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Surfactant Adsorption at the Surface of Mixed Ionic Liquids and Ionic Liquid Water Mixtures

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Abstract

Surface tensiometry and neutron reflectivity have been used to elucidate the structure of the adsorbed layer of non-ionic surfactant tetraethylene glycol tetradecyl ether (C₁₄E₄) at the free surface of the ionic liquids ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN) and their binary mixtures with each other and with water. Surface tensions reveal that the critical micelle concentration (CMC) depends strongly on solvent composition. The adsorbed surfactant structure elucidated by neutron reflectivity shows that the level of solvation of the ethylene oxide groups varies for both the pure and mixed solvents. This is attributed to solvent – solvent interactions dominating solvent – surfactant interactions.

Introduction

Ionic liquids are pure salts which are liquid below 100°C. Many ionic liquids are nanostructured,¹⁻⁸ with alternating polar and non-polar regions present in the bulk liquid. Nanostructure arises from inter- and intra-molecular bonding, and is responsible for many of the physiochemical properties of the ionic liquid. Changing the cation or anion influences interactions between the ions and hence the degree of nanostructure, which allows ionic liquids' properties to be predictably changed. This tunability of key properties such as viscosity, thermal stability, and electrochemical conductivity and stability, has stimulated increased ionic liquid research in many areas.⁹⁻¹⁹ Similarly, ionic liquid interfacial structure and properties depend on the cation and anion,²⁰⁻²⁵ and ionic variations alter the level of surface structure. However, changing the cation or anion to obtain specific interfacial properties may result in undesirable properties within the bulk liquid, or vice versa. The introduction of a cosolvent is an alternative to cation and anion variation, as mixed solvents offer the opportunity to adjust properties continuously via variation in composition. Alternatively, surface active species may be used to selectively modify surface properties. In this work we investigate surfactant adsorption at the surface of

ethylammonium nitrate (EAN), ethanolammonium nitrate (EtAN), water and their binary mixtures using surface tensiometry and neutron reflectivity.

Neutron scattering² and diffraction,⁷ and small- and wide- angle x-ray scattering^{5,26} measurements have shown that EAN is nanostructured in the bulk. The ethyl chains associate together via solvophobic interactions while the anions associate with the ammonium groups through hydrogen bonding and electrostatic interactions. This creates well-defined polar and non-polar regions arranged in a bi-continuous L₃-sponge like structure.⁷ EAN has been shown to support all forms of surfactant self assembly, but CMCs are much higher compared to water because EAN's apolar domains can solvate surfactant alkyl tails.²⁷⁻³⁸ In EtAN, nanostructure is reduced because the incorporation of an alcohol moiety on the cation ethyl chain disrupts the solvophobic interactions that promote alkyl chain aggregation;^{5,7} while the anions still associate with the ammonium headgroups, they also hydrogen bond with the hydroxyl group, which impedes alkyl chain aggregation. Consequently, nanostructure in EtAN is less pronounced, with smaller apolar domains⁷ that are less able to solvate surfactant tailgroups than the larger apolar regions in EAN. Thus, CMCs are significantly lower in EtAN than EAN.³⁸

Differences in the bulk liquid nanostructure of EAN and EtAN are also manifested at their surfaces. X-ray reflectivity has shown that the macroscopic air interface orients EAN's existing bulk nanostructure into alternating layers enriched in polar and non-polar groups.^{21,24} The layers are most well-defined closest to the air interface, and decay to the bulk liquid morphology over a distance of 38 Å, or about seven ion pairs. In EtAN, no such surface layering is detected, consistent with the weaker bulk structure.²⁵

Previously we have investigated the structure of adsorbed C_nE₄ layers at the EAN – air interface using neutron reflectivity and vibrational sum frequency spectroscopy as function of alkyl chain length (n = 12, 14, 16), concentration and temperature.³⁶ The tetra(ethylene glycol) head group layer was found to be thin, compact (incorporating only ~30% EAN by volume), and disordered i.e. there is no preferential orientation of the ethylene glycol groups. Similarly, the alkyl tail groups have a significant number of gauche defects indicating a high degree of conformational disorder. The thickness of this non-polar layer is much less than the fully-extended chain length, but does increase with alkyl chain length. Lowering the concentration of C₁₂E₄, from 1 wt% to 0.1 wt% decreases the surface excess, and the headgroup layer became thinner and less solvated, but

C₁₄E₄ and C₁₆E₄ adsorbed layers were unaffected over the same concentration range, indicating that their CMCs are lower than 0.1 wt%.

