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The Effect of Protic Ionic Liquid and Surfactant Structure on Partitioning of Polyoxyethylene Nonionic Surfactants

Inga L. Topolnicki^a, Paul A. FitzGerald^a, Rob Atkin^b and Gregory G. Warr^{a1}

a. School of Chemistry F11, The University of Sydney, NSW, 2006 Australia
Tel: +612 9351 2106, Fax: +612 9351 3329

b. Discipline of Chemistry, The University of Newcastle, NSW 2308, Callaghan, Australia

Abstract

The partitioning constants and Gibbs free energies of transfer of poly(oxyethylene) n-alkyl ethers between dodecane and the protic ionic liquids (ILs) ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) have been determined. EAN and PAN have sponge like nanostructure consisting of interpenetrating charged and apolar domains. This study reveals the ILs solvate the hydrophobic and hydrophilic parts of the amphiphiles differently. The ethoxy groups are dissolved into the polar region of both ILs via hydrogen bonds. This environment is remarkably water-like and the solubility of ethoxy groups in EAN decreases on warming, just as it does in water, underscoring the critical role of the IL H-bond network for solubility. In contrast, amphiphile alkyl chains are not preferentially solvated by the charged or uncharged regions of the ILs. Rather, they experience an “average” IL composition, so partitioning from dodecane into the IL increases as the cation alkyl chain is lengthened from ethyl- to propyl- because the IL apolar volume fraction increases. Together these results show that surfactant dissolution in ILs is related to structural compatibility between the head or tail group and the IL nanostructure. Thus, these partitioning studies reveal molecular design parameters for effective surfactants in ILs.

¹ Author for correspondence: gregory.warr@sydney.edu.au

Introduction

Ionic liquids (ILs) display an extraordinary range of properties. Among the most important is their striking ability to dissolve diverse types of solutes, and especially to support self-assembly of amphiphilic solutes into micelles and lyotropic liquid crystals. Protic ILs – an important subset of ILs formed by proton transfer between a Brønsted acid and base^[1-4] – generally have smaller ions than aprotic ILs, but because many form hydrogen bond networks they can be more difficult to characterise. These compounds are exemplified by the most studied protic IL, ethylammonium nitrate (EAN).^[5] EAN exhibits extensive hydrogen bonding between multiple donor and acceptor sites on the cationic ammonium and nitrate anion, respectively^[6-9] in the liquid state (melting point = 13°C). This contributes to a solvophobic effect within the liquid itself that causes nanosegregation of the non-polar ethyl moieties away from the H-bonded ionic groups into a bicontinuous structure reminiscent of a microemulsion or sponge phase.^[9-13] This is also seen in many other protic ILs, and the extent of nanosegregation depends on the detailed structure of both cationic and anionic moieties.^[4, 12, 14] Protic ILs are thus arguably the smallest amphiphiles, exhibiting not only surface activity^[15-17] but also bulk amphiphilic self-assembly.^[11] Although knowledge of the amphiphilic nanostructure in ILs is increasing rapidly, its effect on dissolution of various solutes is much less well understood.

Many protic and aprotic ILs are excellent solvents for amphiphilic self-assembly of conventional surfactants and block copolymers,^[18, 19] but among protic ILs EAN is by far the most widely studied. Polyoxyethylene n-alkyl ethers (C_nE_m) and PluronicTM PEO-PPO-PEO co-polymers exhibit a full range of self-assembly behaviour into micelles, liquid crystals, and microemulsions in EAN.^[20-26] Previous work has suggested that most differences in self-assembly behaviour are related to the greater solubility of the alkyl chain in EAN and propylammonium nitrate (PAN) compared to water. The polar polyoxyethylene group, curiously, behaves quite similarly in EAN and water.^[27, 28]

Despite numerous investigations of ILs for solvent extraction and related separations processes,^[29-32] and for studying water-immiscible ILs,^[33] liquid-liquid equilibria have not been exploited to understand the bulk thermodynamic behaviour of protic ILs as solvents for amphiphiles.^[6] The partitioning of suitable candidate solutes between immiscible solvents such as oil and water or IL provides direct measurements of standard free energy, enthalpy and entropy of transfer between solvents. These can be used to construct a solvophile-lipophile balance scale for ILs analogous to the widely-used HLB scale for aqueous surfactants and emulsifiers, and an empirically-predictive, additive solvophobic fragment model for ILs,^[34-36] or to develop linear free energy relationships that characterize IL-solute interactions.^[37]

Polyoxyethylene n-alkyl ethers (C_nE_m) are an important and extensively studied class of nonionic surfactants in water, nonaqueous molecular solvents and ILs.^[20, 38-41] They have particular significance in ILs as they contain no counterion, which can potentially complicate solution behaviour. Here we undertake the first systematic study of the partitioning of dilute (sub-cmc) solutions of C_nE_m surfactants between the protic ILs EAN and PAN and a non-polar solvent, dodecane, as a function of both alkyl and ethoxy chain lengths, as well as the effect of temperature on partitioning. The derived thermodynamic parameters for molecular fragments will reveal just how the solvencies of these ILs are similar to, and differ from, water. The results obtained enable the contribution of the amphiphile head and tail groups to overall surfactant solubility and efficiency to be separated, which elucidates molecular design parameters to optimise surfactants for use in ILs.

