Nanostructured Ionic Liquids and Their Solutions: Recent Advances and Emerging Challenges

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Abstract

Many ionic liquids (ILs), and their mixtures and solutions are amphiphilically nanostructured. Here we review recent advances towards understanding the nature of this nanostructure in ionic ILs and related mixtures and solutions, both in bulk and at or near macroscopic interfaces. We propose nanostructure is key for realising the designer solvent promise of ILs, and highlight its potential for translation to new generations of low-cost and environmentally sustainable cation and anion motifs for large-scale applications.

Keywords: ionic liquids, amphiphilic, nanostructure, scattering

Introduction

One of the most striking features of ionic liquids (ILs) is the widespread occurrence of amphiphilic nanostructure.[1, 2] Far more than simply being low melting-point salts, most ILs are structurally heterogeneous on the nanoscale; the features of this structure are highly variable, but controllable through e.g., polar/apolar structure and composition, charge density, and H-bonding capacity of the cation and anion. This amphiphilic nanostructure is manifested in the bulk liquid as well as near macroscopic interfaces, affecting the physical properties of pure ILs, as well as their performance as solvents and in liquid mixtures. The ability to control properties via nanostructure through structural variation of cations and anions has prompted research spanning process technology, synthesis and catalysis, biotechnology, pharmaceutics, electrochemistry, analytics and functional materials.[3]

X-ray and neutron scattering studies over the past decade have shown how the amphiphilicity of cations and anions determines the bulk structure of ILs.[4, 5] Amphiphilic nanostructure arises when the alkyl chain (or other non-polar moiety) is too long to be accommodated by the charged groups, which in turn depends on the nature of the charged group. Thus, ILs with sterically hindered (e.g. N-alkyl-N-methylpyrrolidinium) or delocalised (e.g. N-alkyl-N'-methylimidazolium) charges develop amphiphilic nanostructure above n-butyl chains,[6, 7] but the more localised and exposed charges of protic alkylammonium ILs lead to nanostructure even with ethyl chains.[8] Bulk amphiphilic nanostructure is controlled mainly by Coulombic forces expelling non-polar groups. Simple packing constraints, similar to those using in surfactant self-assembly, then determine the overall arrangement of polar and non-polar domains.[9] A dense H-bond network, once thought to be critical for amphiphilic nanostructure, is not necessary, and in fact H-bonding plays a secondary role to electrostatics even in protic ILs.[10, 11] This is underscored by the observation that the amphiphilic nanostructure of protic ILs is not found in their H-bonding molecular precursors, which are homogeneous.[12] ILs with a hydrocarbon cation and fluorocarbon anion have even more complex liquid nanostructure, consisting of segregated polar, hydrocarbon and fluorocarbon domains.[13, 14] Figure 1 shows how liquid nanostructure is affected by ion type for three representative protic ILs, with corresponding X-ray scattering patterns.
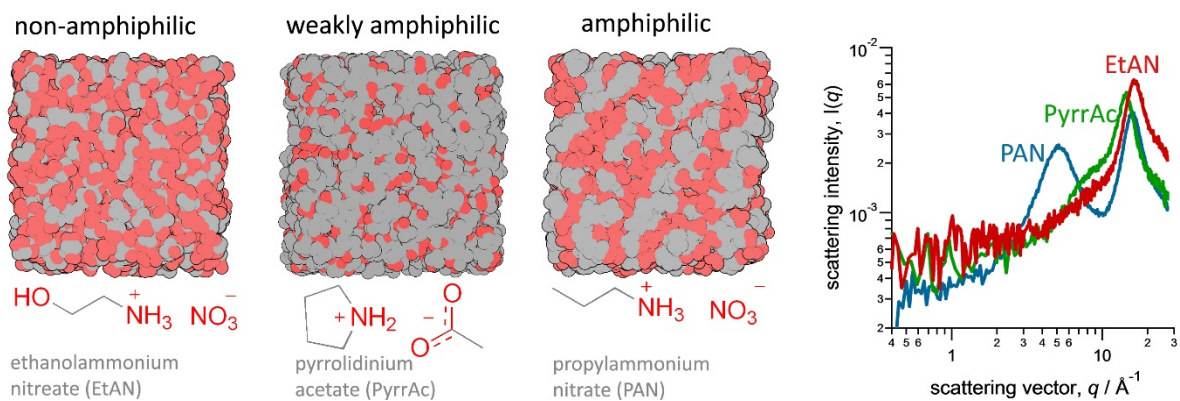
Figure 1. Emergence of amphiphilic nanostructure in protic ILs, as determined from neutron diffraction and X-ray scattering.[10, 15] Longer alkyl moieties on cations are expelled into nonpolar domains, with overall liquid nanostructure influenced by cation and anion structure, packing of polar/apolar sub-volumes, and H-bonding capacity