There are no previous reports of surfactant structure adsorbed at the surface of mixed ionic liquids. However, non-ionic surfactant aggregation and cloud point behaviour in the bulk have been studied using C₁₄E₅ in mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate (emimBF₄) and 1-hexyl-3-methylimidazolium tetrafluoroborate (hmimBF₄).^{39,40} C₁₄E₅ is insoluble in emimBF₄ at room temperature but is completely miscible in hmimBF₄ with no evidence of micelle formation or a cloud point up to at least 100°C. When the two ionic liquids were mixed a cloud point was noted, which increased with increasing hmimBF₄ content. Likewise, micelle formation was observed in the ionic liquid mixtures, and CMCs varied as a function of ionic liquid composition. As the concentration of emimBF₄ increased, the critical micelle concentration decreased, and the micelle size increased, owing to reduced solubility. This shows that surfactant properties can be controlled by varying the ionic liquid composition.

In this work the adsorption of the non-ionic surfactant C₁₄E₄ at the air – liquid interface of ionic liquid mixtures and ionic liquid/water solutions is investigated using surface tensiometry and neutron reflectivity. The behaviour of C₁₄E₄ has previously been extensively characterised at the EAN – air surface,³⁶ in micelles and microemulsions in EAN,^{32,35} other protic ionic liquids,⁴¹ and aqueous systems.⁴² The selected solvents (H₂O, EtAN, EAN/H₂O, EtAN/H₂O, and EAN/EtAN) aim to explore the effect of solvophobicity and solvophilicity on solvent – surfactant and solvent – solvent interactions. Results are compared to aqueous and other ionic liquid systems.

Materials and Methods

Materials: Ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN) were prepared by mixing equimolar amounts of base, ethylamine (Aldrich) or ethanolamine (Aldrich), with nitric acid (Aldrich) in aqueous solution at 10°C. Water was removed from the ionic liquid solutions by rotary evaporation at 45°C, followed by nitrogen purging and heating at 110°C. This led to water contents undetectable by Karl Fischer titration. Partially deuterated EAN and EtAN were prepared by the same method, however after the heating step the ionic liquids were mixed with D₂O (Aldrich). D₂O:EAN was mixed in a 3:1 molar ratio which substitutes the

ammonium hydrogen's with deuterium, and D₂O:EtAN in a 4:1 molar ratio to also replace the exchangeable hydroxyl hydrogen. The solutions were redried via rotary evaporation, nitrogen purging and heating.

Hydrogenous nonionic surfactant, tetradecyl tetraethylene glycol ether (C₁₄E₄) was purchased from Nikkol, Japan, and was used as received. The tail deuterated tetradecyl tetraethylene glycol ether surfactant (d-C₁₄-h-E₄) was purchased from R. K. Thomas, University of Oxford, UK. The surfactant was dried in a vacuum oven prior to use.

Surface tension measurements: The air – liquid interfacial tension measurements were performed on a Dataphysics OCA20 optical tensiometer using the pendant drop method. A volume of liquid is suspended from a capillary and an image of the drop is captured. The Young-Laplace equation is fit to the drop image using SCA20 software to calculate the surface tension. Measurements were conducted at 20°C. The capillary and sample were placed within a transparent container and a Petri dish containing the liquid was positioned below the capillary to minimize water adsorption by the drop. Drops were monitored for 30 minutes and all samples had reached an equilibrium surface tension by this time.

Neutron reflectivity: Measurements were conducted on the INTER reflectometer at ISIS, Rutherford Appleton Laboratories, Didcot, UK. Samples were placed into Teflon troughs inside a chamber purged with nitrogen. A neutron beam (wavelength = 1.5 - 16Å) was directed at the liquid surface at an incident angle, $\theta = 0.8^\circ$. Measurements were performed at 20°C.

Solutions of tail deuterated d-C₁₄-h-E₄ in a series of hydrogenous and partially deuterated EAN/H₂O, EtAN/H₂O, and EAN/EtAN mixtures were prepared at 1.1 – 1.3 x CMC, as determined by the surface tension measurements. This resulted in varied absolute bulk surfactant concentrations ranging from 8.0 x 10⁻⁴ to 2.2 x 10⁻² wt%.