Experimental Methods

EAN and PAN were prepared by carefully adding an equal molar amount of nitric acid (35wt%, Ajax) to a 70wt% aqueous solution of either ethylamine (Aldrich) or propylamine (Acros). Reactions were maintained below 10°C in an ice bath to prevent unwanted side reactions. Water and excess alkylamine were removed by rotary evaporation, followed by a 24 hour nitrogen purge at 105°C. Water contents were below 0.1 %w/w by Karl Fischer titration. n-dodecane (Merck) was passed through an alumina column prior to use to remove any polar impurities.

Polyoxyethylene n-alkyl ethers (Nikko Chemical Company and Fluka) were used as received. Their purities were confirmed by NMR, and by HPLC in the normal course of instrument calibration. Partitioning experiments were conducted for the polyoxyethylene n-alkyl ether surfactants (C_nE_m), from a 1 mM stock solution in the ionic liquid. Dodecane was added on top in a 2mL vial, being careful to avoid emulsification. Volume ratios were varied between 3:1 and 1:10 to optimize conditions for determination of the distribution coefficient, K_{tr} , by HPLC (see below). All samples were equilibrated in a thermostatted water bath at $25 \pm 0.1^\circ\text{C}$ for two weeks before measurement, which was pre-determined to be sufficient to reach equilibrium.^[42] Although widely used in aqueous partitioning studies, n-octanol is unsuitable as a non-polar solvent here due to its partial miscibility with EAN.^[43] Equilibrium partitioning constants^[44] were determined by directly measuring the concentration of surfactant in the IL using HPLC and then using a mass balance to calculate the concentration in the dodecane. In selected samples the dodecane phase was also analysed by way of confirmation. HPLC measurements were performed in isocratic mode using a C_{18} reverse-phase column (Sunfire 5 μm , 4.6mm $\times$ 150mm) at 40°C, 0.7mL min⁻¹ flow rate, 200 μL injection, and using a Waters 2410 RI detector. The eluent was an 8:1:1 volume ratio of methanol (Merck), water (Milli Q filtered) and EAN. Samples were diluted in the methanol:water pre-eluent mixture to give the same solvent ratio as the eluent, which helps to suppress the IL solvent peak.

Results and Discussion

Figure 1 shows partitioning results for a set of C_nE_m amphiphiles between dodecane and EAN at 25°C, expressed as standard Gibbs free energy of transfer, $\Delta G_{tr}^\circ = -RT \ln K_{tr}$, where the partition

constant $K_{tr} = \frac{[C_nE_m]_{IL}}{[C_nE_m]_{dodecane}}$. The distribution constants for a given surfactant into EAN are much greater

than those reported previously for their partitioning between iso-octane and water (see Figure 1(b)).^[45]

The free energy of transfer was found to vary linearly as a function of both alkyl and ethoxy chain lengths, n and m , so the matrix of data for ($10 \leq n \leq 16$, $4 \leq m \leq 8$) variation of fourteen surfactants is fit to a single expression

$$\begin{aligned}\Delta G_{tr}^\circ &= \Delta G_{tr}^\circ(\text{CH}_3-) + \Delta G_{tr}^\circ(-\text{OH}) + (n-1)\Delta G_{tr}^\circ(-\text{CH}_2-) + m\Delta G_{tr}^\circ(-\text{CH}_2\text{CH}_2\text{O}-) \\ &= -10.6 + (2.19 \pm 0.20)(n-1) - (2.69 \pm 0.33)m \quad \text{kJ mol}^{-1}\end{aligned}$$

Note that we are not able to separate the contributions of terminal methyl and hydroxyl groups, which are both present in all C_nE_m surfactants.^[45]

Figure 1. ΔG_{tr}° from dodecane to EAN for C_nE_m amphiphiles as a function of (a) alkyl chain length n and (b) ethoxy chain length m . Closed circles show $C_{12}E_m$ results for the iso-octane/water system.^[45]

Figure 2 shows the effect of replacing the ethylammonium cation with propylammonium (PAN). This is a smaller data set in which m is varied while n is fixed at 10, and n is varied while m is fixed at 4. Again a linear dependence on both n and m is observed. The Gibbs free energies of transfer for methylene and ethoxy groups from alkane into each of these ILs are listed in Table 1, together with literature values for water.^[45, 46]

Figure 2. ΔG_{tr}° from dodecane to EAN and PAN for (a) C_nE_4 as a function of alkyl chain length, n , and (b) $C_{10}E_m$ as a function of ethoxy chain length, m .

