



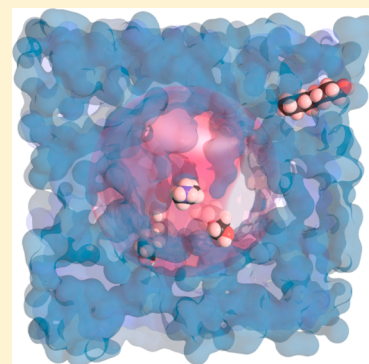
Amphiphilic Self-Assembly of Alkanols in Protic Ionic Liquids

Haihui Joy Jiang,[†] Paul A. FitzGerald,[†] Andrew Dolan,[†] Rob Atkin,[‡] and Gregory G. Warr^{*,†}

[†]School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

[‡]Centre for Advanced Particle Processing and Transport, Chemistry Building, The University of Newcastle, Callaghan, NSW 2308, Australia

ABSTRACT: Strong cohesive forces in protic ionic liquids (PILs) can induce a liquid nanostructure consisting of segregated polar and apolar domains. Small-angle X-ray scattering has shown that these forces can also induce medium chain length *n*-alkanols to self-assemble into micelle- and microemulsion-like structures in ethylammonium (EA⁺) and propylammonium (PA⁺) PILs, in contrast to their immiscibility with both water and ethanolammonium (EtA⁺) PILs. These binary mixtures are structured on two distinct length scales: one associated with the self-assembled *n*-alkanol aggregates and the other with the underlying liquid nanostructure. This suggests that EA⁺ and PA⁺ enable *n*-alkanol aggregation by acting as cosurfactants, which EtA⁺ cannot do because its terminating hydroxyl renders the cation nonamphiphilic. The primary determining factor for miscibility and self-assembly is the ratio of alkyl chain lengths of the alkanol and PIL cation, modulated by the anion type. These results show how ILs can support the self-assembly of nontraditional amphiphiles and enable the creation of new forms of soft matter.



INTRODUCTION

Salts that are molten at or near room temperature, or ionic liquids (ILs), are remarkable liquids.^{1–4} They are typically formed from an organic cation and an organic or inorganic anion with delocalized charges or some other structural feature that destabilizes the crystal. In many ILs H-bonding is an important secondary interaction that influences both physical properties and miscibility with other liquids. Thus, ILs may be broadly classified as hydrophilic or hydrophobic according to their miscibility with water.^{5,6} Many ionic liquids have been found to be good solvents for self-assembly of surfactants and amphiphilic polymers into micelles,^{7–10} liquid crystals,^{11–13} and microemulsions.^{14–16}

Research interest in protic ILs (PILs) is increasing due to their ease of synthesis (by Brønsted acid–base neutralization), low cost, and the simplicity, stability, and low toxicity of their constituent ions.^{17–21} PILs are overwhelmingly water-miscible, and like their aprotic cousins, many have been shown to be excellent solvents for amphiphilic self-assembly.^{22–30}

H-bonding in PILs has been shown to be a key feature in controlling self-assembly behavior.^{31,32} Simple ILs with identifiable polar and nonpolar moieties, exemplified by ethylammonium nitrate (EAN), exhibit an inherent amphiphilic nanostructure in the pure liquid state,³³ the extent and nature of which depend on cation and anion structure and H-bond capacity.^{32,34–36} This is also critical in determining the nanostructures that form in mixtures of PILs with water.^{37,38}

Both protic and aprotic ILs exhibit a complex set of miscibility behavior with aliphatic alcohols. EAN + methanol exhibit many characteristics of ideal mixtures³⁹ but do exhibit some structural complexities.⁴⁰ However, EAN and *n*-octanol are only partially miscible at room temperature and exhibit an

UCST at 47 °C,^{41,42} above which EAN and *n*-octanol are miscible. Hydrophobic aprotic ILs also show partial miscibility with short-chain alcohols; butylmethylimidazolium hexafluorophosphate (bmimPF₆) has a UCST with ethanol at 71 °C and with *n*-propanol at 87 °C,⁴³ and mixtures of ethylmethylimidazolium NTf₂ and *n*-butanol have a UCST at 47 °C.⁴⁴