In the technique of neutron reflectivity, a beam of neutrons is directed at the surface at an incidence angle, θ , and the specularly reflected neutrons are measured as a function of the neutron's momentum transfer, Q , given by:

$$Q = \frac{4\pi \sin \theta}{\lambda}$$

where λ is the neutron wavelength. The reflected intensity is a function of the scattering length density, ρ , defined by:

$$\rho = \sum_i n_i b_i$$

where n_i is the number density of each component, and b_i is the scattering length. Neutron scattering length densities for the components examined in this work are given in Table 1.

Table 1: Calculated lengths, volumes, and scattering length densities of hydrogenous and partially deuterated C₁₄E₄ and the solvents.

	Length (Å)	Volume (Å ³)	Hydrogenous SLD (x 10 ⁻⁶ Å ⁻²)	Deuterated SLD (x 10 ⁻⁶ Å ⁻²)
C₁₄H(D)₂₉	19.2	404.0	-0.38	7.09
(OC₂H₄)₄OH	14.4	253.3	0.74	-
H₂O (D₂O)	2.8	30.0	-0.56	6.37
H(D)OC₂H₄NH(D)₃NO₃ (EtAN)	5.7	170.0	1.70	4.46
C₂H₅NH(D)₃NO₃ (EAN)	5.3	150.0	1.30	3.38
25wt% EAN/75wt% H₂O	-	-	-0.11	5.69
50wt% EAN/50wt% H₂O	-	-	0.29	4.97
75wt% EAN/25wt% H₂O	-	-	0.79	4.20
25wt% EtAN/75wt% H₂O	-	-	-0.12	6.05
50wt% EtAN/50wt% H₂O	-	-	0.38	5.62
75wt% EtAN/25wt% H₂O	-	-	0.99	5.08
10wt% EAN/90wt% EtAN	-	-	1.65	4.35
25wt% EAN/75wt% EtAN	-	-	1.57	4.18
50wt% EAN/50wt% EtAN	-	-	1.48	3.90
75wt% EAN/25wt% EtAN	-	-	1.39	3.65

Neutron reflectivity is sensitive to changes in scattering length density, therefore provides information perpendicular to the surface about the structure of the adsorbed surfactant, provided there is contrast between the

scattering length densities of the adsorbed species and the solvent. In this work, which aims to elucidate information on the surfactant hydrocarbon tail and head group regions, contrast is achieved by selectively deuterating the tail group only. This gives a large contrast between the tail and head groups (Table 1). Additionally, two solvent contrasts are used. The hydrogenous solvents have a scattering length density similar to the surfactant head group, and in these systems the reflectivity is primarily a consequence of the surfactant tails. The deuterated solvents' scattering length density is different from both the surfactant tail and head groups, and hence the reflectivity arises from the entire surfactant molecule.

The neutron reflectivity data was modelled using the *Motofit* reflectivity analysis package.⁴³ A scattering length density model is generated from which a theoretical reflectivity curve is calculated and compared to the measured data. For each system, four parameters were fixed during data fitting: instrumental scale factor (adjusts reflectivity below the critical edge to one), the solvent scattering length density (Table 1), the gas phase scattering length density (set to 0), and the sample background. The data was fit using a slab method which models the interface as a series of layers of uniform scattering length density and constrained by known molecular dimensions (see Table 1). The hydrogenous solvent systems, which provide information on the surfactant hydrocarbon tail, are modelled as a single layer. During the fitting process, the layer thickness was upper bounded by the length of the extended hydrocarbon chain, and the scattering length density was allowed to vary between 0 (the scattering length density value for air) and the value for the deuterated tail (see Table 1). The deuterated solvent systems, which provide information on the entire surfactant molecule, were fit using two layers. The thickness and scattering length density of the uppermost layer, which represents the surfactant tail group oriented towards the gas phase, was set to the same parameters as the hydrogenous system. Roughness was included between the tail layer and the gas phase and the tail layer and the bulk liquid, and was constrained to remain below 5 Å, a common value for surfactant systems. The second layer, which describes the surfactant head groups facing the bulk liquid, was limited by the length of a fully extended tetra(ethoxy) group, and the scattering length density was allowed to vary between the values for the headgroup and the partially deuterated solvent. Again, roughness was included between interfaces of adjacent slabs. The data sets from the both the hydrogenous and deuterated solvents were fit simultaneously, giving confidence in the final model.

