate into a bicontinuous structure. At all compositions the IL nanostructure remains evident, retaining a continuous network of polar

domains. Such alkanol self-assembly has not been observed in simple molecular solvents, or in non-amphiphilic ILs; their formation seems to rely on the combination of intermolecular forces between components being just right.

Polymers in ionic liquids

The solubility and structure, as well as the synthesis of polymers in ILs is of great potential interest for generating innovative materials such as plastic electrolytes and ionogels, and the unique solvent properties of ILs greatly expands prospects for processing of synthetic and biological polymers, particularly cellulose. Exploiting the response of polymer solutions to various stimuli has been proposed as a route to intelligent materials in ILs as well as conventional solvents. Although solubility and phase equilibrium studies of many homo- and copolymers in many ILs are extensive and have been recently reviewed,[106] *in situ* structural studies are relatively scarce. Neutron and X-ray scattering can however yield insights across most relevant length scales for polymer-IL systems from detailed local solvation structure up to overall polymer conformation (radius of gyration, R_g , and structural correlation length, ξ) and association structures.

The solubility, solvation and conformation of poly(ethylene glycol) (PEO) in water has been extensively characterised. PEO is a classic hydrophilic and biocompatible polymer, widely used as a viscosifier, as a surface coating for its effective steric stabilisation, and as a hydrophilic component in both copolymers and non-ionic surfactants. While it retains its high solubility in various ILs, its conformation (determined from Zimm analysis of small-angle neutron scattering (SANS)) suggests that solvent quality ranges widely from near theta in EAN[93]* to a good solvent in BmimBF₄. [92]** Unusually, the concentration dependence of R_g in both ILs resembles that of polyelectrolytes in salt-free solutions. In EAN, it was suggested that ether oxygens may be preferentially solvated by EA⁺ cations, inducing charges and short range interactions along the PEO chain, analogous to polyelectrolytes, and recent simulations of short PEO chains in BmimBF₄ have also predicted good solvency and polyelectrolyte-like R_g scaling.[94] PEO conformation in the solvate IL [Li(G4)]TFSI has also recently been investigated by SANS, where it was found to be a somewhat better solvent than EAN (θ),[95] but here the concentration dependence of R_g was unremarkable. Using null-contrast conditions, the isolated chain conformation was shown to decrease towards its θ limit as PEO concentration increased through the semi-dilute and concentration regions towards the melt.

More recently, this has been complemented by studies of the short-range PEO solvation structure in EmimBF₄, TFSI and bis(fluorosulfonyl)amide (FSA) using HEXRD with MD simulations.[107]* Variations in PEO molecular weight and branching were found not to influence the local structure, which lends credence to modelling polymer solvation using monomers as models. Emim cations were found to preferentially solvate PEO chains via H-bonding through the C2 hydrogen, leaving anions randomly distributed about the PEO chain. This preferential solvation is potentially the cause of the strong R_g :concentration dependence previously reported in both BmimBF₄ and EAN.

Local solvation structure of polymer-IL solutions has been examined by neutron and X-ray scattering using monomers such as benzyl methacrylate in Emim acetate,[108] and glucose (as a model for cellulose) in Emim acetate[91]* and MmimCl.[90] In MmimCl[90] glucose hinders the cation-cation stacking seen in the pure IL, but cation-anion correlations are relatively unperturbed. Glucose was found to H-bond extensively with Cl^- , and weakly to the cation C2 hydrogen. Few glucose-glucose H-bonds were found, with closely separated glucose molecules bridged by Cl^- . Conversely, in Emim acetate[91]* the nearest-neighbour ionic structure is not significantly perturbed by glucose. Only a small reduction in the total number of anion-cation H-bonds (including complex, bifurcated H-bonds, and bidentate-like sharing of H atoms) are observed. Here again the anion is critical in determining structure via H-bonds which bridge adjacent $-\text{OH}$ groups around the glucose ring.