Here we examine the miscibility of protic ILs and aliphatic alcohols through a systematic variation of cation (ethyl-, propyl-, and 2-hydroxyethylammonium) and anion (nitrate and formate) structure and aliphatic chain length from ethanol through dodecanol. The ILs examined are shown in Figure 1. Using small-angle X-ray scattering, we demonstrate amphiphilic self-assembly of the alkanols, which in turn reveals the connections between amphiphilicity, structure, and miscibility in these systems. The miscibility of a number of protic ILs with aliphatic alcohols has been examined recently, and we will also discuss some discrepancies between ours and these previously reported results.⁴⁵

EXPERIMENTAL SECTION

Materials and Methods. Analytical-grade *n*-alcohols were dried, and their purity was confirmed by melting point, TLC, and mass spectrometry prior to use. Ionic liquids were prepared from ethylamine (Aldrich), propylamine (Acros), and ethanolamine (Merck) bases and either nitric acid (AJAX) or formic acid (Aldrich). All of the ionic liquids were synthesized by slow acid neutralization of the relevant alkylamine base with the relevant dilute acid as reported previously.²⁴ The reaction was

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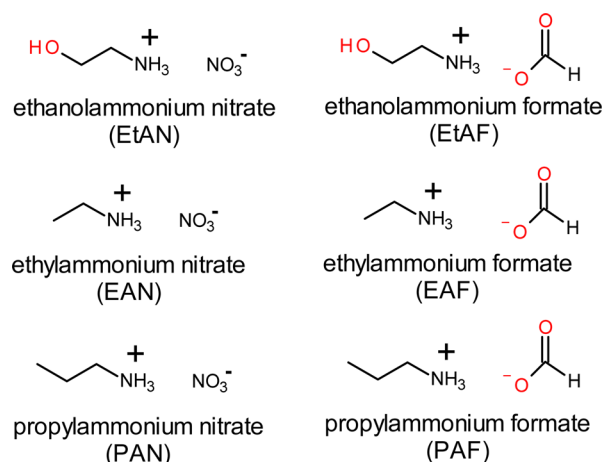


Figure 1. Structures of the ILs used in this work.

kept below 10 °C in an ice bath. The nitrate ionic liquids (EAN, PAN, EtAN) were dried first to less than 10 wt % water content on a rotary evaporator and then to less than 0.2 wt % water content under nitrogen at 110 °C for at least 16 h. Note that formate PILs have a tendency to form amides and could not be heated during the synthesis or the drying process. Instead, they were dried under vacuum while the amide content was monitored by NMR on regularly collected samples. Aqueous EtAF could not be dried below 2 wt % water content without heating, so dry EtAF was made in THF. THF (AJAX) was dried over molecular sieves (to <0.01 wt % water), ethanolamine was dried by vacuum distillation (to 0.03 wt % water), and formic acid was dried over boric anhydride (B₂O₃) and then distilled (to 0.18 wt % water). After the EtAF synthesis the THF was removed under vacuum. Water contents were measured by Karl Fischer titration to be less than 0.2 wt % (typically much lower) for all ILs after drying.

Small- and Wide-Angle X-ray Scattering. Small- and wide-angle scattering (SAXS/WAXS) was performed on a point collimated Anton Paar SAXSess on a single image plate which was radially averaged and normalized to a direct beam intensity of 1 before subtraction of the empty cell scattering. Scattering was measured at 25 °C from 1 mm quartz capillaries for 10 min per sample.

Miscibility Measurements. Samples for miscibility measurements were prepared by mass in 1 mL glass vials at approximately 10 wt % intervals. The samples were mixed by mechanical agitation on a Vortex mixer for between 1 and 5 min, followed by bath sonication for 30 s, and then left to equilibrate in a water bath thermostated at 25 °C. Miscibility or

otherwise was determined after 30 min equilibration and confirmed after 1 week. Immiscible samples were identified by the formation of a meniscus and by optical turbidity when mechanically agitated after having equilibrated. Note that some of the EAF samples initially appear opaque or two phase when first made (probably from slow mixing due to the high viscosity of the ionic liquid) but are miscible at equilibrium. Small amounts of adventitious water were also found to decrease miscibility in some systems examined (e.g., PAN + dodecanol). Hence, dryness was reconfirmed by Karl Fischer titration for any mixed systems exhibiting such ambiguities. These difficulties are probably responsible for previously published results⁴⁵ that are inconsistent with our results.