Results and Discussion

Surface Tension: Surface tension measurements were performed on a series of EAN/H₂O/C₁₄E₄, EtAN/H₂O/C₁₄E₄, and EAN/EtAN/C₁₄E₄ mixtures. Figures 1a-c shows the data for surface tension versus the surfactant concentration. For all samples, as surfactant concentration is increased the surface tension decreases until a minimum value is reached, after which the surface tension remains constant. The minimum surface tension value is similar for all solvents studied, ranging from 29.5 to 30.8 mN.m⁻² (c.f. Table 2). The concentration at which the surface tension plateau is reached is the critical micelle concentration (CMC). This behaviour is reminiscent of well studied aqueous surfactant systems,^{44,45} and more recently probed ionic liquid surfactant systems.^{27,38,46-48} CMCs for surfactant – solvent mixtures determined this way are listed in Table 2.

Surface tension – ln surfactant concentration data were analysed using the Gibbs equation to determine the maximum surface excess concentration, Γ :

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln C}$$

where γ is the surface tension, C is the surfactant concentration, and R and T the gas constant and temperature, respectively. The surface excess was then used to determine the monolayer molecular area:

$$A = \frac{1}{N_A \Gamma}$$

where N_A is the Avogadro constant.

The standard free energies of micellisation, ΔG_{mic}° , and adsorption, ΔG_{ads}° , were calculated using:⁴⁵

$$\Delta G_{mic}^\circ = RT \ln CMC$$

and:

$$\Delta G_{ads}^\circ = \Delta G_{mic}^\circ - \pi_{cmc} \cdot A$$

where π_{cmc} is given by:

$$\pi_{cmc} = \gamma_{solvent} - \gamma_{cmc}$$

The values determined from this analysis are reported in Table 2.

Figure 1: Surface tension versus concentration for $C_{14}E_4$ in mixed solvent systems. (A) EAN/H₂O; (B) EtAN/H₂O; (C) EAN/EtAN. (Data series for different compositions are vertically offset for clarity as indicated in the Figure). Solid lines are used as a visual guide to indicate the two regions of surface tension used to determine the CMC. (D) CMC as a function of solvent composition.

The solvent has a significant effect on the CMC of $C_{14}E_4$, with CMC's in pure EAN being much greater than EtAN or water, c.f. Table 2. High solubility in EAN compared to water has been observed for other surfactants,^{27,35} and can be attributed to EAN's amphiphilic nanostructure; EAN's non-polar domains solubilise the surfactant hydrocarbon tails. Hydrogen bonding between the ethylammonium cation and ethylene oxide units in the surfactant headgroup may also contribute to surfactant solubility,³⁸ but neutron reflectivity³⁶ and scattering,^{32,49} and atomic force microscopy^{50,51} measurements have shown that ethylene oxide monomers are poorly solvated by EAN compared to water, so associations are expected to be weaker. EtAN has smaller apolar domains than EAN and is thus less able to solvate surfactant tailgroups, decreasing surfactant solubility, resulting in CMCs in EtAN that are similar to those in water.

Table 2: Summary of surface tension analysis for C₁₄E₄ adsorbed at the air interface of ionic liquid and water mixtures.