Amphiphile self-assembly in ILs

Micelles and Lyotropic Phases in ILs

As of 2013, 37 protic and 11 aprotic ILs were known to support amphiphilic self-assembly into micelles or lyotropic phases, vastly outnumbering known molecular solvents.[21]* Since Evans *et al.* demonstrated micelle formation by cationic and non-ionic[4] surfactants in EAN, it has become a sort of gold-standard for (at least, protic) ILs. However studies of micelle formation and structure in this and other ILs has not yet been undertaken as a function of the systematic variables (such as alkyl chain length and head-group structure, counterion type, electrolyte, or temperature) to anything like the same degree as in water. This is partly due to the difficulty in measuring critical micelle concentrations (cmcs) of such concentrated electrolytes (ruling out conductivity) with low surface tensions and high viscosities (limiting the utility of surface tension), and unusual polarity and nanostructure (complicating the use of molecular probes like pyrene), and partly due to their expense as deuterated solvents for SANS. Add to this the inherent structural variations possible among known ILs, and the mammoth scale of understanding amphiphile self-assembly in ILs begins to emerge.

Poly(oxyethylene) alkylphenol and alkylether non-ionic surfactants ($\text{C}_i\phi\text{E}_j$ and C_iE_j) have been studied in both protic and aprotic ILs. Micelle formation by various C_iE_j was reported to occur in Bmim PF_6 and BF_4 , but not TFSI.[18]* Micelle radii derived from Guinier fits to SANS profiles for C_{14}E_8 in Bmim PF_6 were much smaller than in water, and cmcs (from surface tensiometry) at least two orders of magnitude higher. (Bmim BF_4 could not be examined due to the high neutron absorption coefficient of boron.)

C_iE_j micelle structures in EAN were systematically examined using SANS.[109]* This showed numerous strong similarities with self-assembly patterns in water, including increasing micelle size with i , decreasing micelle size with j , a sphere-to-cylinder transition at low j , and a lower critical solution temperature or cloud point. The weaker solvophobic driving force in EAN results in an effective offset, requiring an alkyl chain about four methylenes longer in EAN than in water. The trends in self-assembly are otherwise consistent

with normal surfactant packing considerations. As noted for $C_{14}E_8$ in $BmimPF_6$, EAN induces higher curvature structures than water. This is explained by the greater molar volume of EAN compared to water, increasing steric interactions between solvated ethoxy groups in the coronas around C_iE_j micelles. These trends continue in propylammonium nitrate (PAN),[15] and were recently shown to extend to Brij 97 ($C_{18:1}E_{10}$),[110] which transforms from spheres into short cylinders with increasing concentration in EAN.

The capacity of 20 protic ILs to support self-assembly by $C_{12}E_j$ ($j = 3-8$) was examined using SAXS.[111] Solubility was so high in ILs with long alkyl chains (and large apolar domains) that no self-assembly was detected, whilst in ILs lacking nanostructure the amphiphiles were only sparingly soluble. Between these extremes, self-assembly was reported in EAN, PAN, and also in di- and tri-ethylammonium formate, with non-polar domains between 6 and 12 Å, although low Q scattering in formates was too weak to be satisfactorily fit. Upon addition of amphiphile, the low Q peak shifted to lower Q until micellisation occurred, after which there was no further change in the peak position. This was attributed to amphiphile molecules swelling the IL apolar domains until they were saturated. Above the *cmc*, amphiphiles are incorporated into micelles where they have no further effect on the IL nanostructure.

This highlights the importance of solvation in determining surfactant self-assembly structure. The larger volumes of IL ions lead to larger solvation layers and stronger steric repulsions between surfactant polar groups and more curved aggregates, even though water may be a better solvent than an IL (e.g. for PEO compared to EAN).[11-13, 15]

Due to their high ionic strength, steric effects are also important determinants of self-assembly structure in ionic surfactants. These have thus far attracted less attention in ILs, probably due to potential complications from metal salts or halides formed by using anionic or cationic surfactants, respectively. A recent SAXS study[110] of the cationic surfactants hexadecyltrimethylammonium chloride (CTAC) and hexadecylpyridinium bromide (HDPB) showed that both formed smaller globular micelles in EAN than in water at low concentrations, and transform into short cylinders with increasing concentration.

A recent systematic SANS study of primary through quaternary ammonium surfactant micelles has shown strong counterion effects on their cmcs and micelle sizes in various protic ILs.[112] These are attributed to the IL's capacity to accommodate both the ammonium head group and counterion within its H-bond network. Unexpectedly, IL nanostructure was found to have a negligible effect on cmcs, except for quaternary ammoniums which are unable to H-bond with the IL. The implication is that generalisation of behaviour from one IL to another, or one surfactant to another must be undertaken cautiously, as interactions over multiple length scales can affect self-assembly structure.