Partially miscible samples were examined as a function of warming in 5 °C increments, allowing us to determine or confirm the phase boundaries in, for example, EAN + *n*-octanol.⁴¹

RESULTS AND DISCUSSION

Table 1 summarizes the observed liquid–liquid miscibilities of protic ILs with aliphatic alcohols at 25 °C. This includes the behavior of long-lived, metastable but subcooled EtAN. An immediate distinction can be drawn between ILs with the ethanolammonium cation, which only mix with ethanol, and the ethylammonium and propylammonium salts, which are miscible with much longer alkanol chain lengths. Mixtures of between 20 and 80 wt % butanol in EtAN remained mutually immiscible between 5 and 70 °C, well above its equilibrium melting point. This and the absence of any precipitation confirms that the observed immiscibility is not a consequence of EtAN being a metastable liquid at room temperature. The temperature dependence of EtAF miscibilities was not pursued due to the risk of amide formation.

EAN is miscible with all (even-chained) alcohols up to hexanol, and partially miscible with octanol, becoming fully miscible above its UCST.⁴¹ EAF is miscible with all the alcohols examined up to decanol and PAN up to dodecanol at 25 °C. PAF is a solid at room temperature where its solubility in hexanol and octanol is below 10% w/w. Above its melting point PAF is completely miscible with both alkanols. Our results show miscibility of much longer alkanols with some of these PILS than previously reported.⁴⁵ As discussed in the Experimental Section, we attribute this to two factors: many of these mixtures become immiscible in the presence of small amounts of water, and mixing is sometimes quite slow due to the high viscosity of some PILs.

Previous studies of IL structure by neutron³⁴ and X-ray³⁶ diffraction have shown that EtAN and EtAF both lack the

Table 1. Miscibility of *n*-Alkanols with PILs^a

mp =	EAN 13 °C ²²	PAN 6 °C ²⁰	EtAN 51 °C ²⁰	EAF −15 °C ²⁰	PAF 48 °C ⁴⁶	EtAF −82 °C ⁴⁷
ethanol	miscible	miscible	miscible	miscible	—	miscible
butanol	miscible	miscible	immiscible	miscible	—	immiscible
hexanol	miscible	miscible	immiscible	miscible	<10 wt % ^c	immiscible
octanol	partial ^b	miscible	immiscible	miscible	<6.4 wt % ^c	immiscible
decanol	immiscible	miscible	—	miscible	—	—
dodecanol	immiscible	miscible	—	partial	—	—

^aData are for liquid mixtures at 25 °C, except for PAF which melts at 48 °C. Note that EtAN is a metastable liquid at this temperature. “—” denotes mixtures not examined in this study. ^bPartly miscible at room temperature. Octanol becomes fully miscible with EAN above its UCST.⁴¹ ^cSolubility of solid PAF in alcohol at 25 °C. PAF is fully miscible with both alcohols above 48 °C.

characteristic amphiphilic nanostructure exhibited by EAN, PAN, and EAF, generated by a solvophobic effect. Ethanolammonium ILs are among the most water-like as judged by surface tension and surface structure⁴⁸ and by comparison of critical micelle concentrations and solubility behavior of representative nonionic surfactants.^{49,50} Indeed, EAN behaves as a surfactant at both the EtAN/air and water/air interfaces.⁵¹

Primary alkylammonium ILs form pronounced, bicontinuous, sponge-like nanostructures composed of interpenetrating domains of polar, charged, and H-bonding groups, with nonpolar domains. These are reminiscent of surfactant microemulsions or sponge phases, even to the extent that water dissolves into the H-bonding regions of such ILs.³⁷ The degree of this amphiphilic structuring depends slightly on anion (nitrate > formate)³² and more on alkyl chain length (butyl- > propyl- > ethylammonium).^{34,35} A signature of this is the presence of a low-angle peak or shoulder in the neutron³³ or X-ray³⁶ scattering patterns of these ILs. This is sometimes referred to as a prepeak, which we denote q_1 . Figure 2 shows