AFM studies have shown the existence of distinct surface and near-surface amphiphilic nanostructures that differ from, but are related to the bulk structure, which can also be controlled by varying ion structure.[16] The bulk, isotropic nanostructure of the IL becomes increasingly anisotropic as the polar and non-polar domains align parallel to a macroscopic interface in response to geometric constraints, its charge, and its chemical composition. The structure of ILs near a solid surface is important for diverse applications from electrodeposition to lubrication.[17, 18]

The existence of degrees of amphiphilic nanostructure renders ILs structurally more akin to microemulsions than conventional molecular solvents, which requires a paradigm shift beyond current ideas of uniform solvent polarity. Traditional methods based on a partition coefficient (logP) or a solvatochromic dye yield a single parameter describing an average solvent environment. The three-parameter Kamlet-Taft approach, which characterizes solvents according to their polarizability (π^*), hydrogen-bond acidity (α) and hydrogen-bond basicity (β) is widely used to compare ILs to other green solvents.[19] Amphiphilic nanostructure disrupts the interpretation of such experiments due to selective solvation or partitioning of probes between polar and apolar domains within the IL itself. For example, partitioning studies of homologous series of poly(oxyethylene)-n-alkyl ether surfactants between ILs and octane showed that while the alkyl chains experienced a more-or-less average of the polar and non-polar environment, the ethoxy groups were exclusively located within the polar domains of IL nanostructure. Likewise, different choices of solvatochromic probe give rise to different polarity scales of ILs.[20] [21]

With recent advances in computation methodologies, multi-scale studies of IL nanostructure are redefining the concept of solvent polarity.[22] Atomistic *ab initio* calculations, such as Density Functional Theory, probe intra- and intermolecular interactions in detail, with a computation capacity up to a few ion pairs. To explore IL structure at the nanoscale, methods such as Molecular Dynamics accommodate hundreds of ion pairs with statistical information on atom-atom pair correlations. Most neat ILs have domain sizes that fall within this length scale. However, if the system of interest includes dissolved polymer, surfactant self-assembly structures, or dispersed nanoparticles, it is currently necessary to use coarse-grained methods with compromises on atomic resolution.

X-ray and neutron scattering have proven to be powerful experimental tools for studying nanostructured ionic liquids with and without solutes.[4] However, the nanostructure of ILs is less-well defined than, for example, aqueous surfactant micelles, and cannot be accurately described by geometric models such as spheres, ellipsoids or bilayers. Flexible models or simulation methods to fit experimental data over wide length scales will emerge.

The "green credentials" of many conventional (*i.e.* imidazolium) ILs have recently been subjected to well-deserved scrutiny. Their high synthesis cost and reliance on fluorous components compromises the advantages of negligible vapour pressure, and limits the potential for sustainable exploitation of the performance advantages of amphiphilic nanostructure. To achieve broad uptake, ILs must be both economical and environmentally-friendly. Instead of using aprotic ILs which typically cost over $50 kg^{-1}, protic ILs can be as cheap as $1.25 kg^{-1}, significantly lowering the industrial processing cost.[23] Adding a molecular co-solvent such as water or alcohols further reduces solvent cost, while preserving structural features and functionality of the neat IL. Moreover, ILs made from renewable starting materials are of environmental interest and with potential biomedical uses. These include amino-acid based ILs and the related but distinct deep eutectic solvents (DESs).

In this context, it is important to note that some ILs, both aprotic and protic, have been shown to retain amphiphilic nanostructure in the presence of significant amounts of water. Aggregation of cation alkyl tails, driven by preferential anion-water interactions, largely preserves liquid nanostructure up to at least 25 wt% water in imidizolium ILs.[24, 25] Protic ethylammonium nitrate-water mixtures (as well as ethylammonium formate-glycerol) at 50% v/v also exhibit amphiphilic nanostructure comparable with pure ILs, but with a modified structure due to the different polar/apolar volume fractions.[26, 27] Incorporation of the amphiphilic butanoate anion changes packing constraints, rendering the IL more like a catanionic surfactant. This affects how nanostructure changes on upon water dilution.[28] (At the limit, many long-chain analogues of ammonium, pyridinium and imidazolium ILs are of course cationic surfactants that form micelles in water.) Adding water into ILs reduces their cost, often with the additional benefit of lowering viscosity, thereby retaining or improving performance. Biomass pre-treatment is an important example of using ILs as a processing solvent, which involves water as a by-product, and therefore the chosen ILs must be water compatible.