Table 1. Standard Gibbs free energies of transfer of methylene and ethoxy moieties from an alkane (isooctane or dodecane) into water or protic IL.

Polar solvent	$\Delta G_{tr}^{\circ}(-CH_2-)$	$\Delta G_{tr}^{\circ}(-CH_2CH_2O-)$
	(kJ mol ⁻¹)	(kJ mol ⁻¹)
Water	3.45 ^[35]	-2.61, ^[45] -2.52, ^[46] -2.68 ^[47]
EAN	2.19±0.20	-2.69±0.33
PAN	1.3	-2.5

$\Delta G_{tr}^{\circ}(-CH_2-)$ decreases with the progression from water to EAN to PAN, as the volume fraction of nonpolar components (i.e. the cation alkyl group) increases, and the average polarity of the solvent decreases. Such increased alkyl chain solubility correlates well with elevated critical micelle concentrations reported in EAN.^[48] In fact $\Delta G_{tr}^{\circ}(-CH_2-)$ into EAN is about 60% of its value for water (Table 1). This is comparable to the reduction seen in free energy for dissolution of alkane gases in water *versus* EAN.^[6]

A very similar reduction was also reported for micelle formation in EAN by Evans *et al.*, derived from the alkyl chain length dependence of cmcs of ionic surfactants.^[48] They found a Gibbs free energy of transfer of -1.5 kJ mol⁻¹ per methylene group from EAN into a micelle (at 50°C)

compared to -2.9kJ mol^{-1} for aqueous micelle formation. More recently this has been extended from EAN to PAN at 25°C by Fernández-Castro *et al.*^[49] Using their measured cmcs for alkyltrimethylammonium bromide cationic surfactants which, for the case of ILs acting as swamping electrolytes the standard free energy of micellization is $\Delta G_{mic}^\circ = RT \ln(\text{cmc})$, we obtain $\Delta G_{mic}^\circ (-\text{CH}_2-)$ = -1.2kJ mol^{-1} in EAN and -0.6kJ mol^{-1} in PAN. This trend closely parallels that shown in Table 1 for the transfer of a methylene between polar solvent and an alkane.

This result is also consistent with our qualitative observation of increasingly lower efficiency of C_nE_m surfactants for microemulsion formation in EAN and PAN compared to water.^[23, 41]

In contrast, $\Delta G_{tr}^\circ (-\text{CH}_2\text{CH}_2\text{O}-)$, remarkably, is the same within experimental error for EAN, PAN and water. Put another way, the standard free energy of transfer of an ethoxy group from water into either PAN or EAN is zero. Like many ILs, EAN and PAN are both known to undergo nanosegregation into a sponge-like arrangement of interpenetrating polar and non-polar domains.^[9, 11, 12] We attribute the constant $\Delta G_{tr}^\circ (-\text{CH}_2\text{CH}_2\text{O}-)$ to the ethoxy groups being specifically dissolved into and solvated by the polar components of the ILs, rather than sensing the average environment of the IL, which would include nonpolar domains comprised of ethyl- or propyl- chains.

The behaviour of the polar ethoxy groups is thus similar to that of water dissolved in EAN. Water dissolves into EAN by incorporation into the polar, H-bonded network of ammonium and nitrate charged groups, with negligible dissolution into the non-polar ethyl domains.^[14, 50] Ideal mixing of methanol with EAN has also been reported previously.^[51] The similarity of the $\Delta G_{tr}^\circ (-\text{CH}_2\text{CH}_2\text{O}-)$ values suggests they are also dissolved exclusively into the polar domains of EAN and PAN. Given the well-known H-bonding complementarity between ethoxy groups and water,^[52] this suggests further that the H-bond network within the polar domain of alkylammonium nitrates may be even more similar to water than previously suspected.^[6]

This behaviour is also consistent with SANS investigations of C_nE_m micelle formation in EAN and PAN,^[21, 23] which showed that the ethoxy groups are strongly solvated, and with the pattern of lyotropic phase behaviour^[20] and microemulsion formation,^[41] which both suggested that the solvation volumes of ethoxy groups are greater in EAN than in water; this is because the solvating ions in an IL have greater molecular volume than water. Our previous studies of the conformation of poly(ethylene glycol) also showed that EAN is a good solvent.^[27]

The cmcs of the $C_{12}E_m$ series in EAN have been reported by Greaves *et al.*^[53] As with alkyl chain length variation, this can be used to obtain $\Delta G_{mic}^\circ (-CH_2CH_2O-) = 0.4 \text{ kJ mol}^{-1}$ in EAN, which is indistinguishable from the value obtained from cmcs in water.^[54] Of course, these values are much smaller than the $\Delta G_{tr}^\circ (-CH_2CH_2O-)$, as they reflect only that the ethoxy groups remain relatively in their polar environment, and are largely unaffected by micelle formation.