There have been too many studies of block copolymer assembly in a wide range of ILs over the past few years to be included here.[106] Here we single out PEO-PPO-PEO (Pluronics) for mention, as they are so frequently compared with small-molecule surfactants in water.

Like small-molecule surfactants, many of the properties of Pluronic copolymers in EAN and other ILs echo their behaviour in water. SANS and SAXS have shown that P65,[14]* F127,[113] and P123[110],[113] form globular, core-shell micelles in EAN, while the more hydrophobic L121 forms unilamellar vesicles. However these have less well-defined interfaces between polar and non-polar regions than they do in water.[114] As in water, self-assembly in EAN is temperature-dependent: at low concentrations and temperatures P65 and L81 dissolve as monomers with random flight conformations, but self-assemble into micelles and lamellar stacks, respectively, when heated to 65 °C and the PPO solubility is decreased.

Lyotropic liquid crystal phases, formed at high concentrations by ordering of micellar aggregates, recapitulate many of the observations on micellar solutions in ILs: aggregate curvature is generally higher in ILs than water, contrary to expectations based on ionic strength effects, the ordering is dominated by steric interactions between aggregates as electrostatics are highly screened, and the underlying solvophobic driving force for assembly is weaker. SAXS and SANS have been extensively used to characterise hexagonal, cubic and lamellar mesophases in binary and ternary systems, including a phospholipid in EAN,[7] Pluronic P123 in BmimPF₆,[17] P65, P123 and F127 in EAN,[14, 113] ethoxylated phytosterol in EAN, BmimPF₆[115] and BmimBF₄,[116] as well as symmetric[117] and asymmetric[118] dialkylammonium Gemini surfactants in alkylammonium nitrate PILs and IL-derived surfactants C_nmimCl,[54]**,[119, 120] and N-alkyl-N-methyl-pyrrolidinium[120] in EAN. Vesicle formation by DDAB in EAN[121] and its relationship to sponge and lamellar phases[122] was recently examined by SANS, as was the relationship between vesicle and micelle formation by novel PEO-poly(ethyl glycidyl ether) and PEO-poly(glycidyl propyl ether) di-block copolymers in EAN and PAN.[16].

As observed with micelle formation, many water immiscible ILs (e.g. BmimPF₆) are found to behave as polar solvents for lyotropic phases, whereas others (e.g. C_nmimTFSI) yield no aggregates. This prompted a recent investigation of mesophase structure and miscibility in binary and ternary Pluronic mixtures with water and two different ‘hydrophobic’ ILs, BmimPF₆ and BmimFAP.[123] Here, strong solvation of P123 by PF₆⁻ but not FAP⁻ facilitated the formation of numerous lyotropic phases in BmimPF₆, but induced the demixing of BmimPF₆ and BmimFAP, as well as promoting the mixing of water and BmimPF₆. Structured ternary mixtures such as these border the behaviour of microemulsions.

IL Microemulsions

Scattering techniques provide rich and frequently critical information on microemulsion structure. Prior to the 2005 SANS study of a BmimPF₆:Triton-X100:cyclohexane IL-in-oil microemulsion,[124]** reports of IL based microemulsions were contentious, as light scattering indicated droplet sizes outside the typical range. Here again BmimPF₆ is acting as the polar component, and shortly thereafter, structurally-diverse non-aqueous microemulsions with EAN polar phases were reported and characterised by SAXS.[125]** Fitting to a Teubner-Strey model[105] (**Figure 5**) demonstrated longer-range order in EAN-based microemulsions than their aqueous analogues, due in part to the lower amphiphile efficiency ($\bar{\chi}$). As found in micelles and

lyotropic phases, headgroup areas per surfactant molecule (derived from Porod scattering[126]) are much higher than in water. SANS studies of PAN-based microemulsions,[15] revealed even lower efficiency and larger molecular areas, with evidence suggesting that PAN acts as a co-surfactant.