	CMC (wt%)	CMC ($\times 10^{-3}$ mol.dm ⁻³)	γ_{solvent} (mN.m ⁻¹)	γ_{cmc} (mN.m ⁻¹)	Γ_{max} ($\times 10^{-6}$ mol.m ⁻²)	Area per molecule at CMC (Å ²)	$\Delta G^{\circ}_{\text{mic}}$ (kJ.mol ⁻¹)	$\Delta G^{\circ}_{\text{ad}}$ (kJ.mol ⁻¹)
100% EAN	<1 x 10 ⁻¹ (a,b)	-	47.8 ^(c)	-	-	-	-	-
100% EtAN	5.0 x 10 ⁻⁴	1.3 x 10 ⁻⁵	72.1 ± 0.1	30.3 ± 0.3	4.0 ± 0.5	41.3 ± 2.1	-27.5	-37.9
100% H₂O	2.0 x 10 ⁻⁴ (d)	5.1 x 10 ⁻⁶ (d)	72.1 ^(d)	30.0 ^(d)	4.4 ^(d)	37.7 ^(d)	-29.7	-39.3
25wt% EAN/ 75wt% H₂O	7.0 x 10 ⁻⁴	1.8 x 10 ⁻⁵	66.0 ± 0.2	29.8 ± 0.3	4.4 ± 0.3	42.7 ± 1.8	-26.6	-35.9
50wt% EAN/ 50wt% H₂O	2.0 x 10 ⁻³	5.1 x 10 ⁻⁵	58.8 ± 0.2	29.9 ± 0.1	3.9 ± 0.3	42.7 ± 2.3	-24.1	-31.5
75wt% EAN/ 25wt% H₂O	2.0 x 10 ⁻²	5.1 x 10 ⁻⁴	53.0 ± 0.1	30.5 ± 0.2	3.9 ± 0.3	37.9 ± 2.5	-18.5	-23.6
25wt% EtAN/ 75wt% H₂O	5.0 x 10 ⁻⁴	1.3 x 10 ⁻⁵	72.3 ± 0.1	30.5 ± 0.4	3.9 ± 0.5	43.2 ± 1.7	-27.5	-38.3
50wt% EtAN/ 50wt% H₂O	7.0 x 10 ⁻⁴	1.8 x 10 ⁻⁵	72.6 ± 0.4	30.7 ± 0.2	3.9 ± 0.3	42.9 ± 1.8	-26.6	-37.5
75wt% EtAN/ 25wt% H₂O	5.0 x 10 ⁻⁴	1.3 x 10 ⁻⁵	72.1 ± 0.1	29.5 ± 0.5	3.7 ± 0.5	45.1 ± 2.9	-27.5	-39.0
10wt% EAN/ 90wt% EtAN	1.0 x 10 ⁻³	2.6 x 10 ⁻⁵	61.2 ± 0.3	30.5 ± 0.4	4.4 ± 0.5	38.3 ± 3.2	-25.8	-32.9
50wt% EAN/ 50wt% EtAN	2.0 x 10 ⁻²	5.1 x 10 ⁻⁴	51.8 ± 0.1	30.0 ± 0.6	4.5 ± 0.5	37.2 ± 2.6	-18.5	-23.4
75wt% EAN/ 25wt% EtAN	2.0 x 10 ⁻²	5.1 x 10 ⁻⁴	49.3 ± 0.1	30.8 ± 0.2	4.4 ± 0.3	36.9 ± 2.8	-18.5	-22.6

(a) Value taken from³⁶; (b) Value taken from³⁵; (c) Value taken from³⁸; (d) Value taken from⁵²

Changing solvent composition also affects the CMCs, c.f. Figure 1D and Table 2. Small- and wide-angle x-ray scattering⁵³ and small angle neutron diffraction⁵⁴ studies have shown that EAN's non-polar domains remain intact up to quite high water content. Therefore, it could be expected that the EAN/water mixtures would be capable of dissolving high concentrations of surfactant, like pure EAN. However, as water is added the volume fraction of the apolar region is lowered, reducing alkyl chain solubility. Neutron diffraction has also revealed strong hydrogen bonding between EAN and water,⁵⁴ with each water molecule forming, on average, 1.5 hydrogen bonds with EAN in a 50/50 wt% EAN/water mixture. If these inter-solvent hydrogen bonds form in preference to hydrogen bonds between the mixed solvent and the surfactant headgroup, this could further lower surfactant solubility. Both effects favour lower CMCs. Similarly, $\Delta G^{\circ}_{\text{mic}}$ and $\Delta G^{\circ}_{\text{ads}}$ become more negative with increased water concentration, indicating aggregation and adsorption are favoured, in accordance with reduced

surfactant solubility. Surfactant CMCs are highest, and $\Delta G^{\circ}_{\text{mic}}$, and $\Delta G^{\circ}_{\text{ads}}$ values least negative, in the 75wt%EAN/25wt%H₂O mixture. As the volume of the alkyl regions in this mixture is lower than for pure EAN, which will reduce surfactant solubility, incorporation of water into the charged domains must increase surfactant headgroup solubility. These two effects are competing, and as the water content is further increased the reduced hydrophobic volume dominates and CMCs are reduced.

CMCs and $\Delta G^{\circ}_{\text{mic}}$ of C₁₄E₄ in EtAN and water are similar, and do not vary appreciably in EtAN/water mixtures. Likewise, the amount of surface adsorbed surfactant and $\Delta G^{\circ}_{\text{ads}}$ are constant within error. This, too, is consistent with the very weak amount of amphiphilic nanostructure in EtAN compared with EAN.

It is expected that a 1:1 molar ratio of EAN and EtAN will have bulk nanostructure intermediate to the L₃-sponge structure of EAN and the clustered arrangement of EtAN. Therefore, as the concentration of EtAN increases the average size of the non-polar domains decreases, reducing the mixtures' ability to solubilise the surfactant tailgroups, resulting in lower CMCs and more negative $\Delta G^{\circ}_{\text{mic}}$, and $\Delta G^{\circ}_{\text{ads}}$ values. This behaviour is consistent with previous investigations of surfactant aggregation in aprotic ionic liquid mixtures.⁴⁰ The surfactant surface excess in these mixtures is greater than for the other solvents, resulting in lower areas per molecule. This is a surprising result given the high surfactant solubility and CMC values in these mixtures, and is discussed further below.