The temperature dependence of the partitioning of $C_{10}E_8$ surfactants between EAN and dodecane is shown in Figure 3. This yields the standard enthalpy and entropy of transfer of $C_{10}E_8$ from dodecane into EAN, $\Delta H_{tr}^\circ (C_{10}E_8)$ and $\Delta S_{tr}^\circ (C_{10}E_8)$, shown in Table 2. Also shown for comparison are corresponding data for transfer of $C_{12}E_8$ from iso-octane into water.^[45] Although the alkyl chain lengths are different, both enthalpies and entropies are remarkably similar between the two polar solvents. For both EAN and water, nonionic surfactants partition increasingly into the non-polar phase on warming, and to virtually the same extent.^[45, 46] This underscores the critical role of H-bond structure in the solvation of ethoxy groups by EAN (and PAN), and its similarity to water, consistent with the observation of lower consolute boundaries for C_nE_m surfactants,^[20, 21, 38, 55] in the phase behaviour of ternary microemulsions of C_nE_m ,^[23, 41, 56-58] [59] and the temperature-dependent self-assembly of Pluronic amphiphiles in EAN.^[22, 25, 60, 61]

Figure 3. Temperature dependence of ΔG°_{tr} between alkanes and EAN or water.^[45]

Table 2. Standard enthalpies and entropies of transfer from nonpolar into polar solvents.

Nonpolar solvent	polar solvent	surfactant	ΔH°_{tr} (kJ mol ⁻¹)	ΔS°_{tr} (J K ⁻¹ mol ⁻¹)
iso-octane	water ^[45]	C_{12}E_8	-57±4	-216±14
n-dodecane	EAN	C_{10}E_8	-61±12	-160±40

The average environment experienced by the alkyl groups of these surfactants explains their low efficiency (high cmc and microemulsification concentration) in both EAN and PAN, and also contrasts with the specific solvation environment of the polar ethoxy groups. Together these suggest strategies for improving surfactant efficiency in these and other ILs. Reducing the IL's amphiphilicity and capacity to nanostructure while maintaining a strong H-bond network, e.g. ethanolammonium nitrate,^[9] should reduce alkyl chain solubility. Alternatively, introduction of non-alkyl non-polar groups would reduce miscibility with the alkane component and should lower solubility, favouring adsorption and micellisation.^[62] This strategy mirrors that taken successfully in optimizing design parameters for amphiphiles in supercritical CO₂.^[63, 64] On the other side, an amphiphile with a polar head-group with reduced H-bonding capacity might lower its solubility in the polar domains, but risks greater solubility in the nonpolar regions and hence no improvement in efficiency. Partitioning

experiments such as these are a rapid, efficient way of screening potential polar and non-polar functionalities, which may already exist among known aqueous amphiphiles.

Conclusion

Partitioning of homologous series of C_nE_m amphiphiles between dodecane and EAN or PAN shows that the amphiphilic IL nanostructure determines how they behave as solvents for different kinds of functional groups. Although a straightforward macroscopic measurement, Gibbs free energies of transfer are a sensitive probe of the microenvironment around various solute moieties, and are amenable for the investigation of relatively complex molecular structures. This yields a new route for rapid screening of solutes in various ILs, and for the prediction of macroscopic properties from the molecular structure and H-bonding capacities of the constituent ions, complementing the more detailed information obtained from more labour-intensive neutron and x-ray diffraction studies of liquid mixtures and solutions.

Comparison of the solvation behaviour of ethoxy groups by EAN, PAN and water seems to have revealed a “Goldilocks” H-bond network structure which makes them just right for dissolving certain water-soluble molecular species, as indicated by a near zero $\Delta G_{tr}^\circ(-CH_2CH_2O-)$ between water and either IL. This also renders them good solvents for poly(ethylene glycol). The low efficiency of C_nE_m amphiphiles in these ILs compared with water is primarily a consequence of the much greater solubility of the alkyl moiety, although the specific role of the terminal $-OH$ merits further investigation.

Acknowledgements

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Table of Contents Figure

Surfactants in Ionic Liquids: The dissolution and solvation of the hydrophilic and hydrophobic components of nonionic surfactants in ionic liquids is affected by solvent nanostructure and H-bonding. The polar domains of the protic ionic liquids ethyl- and propyl-ammonium nitrate are, thermodynamically-speaking, remarkably water-like.