Formulation of and structure in IL-based microemulsions was reviewed recently, including scattering-based approaches to structure.[127] The underlying nanostructure and complex solubility and miscibility characteristics of ILs complicates scattering analysis, particularly due to the difficulty of determining composition, and therefore scattering length density, of the microemulsion domains:[128] From this point of view, a notionally three-component IL-surfactant-IL microemulsion has more in common with a quinary aqueous microemulsion than a water-surfactant-alkane system.

Although the range rapidly-expanding of components used to produce microemulsions now routinely includes Pluronic,[123] ethoxylated phytosterol,[129] sodium dioctyl sulfosuccinate (AOT),[130] Triton-X100,[124] and C_iE_j [15, 125, 131] surfactants in combination with protic ammonium[15, 128, 132, 133] and aprotic imidazolium[130] IL polar phases, together with hydrocarbons, this barely scratches the surface of the set of possible combinations.

Figure 6. Left: Vertical sections through the phase prisms for $C_{12}E_3$ (Top), and $C_{14}E_4$ (Bottom) with equal masses of EAN and dodecane. The open circles denote samples examined by SAXS. Top Right: SAXS patterns of 45 wt% $C_{12}E_3$ -EAN-dodecane as a function of temperature. The solid lines show fits using the Teubner-Strey model. Bottom right: Partial small-angle X-ray scattering spectra of symmetric $C_{14}E_4$ -EAN-dodecane mixtures as a function of surfactant concentrations at temperatures straddling the lamellar (L_α)-microemulsion phase boundary. The lines are to guide the eye for the L_α phase and fits using the Teubner-Strey model for the microemulsion phase. Reproduced with permission from reference [125]**.

IL-based surfactants, such as C₁₆mimCl,[128, 132] are finding wide application in microemulsions with both protic (EAN) and aprotic (BmimBF₄ and PF₆) IL polar phases. Porod scattering revealed larger specific areas with BmimBF₄ than EAN, which was suggested to be due to IL cations acting as cosurfactants, with Bmim⁺ both larger and more amphiphilic. However, this may also be due to strong, specific π - π stacking in C₁₆mim/Bmim mixtures. Comparing periodicity and specific areas from SAXS patterns indicated higher interfacial film rigidities in the BmimPF₆ than in EAN microemulsions. The wide range of potential cation and anion components of ILs also enables the use of the FeCl₄⁻ anion to produce magnetic microemulsions.[134] SANS indicates a highly ordered structure at near-equal IL:oil volumes, with correlation lengths approaching the effective length of the C₁₆mimCl and indicating a low interface rigidity.

Another recent development has been to employ hydrophobic ILs containing the PF₆,[123, 131] FAP[123] and TFSI[130] anions as the apolar phase in aqueous microemulsions, and to use mutually immiscible ILs (e.g. propylammonium formate (PAF) and C₈mimPF₆) as both the polar and apolar phases.[133]* SAXS reveals that PAF-continuous microemulsions contain near-spherical C₈mimPF₆ droplets, which swell with C₈mimPF₆ volume fraction, which have been employed to synthesise a La-BTC metal-organic framework. This combines the concept of microemulsions as nanoreactors with the well-documented advantages of ILs as selective and tunable synthetic solvents.

Conclusion and outlook

The earliest scattering studies examined self-assembled amphiphile structures. However, it soon became apparent that the IL solvents were themselves highly structured. Radiation scattering has provided rich insights into the nanostructure of pure ILs, clarifying morphologies and structure-property relationships. However, the understanding of IL-co-solvent binary mixture structures is still poorly characterised. Understanding the interplay between co-solvent identity and concentration and IL-solution nanostructure will be critical for the successful application of IL based systems. Additionally, new avenues are emerging. Notably, solvate ILs (SILs) and IL-related systems, deep eutectic solvents (DESs) have undergone recent surges in research interest. Research into both solvent classes will benefit from the structural insights scattering can provide.

It has been generally well agreed that amphiphilic self-assembly in ILs is strongly dependent on IL nanostructure. Large apolar domains are thought to easily accommodate added amphiphiles while unstructured ILs are poor amphiphile solvents, precluding amphiphilic self-assembly, in between these extremes self-assembly can be mediated. However, there is evidence suggesting overall IL polarity may be the more important factor, with unexpected counter-ion and headgroup effects also observed. Detailed, systematic investigations using scattering techniques will help resolve how IL structure and nanostructure controls the hydrophobic (solvophobic) effect influences aggregate morphologies.

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