Other simple solutes can have surprisingly complex effects. For example, amphiphilic and non-amphiphilic protic ILs have been shown to undergo starkly different, ion-specific, structural changes in the presence of dissolved salts.[29, 30] In ethylammonium nitrate for example, chloride weakens amphiphilic nanostructure by selectively binding to the ammonium charge centre. Lithium – solvated by the nitrate anion – weakens existing nanostructure but, perversely, induces it for the marginally amphiphilic ethanolammonium cation. Similar observations were found in aprotic imidazolium and pyrrolidinium bis(trifluoromethanesulfonyl)imide (TFSI) ILs.[31] As heterogeneity affects the transport mechanisms of various solutes in ILs,[32] these short-range effects on amphiphilic nanostructure can have macroscopic implications, e.g. for the performance of ILs as electrolytes for Li-ion batteries.

Addition of more complex solutes or molecular components can dramatically modify nanostructure. Many nanostructured ILs are miscible with medium chain length n-alkanols, accommodating their hydroxyl groups into polar nano-domains containing IL charged groups, while stabilizing the non-polar domains that can be substantially swollen by the alkanol, and may lead to substantially longer-range periodic order than the IL alone (see Figure 2),[33-35] bringing these binary mixtures even closer in concept to conventional microemulsions. Additional components may then dissolve into or swell polar or non-polar domains. This behaviour is unlike water and other polar molecular solvents, in which alkanols cannot self-assemble. Pre-existing amphiphilic nanostructure is essential.

propylammonium nitrate – **octanol** binary mixtures
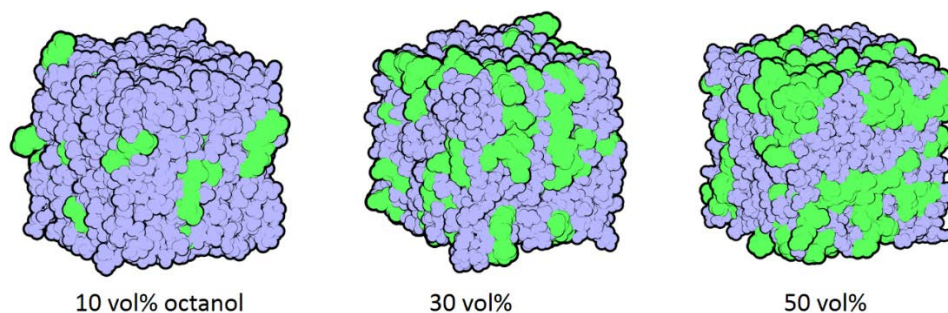
10 vol% octanol   30 vol%   50 vol%

Figure 2. Structure of propylammonium nitrate/n-octanol mixtures from neutron diffraction, showing development of octanol tail-rich non-polar domains stabilised by the IL's amphiphilic nanostructure**[34]

Exploiting Nanostructure in Applications

ILs are important solvents for the processing of various biomaterials, such as lignocellulosic biomass, microalgae, and coal, from which a range of chemical compounds including lipids, biopolymers, aromatics and other small molecules are extracted. Badgujar *et al*. identified many individual structural factors that govern lignocellulosic biomass dissolution including IL anion (H-bond basicity), IL cation structure, functional group, cation size, and side chain length, as well as Kamlet-Taft solvation properties.[36] Although no direct link between nanostructure and biomass dissolution was explored, many of these factors are the same as those that determine solvent nanostructure, which we expect will prove to be an important unifying concept.

Microalgae are another rich potential sustainable source to produce fuels and other chemicals. Lipid extraction by ILs has been investigated, including exploiting their water miscibility to bypass costly dewatering and drying stages needed with most current solvents.[37] Although much of the detailed mechanism remains unknown, including the chemical roles of IL and water, ILs are known to facilitate lipid extraction by disrupting cell structure, including lipid bilayers. Two recent studies have shown that the stability of phospholipid vesicle bilayers depends on amphiphilicity of ILs.[38, 39] Non-amphiphilic ILs preserve lipid bilayers, whereas amphiphilic ILs with longer alkyl chains disrupts lipid bilayers.