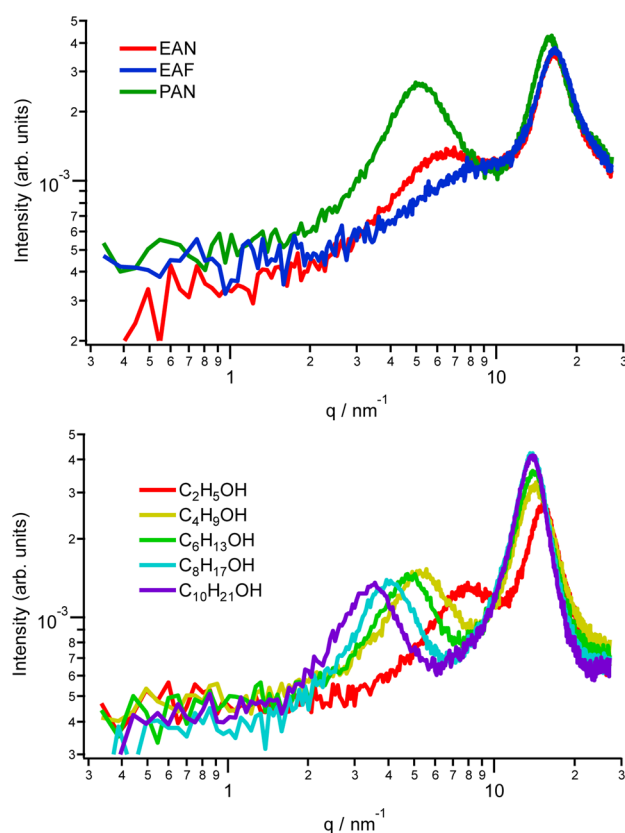


Figure 2. SAXS/WAXS patterns of pure ionic liquids and aliphatic alcohols at 25 °C.

the increasing prominence of this peak in the SAXS patterns of pure EAF, EAN, and PAN, and that the periodicity or repeat spacing of the amphiphilic nanostructure ($2\pi/q_{\text{peak}}$) increases with cation alkyl chain length from 10 Å for ethylammonium to 12 Å for propylammonium salts, and is relatively insensitive to anion. (Note that peak intensity depends on the contrast conditions for the radiation used, so that quantitative structural comparison between formate and nitrate is not possible based on this single contrast condition.³²)

The second peak in IL scattering patterns (q_2) observed near 20 nm⁻¹ has been shown to arise from a combination of

multiple shorter-range correlations (cation–cation, anion–anion, and anion cation or polar–polar, polar–nonpolar, and nonpolar–nonpolar depending on the contrast conditions and ion structures) between nearest neighbors.⁵² This peak is also observed in many nonamphiphilic ILs, including EtAN.^{34,53}

Figure 2 also shows that aliphatic alcohols exhibit similar scattering patterns, as has been documented many times previously.^{54–57} The inherent amphiphilicity of primary *n*-alkanols with alkyl chain lengths from 2 to 10 gives rise to a low-angle (q_1) peak with a repeat spacing that increases from around 8 Å to 20 Å. From the earliest studies this was identified with a nanosegregation of polar and nonpolar moieties into a locally bilayer-like structure,⁵⁴ and concentrated ethanol–water mixtures have been shown, like EAN and water, to exhibit molecular segregation.⁵⁸

Figure 3 shows a matrix of the room temperature SAXS/WAXS patterns of mixtures of EAF, EAN, and PAN with various 1-alkanols. Each mixture is shown over the composition ranges where they are miscible. Only in very few cases can the SAXS patterns of IL–alcohol mixtures be interpreted as an “average” liquid structure in which the two peaks shift smoothly and monotonically between the two pure liquids as a function of composition. Instead, the low-angle scattering increases and the position of q_1 develops nonmonotonically as composition changes. In some cases q_1 disappears completely at intermediate compositions. This provides clear evidence of large changes in liquid nanostructure and the presence in the mixtures of aggregates or domains much larger than in either pure liquid.

In contrast, q_2 shifts smoothly and monotonically with varying composition between the pure liquid components in all systems studied. This confirms that the two components are indeed intimately mixed and that nearest-neighbor distances can be interpreted as simple averages.

The closest approximation to simple mixing of components occurs with EAF + ethanol (Figure 3, top right). Even here, addition of ethanol causes q_1 of EAF to gradually become more prominent and move toward lower wave vector (larger spacing) and through a minimum at around 50 wt %, before moving back to the higher wave vector of pure ethanol. This peak also broadens, and the low angle scattering increases at all intermediate compositions well above the baseline of either pure liquid. This indicates disruption of the pure IL structure; peak broadening is consistent with a less regular arrangement of polar and nonpolar domains, and the increased low- q scattering suggests formation of larger and possibly polydisperse nanostructures.

These changes in longer-range nanostructure become more evident upon changing either component. As the alkanol length is increased to 1-butanol, the minimum in q_1 versus composition becomes more pronounced and shifts toward lower alkanol concentration. This trend continues upon further increasing chain length to 1-hexanol and beyond. The increase in low-angle scattering also becomes clearer, itself adopting a pronounced structure. In all systems examined q_2 continues to shift smoothly and monotonically from pure IL to pure alkanol with changing composition.

At some concentrations of 1-hexanol (20–40 wt %), 1-octanol (20–40 wt %), and 1-decanol (10–40 wt %) in EAF, the q_1 peak is completely absent, exhibiting instead the intense small-angle scattering profile expected from micelles or dilute microemulsions. This suggests that, while the amphiphilic nanostructure inherent in EAF can be altered to accommodate