In the synthesis of both inorganic materials and organic compounds, mechanisms, selectivity, and rates can also be controlled by IL steric factors, H-bonding, solvophobic interactions, ion self-assembly and clathrate formation.[40] Here also the amphiphilic nanostructure of ILs, which resemble self-assembled nanoreactors, has been implicated as a determining feature.[41] Ordered structures of liquid-crystalline ILs can influence the stereochemical outcome of the Diels-Alder reaction.[42] We expect nanodomains to bring otherwise immiscible reactants into contact, to facilitate a cascade reaction (e.g. from polar reactants, to amphiphilic intermediates, to apolar products), and to allow easy separations. Beyond a static picture of amphiphilic nanostructure, understanding the dynamics of assembly/disassembly and the relative "stiffness" of polar and apolar nanodomains[43] will help to realise the full potential of ILs as designer solvents for a diverse range of chemical processes.[44]

Systematically studying ILs with a variety of model solutes would enable the rational design of ILs by identifying key solvent-solute interactions and extending the "like dissolves like" rule to amphiphilically nanostructured solvents.[10]

At the solid-IL interface, the strong interaction of imidazolium-based ILs with carbon nanomaterials leads to confined ion layers on graphene sheets and in carbon nanotubes.[45] Nanomaterials and functional surfaces have been templated via ion self-assembly.[46, 47] On metal electrodes, the ion-surface interactions and therefore the near-surface IL structure controls the size and morphology of the deposit.[48]

The majority of the ILs studied for processing biomaterials are imidazolium based, due to their commercial availability.[49] In addition to the emerging interest of studying mixtures of ILs,[50] more sustainable processes will be achieved with lower cost and more environmentally friendly solvents, such as protic ILs prepared by one-step synthesis, biocompatible solvents such as amino-acid ILs[51] and DESs, as well as utilising mixtures with water and other benign molecular solvents where suitable.

Cholinium ILs with amino acid anions and their water mixtures have been investigated for extraction from sources ranging from fruit peel,[52] to straw,[53] to coals.[54] Some correlation with e.g. anion basicity, charge density, or local structure have been identified,[55] but a fuller understanding awaits systematic studies that correlate performance with structural variation. The diversity of naturally-occurring (and synthetic amino acid) structures includes potentially amphiphilically nanostructured ILs and their solutions, but how this may correlate to process efficiency remains an open question.

Deep eutectic solvents (DESs) are two- (or more) component systems comprising at least a hydrogen bond donor and acceptor, one of which is often a salt. They share many of the structural features and advantageous characteristics of ILs and IL solutions for synthesis and processing applications.[56] The most widely-studied DES – choline chloride/urea – is formed from naturally-occurring components, and retains its underlying structure up to 40 wt% water.[57] Such water-compatible DES are potential candidates for applications such as biomass processing. The changes in properties observed on replacing urea by ethylene glycol and glycerol highlights the importance of hydrogen bond donor-to-acceptor ratio and strengths.[58] To date, the majority of DESs studied are non-amphiphilic, with hydrogen bonding and Coulomb forces governing bulk structure. Recent studies have shown not only that it is possible to design DESs analogous to protic IL – solvent mixture with amphiphilic nanostructure, but that they exhibit similar structures and tunability across diverse properties,[59, 60] both in bulk and at interfaces.[61] The structural understanding of ILs is a decade ahead of DESs, and exciting questions are to be answered. DESs allow sustainable and efficient separations in oil and gas industries, with selective solubility of small aromatics, acidic gases such as CO_2 and H_2S.[62] Ionic liquid-formulated hybrid solvents containing amine have similar functions for CO_2 capture.[63] Future research should further strengthen the nanostructure/property correlation between DESs and protic ILs.

Conclusion and Outlook

The nanostructure of ILs differs substantially from both molecular solvents and simple molten salts. Although the understanding of factors that affect nanostructure in first-generation ILs is relatively mature, some outstanding challenges for modelling intermediate and long-range structures remain. Better understanding of the structural and dynamic coupling between length scales will enabling better *a priori* design of ILs and improve process efficiency.

The translation of the understanding of IL nanostructure into more environmentally benign, lower cost, and sustainable components (protic ILs, mixtures, bio-based ILs and DESs) will enable the advantages of ILs to be exploited more widely and in larger scale applications utilising the next generation of solvent technology. This will complementary structure and application-oriented performance studies, such as examining ILs with dissolved model solutes, alongside multi-scale simulations.

Acknowledgments

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