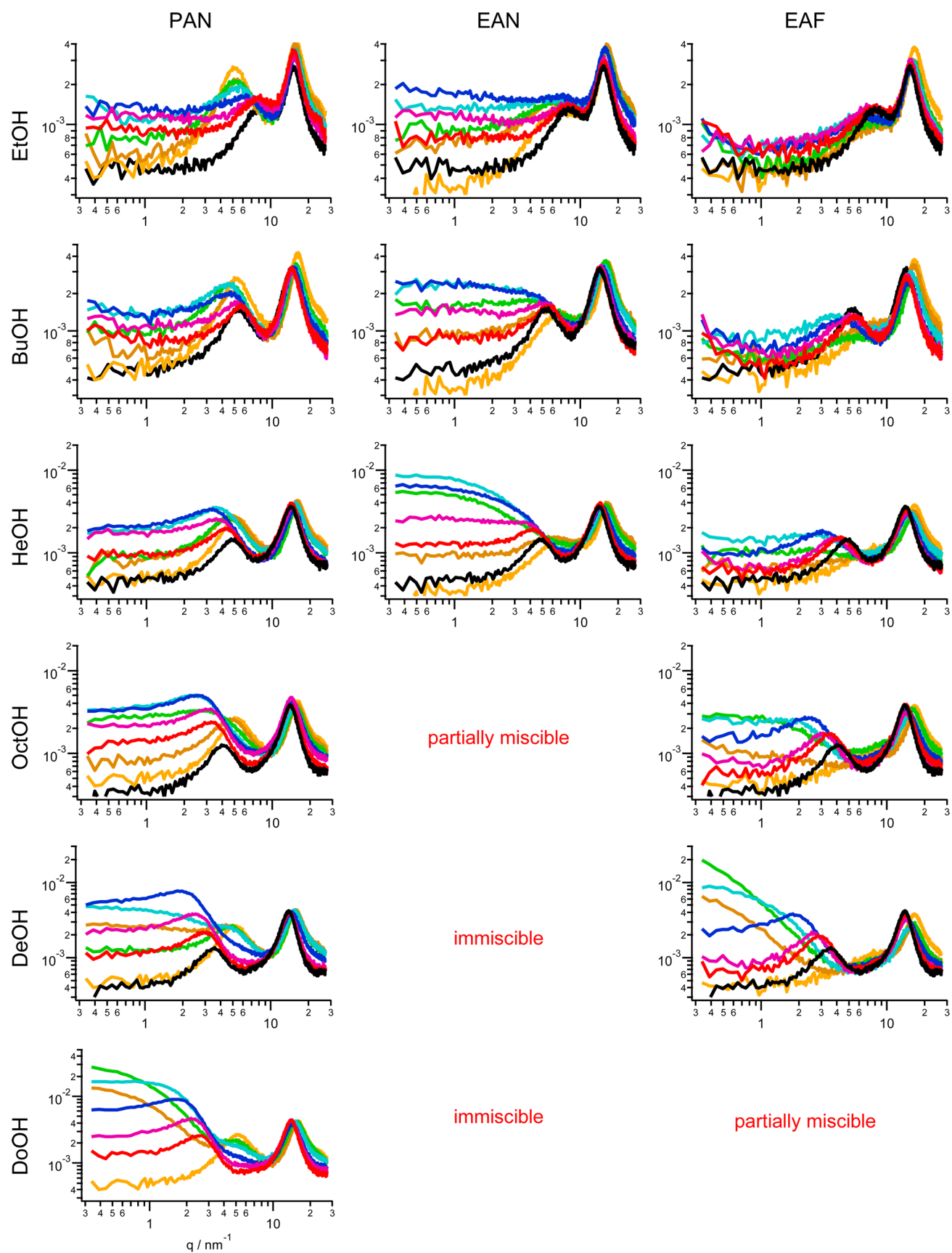


Figure 3. SAXS/WAXS of amphiphilic ionic liquid + aliphatic *n*-alcohol mixtures of various compositions at 25 °C: yellow, IL; brown, 10 wt % alkanol; green, 20 wt %; light blue, 40 wt %; blue, 60 wt %; purple, 80 wt %; red, 90 wt %; black, alkanol.

short alkyl chains, longer alkyl chains cannot. Instead, the solvent drives the amphiphilic self-assembly of the alkanols on a distinct and larger length scale than in either of the pure components. In EAF this occurs once the chain length of the alkanol exceeds twice that of the PIL cation. The pronounced low-angle scattering shifts toward progressively lower angles, indicating larger alkanol aggregates, as the chain length increases up to dodecanol, which is only partially miscible with EAF.

The same pattern of behavior occurs in mixtures of alkanols with both EAN and PAN. Ethanol/EAN mixtures behave similarly to ethanol and EAF; nonmonotonic changes in q_1 and increase in low-angle scattering signal modification of the inherent PIL nanostructure, while monotonic changes in q_2 show that the components are well-mixed. Increasing alkanol chain length to 1-butanol and 1-hexanol shows the emergence of a distinct new structural length scale, which is both more pronounced and becomes evident at shorter alkanol chains than in EAF. In EAN, this new structure seems to arise in butanol rather than hexanol—but still at approximately twice the cation alkyl group length. Partial miscibility is also encountered earlier for EAN, with octanol rather than dodecanol at 25 °C. Longer alkanols are almost completely immiscible with EAN.

Although similar in many respects, the amphiphilic nanostructure of pure EAN has previously been shown to be stronger than that in EAF.³² This has been attributed to a greater density of H-bond donors and acceptors and to their more efficient arrangement into a dense H-bond network. It is thus unsurprising that EAN has a lower “tolerance” for long alkanols and the disruption of the underlying domain structure that accompanies their dissolution. EAN/butanol mixtures already display the small-angle scattering features attributed to small micelles or microemulsions that only emerge in EAF with hexanol or longer chains. The partial miscibility of EAN and octanol is also consistent with its reduced tolerance for disruption of the existing PIL structure.

In their groundbreaking study of the miscibility behavior of the EAN + octanol system, Weingärtner et al.^{41,59} incorporated hydrogen-bonded ion pairs and triple ions into their model of mixtures and their conductivity. While they also considered the possibility of “solvophobic” demixing, the results presented here constitute the first direct evidence of such long-range structural effects.

The same general pattern of behavior is seen again in PAN/alkanol mixtures. Short alkanols disrupt the nanostructure and regular periodicity of the PIL just as they do in EAN and EAF. However, PAN has both a more pronounced underlying amphiphilic nanostructure than either EAN or EAF,³⁵ but also longer propyl chains which lead to larger nonpolar domains. This gives PAN a greater tolerance for incorporating longer alkanol chains before it drives their amphiphilic assembly. This greater solubility is also reflected in, for example, the lower surfactant efficiencies of nonionic surfactants in PAN than in EAN⁶⁰ and the smaller free energies of transfer of alkyl groups from alkanes into PAN versus EAN.⁶¹

PAN is miscible with alkanols from ethanol through to at least dodecanol at 25 °C. Figure 3 shows that mixtures with hexanol and shorter alkanols exhibit the same nonmonotonic evolution of nanostructure as reflected in the position of q_1 , accompanied by an increase in low angle scattering. Mixtures with 1-octanol and longer alkanols yield characteristically micellar small-angle scattering patterns with no q_1 peak over at least part of their composition ranges. As with the two

ethylammonium PILs, a distinct nanostructure only arises when the alkanol length reaches at least twice the cation alkyl chain length.

The emergence of larger (but still nanoscale) structures within these PIL/alkanol mixtures is most clearly seen in systems with large alkyl chain length differences between cation and alcohol, which lie near the miscibility limit. The low-angle scattering component of these systems can be treated approximately by a continuum or small-angle scattering approach, in which the background is treated as constant over the angular or q -range of interest. The low-angle scattering patterns from low concentrations of alkanols can be fit to conventional models of polydisperse spherical or spheroidal micelles.⁶² Such fits do yield physically plausible micelle radii that are slightly smaller than the fully extended lengths of the alkanol chains and which increase with alkanol chain length. However, it is not possible to determine the aggregate structures unambiguously, as the best-fit dimensions are sensitive to the solvent scattering, which is itself structured.

At higher concentrations of alkanol, the peak in the scattering reveals long-range order different from that present in either pure liquid. This may arise due to correlations between micelle-like aggregates (likely for dilute alkanol-in-PIL systems) or from percolation of aggregates into a bicontinuous structure.^{26,63} Again, physically plausible dimensions can be obtained assuming a variety of models ranging from bicontinuous (e.g., Teubner–Strey)^{63–66} to discrete micelle model with (e.g., excluded volume) interactions. However, the reliability of the quantitative results of either discrete or bicontinuous models is again compromised by the structured scattering of the underlying liquid components, which itself changes with composition. Unlike micelles formed from conventional surfactants,²⁵ the separation of length scales between n -alkanol aggregates and the alkylammonium ionic liquid nanostructure is too small to apply the small-angle scattering approximation.

The progression of the small-angle scattering component of these mixtures is also highly reminiscent of that seen in binary poly(oxyethylene)- n -alkyl ether/water mixtures.⁶⁷ We conclude, therefore, that the low-angle component of the scattering is due to self-assembly structures formed by medium to long-chained aliphatic alcohols, driven by the solvophobic effect in these PILs. Multiple isotopically labeled contrast variation neutron scattering is expected to resolve the structure in greater detail.

The formation of discrete micelles and/or bicontinuous microemulsions by primary alkanols in these PILs is itself remarkable. Although surface active, alkanols are not normally regarded as surfactants and do not self-assemble in aqueous solution. The SAXS patterns presented in Figure 3 reveal trends in behavior consistent with the sequestering of alkyl groups and amphiphilic self-assembly in these PILs. Addition of 10 wt % hexanol to EAN causes a small increase in low-angle scattering, but at 20 wt % the presence of a population of aggregates is clearly signaled by the low-angle scattering. Octanol behaves similarly in both PAN and EAF, but increasing alkanol chain length to 10 or 12 lowers the amount of alkanol required to generate such structures. This mimics the well-known trends in the critical micelle concentrations of surfactants in water as a function of alkyl chain length.

Laughlin⁶⁸ has reported that, while a single hydroxy group is insufficiently hydrophilic to cause self-assembly in water, alkane-1,2-diols can exhibit lyotropic surfactant phase behavior in aqueous systems. This is consistent with the observed

immiscibility of the *n*-alkanols examined in this study with both EtAF and EtAN, clearly pointing at the amphiphilicity of the EA⁺ and PA⁺ cations as a critical contributor to miscibility and self-assembly structure. This suggests that the micelles, and other structures at higher alkanol contents, include some alkylammonium cations on their surface, oriented such that the alkyl chains are solubilized into the hydrophobic regions of the alkanol tails. These PILs (cations) may thus be acting as cosurfactants or hydrotropes as well as solvents that promote self-assembly. Alkanol self-assembly does not occur in EtAN and EtAF because the PIL cation alcohol group renders the cation nonamphiphilic,⁴⁸ preventing it from acting as a cosurfactant.

Indeed, these mixtures are highly reminiscent of “surfactant-free microemulsions” and structures reported in the so-called pre-Ouzo regime of ternary mixtures such as water, with short- and long-chained alcohols near their miscibility limit.^{69,70} Here, however, the PIL is a single component that plays the same role as the water/hydrotrope mixture.

The formation of these hierarchical amphiphilic nanostructures in alkanol–PIL mixtures rests on several conditions being met. The solubility of the alkanol in the PIL at low concentrations is favored by the presence of a pre-existing amphiphilic domain nanostructure, as in EAF, EAN, and PAN, but not EtAN or EtAF. Dissolution of short alkanols disrupts the periodicity of this structure while retaining its domain-like character. The tolerance of a given PIL for this disruption depends on the Coulombic and H-bonding driving force for solvophobic segregation, and hence cation and anion structure, but also on nonpolar domain size. In these PILs this is determined solely by cation alkyl chain length. When the alkanol chain length or concentration is increased, the PILs capacity to incorporate the alkanol into its nanostructure is compromised which drives the separation of the alkanols into larger amphiphilic aggregates. These aggregates are not simply alkanol micelles existing in a PIL solvent (like conventional surfactant micelles in water) but also include the inherently amphiphilic PIL cations in their surface. From the perspective of a pseudophase model of self-assembly⁷¹ these liquid mixtures are composed of regions that are alcohol-rich and PIL-poor, and *vice versa*, but no regions or aggregates that are either pure alcohol or pure PIL. Although the solution structures give well-defined scattering patterns, they are in this sense weakly segregated.⁷² Importantly, these mixtures can in no way be interpreted as molecularly homogeneous and exhibit structure on two distinct length scales.

ILs, and in the present context particularly PILs, have dramatically expanded the number of solvents known to support self-assembly by traditional surfactants.^{30,73–76} The results presented here show that the potential of PILs is in fact much broader, enabling self-assembly by solutes outside the current, “water-centric” definition of surfactants, leading to the formation of new kinds of soft, self-assembled matter.

CONCLUSIONS

We have shown that mixtures of aliphatic alcohols with protic ionic liquids exhibit complex miscibility behavior and solution structure, but one which follows an internally consistent pattern. While EtAN and EtAF mix only with ethanol, ethyl- and propylammonium ILs are completely miscible with much longer alkanols.

Both the miscibility and the solution structure of these mixtures are primarily sensitive to the ratio of alkyl chain

lengths of the alkanol and the ammonium cation. Alkanols shorter than twice the alkylammonium cation disrupt the inherent amphiphilic nanostructure of the PIL, reducing its periodic order, but do not generate a qualitatively different solution structure. Longer alkanols cannot be accommodated within the PIL nanostructure to any significant extent and instead are expelled into larger amphiphilic aggregates. The self-assembled structures thus formed depend on composition: globular micelles form at low concentrations, and it is likely that these percolate into bicontinuous structures at higher concentrations. These larger aggregates are alkanol-rich but contain some PIL cations acting as cosurfactants or hydrotropes. For ethanolammonium PILs, which cannot act as cosurfactants, no self-assembly of alkanols is possible, and immiscibility results once the alkanol exceeds twice the cation chain length.

The transition to alkanol immiscibility with alkylammonium PILs only occurs at much larger alcohol:cation chain length ratios (near 4–5). Both transitions are affected by the anion and its H-bonding capacity, so it is expected that replacing the alcohol with other similar solutes would also affect the boundaries between the domains described above, i.e., disruptive nonideal mixing, amphiphilic self-assembly, and partial miscibility. Understanding solution structure in these systems is an important step toward understanding how ILs function effectively as solvents and reaction media for a diverse range of solutes and how they can be used to assemble new forms of soft matter.

AUTHOR INFORMATION

Corresponding Author

*E-mail gregory.warr@sydney.edu.au; Tel (+61 2) 9351 2106 (G.G.W.).

Notes

The authors declare no competing financial interest.

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