Neutron Reflectivity Measurements: The neutron reflectivity profiles for tail deuterated C₁₄E₄ (d-C₁₄h-E₄) adsorbed at the H₂O (D₂O) – air interface, EtAN – air interface, and the surface of EAN/H₂O, EtAN/H₂O, and EAN/EtAN mixtures at 20°C are shown in Figure 2. The bulk surfactant concentration in each case is 1.1 – 1.3 x CMC, so monolayer surface coverage is expected. C₁₄E₄ adsorbed at the EAN surface, reported previously,³⁶ is also included in Figure 2 for comparison. The best fits to the experimental data are the solid lines in Figure 2, and the fitted parameters are summarised in Table 3. The surfactant surface excess, Γ , can be determined using:

$$\Gamma = \frac{1}{N_A A}$$

The calculated values are listed in Table 3.

Figure 2: Neutron reflectivity profiles for d-C₁₄h-E₄ adsorbed at the surface of A) $\blacktriangle$ H₂O, $\square$ D₂O, Δ pd-EtAN, and $\circ$ pd-EAN³⁶; B) D₂O/pdEAN mixtures; C) D₂O/pd-EtAN; D) pd-EtAN/pd-EAN. Data sets within each series (except D₂O and H₂O) are incrementally offset vertically by 2 decades for clarity. Solid lines are the fits to the data using the parameters listed in Table 2. All measurements were recorded at 20°C.

For all pure and mixed solvents examined, the thickness of the adsorbed alkyl group layer is constant, within error, at 11.1 ± 1.3 Å. These values are much shorter than the length of a fully extended C₁₄ chain (19.2 Å⁵⁵). The corresponding molecular areas are also all much greater than would be expected for a close-packed vertical monolayer of an all-*trans* tetradecyl chain. However, fitted scattering length densities for the deuterated alkyl chains are consistent with densely-packed layers at over 80% (in most cases >90%) of their liquid density (except in EAN, but see below). This indicates the surfactant chains are either tilted towards the surface, contain gauche defects, or both. Gauche conformers have previously been detected in the hydrocarbon chain of C₁₄E₄ adsorbed at the EAN – air interface using vibrational sum frequency spectroscopy,³⁶ and in the alkyl chains of C₁₂E₃ and C₁₂E₅ adsorbed at the water – air interface using neutron reflectivity⁵⁶ and vibrational sum frequency

spectroscopy,⁵⁷ respectively. Therefore, it can be reasonably expected that gauche defects are present within the C₁₄ chains in these tailgroup layers.

Table 3: Neutron reflectivity data fit parameters for C₁₄E₄ adsorbed at the air interface of ionic liquid and water mixtures at 1.1 – 1.3 x CMC.

	Area per molecule at CMC (Å ²)	$\Gamma_{\max}$ (x10 ⁻⁶ mol.m ⁻²)	C ₁₄ (tail)		E ₄ (headgroup)		
			Layer Thickness (Å)	Scattering Length Density (x 10 ⁻⁶ Å ⁻²)	Layer Thickness (Å)	Scattering Length Density (x 10 ⁻⁶ Å ⁻²)	Solvent Volume %
100% EAN	47.5 ± 1.3 ^(a)	3.5 ± 0.2	12.0 ± 1.0 ^(a)	5.1 ± 0.1 ^(a)	7.4 ± 0.2 ^(a)	1.5 ± 0.1 ^(a)	22.5 ± 3.0
100% EtAN	41.2 ± 1.4	4.0 ± 0.5	11.5 ± 1.0	6.0 ± 0.7	9.0 ± 1.0	1.9 ± 0.3	26.0 ± 6.7
100% H ₂ O	42.0 ± 1.7	4.0 ± 0.3	11.0 ± 1.0	6.1 ± 0.7	10.5 ± 1.0	3.2 ± 0.4	38.6 ± 6.3
25wt% EAN/ 75wt% H ₂ O	43.0 ± 1.0	3.9 ± 0.2	11.0 ± 1.0	6.5 ± 0.5	8.0 ± 1.0	2.5 ± 0.5	30.9 ± 8.8
50wt% EAN/ 50wt% H ₂ O	42.5 ± 1.5	3.9 ± 0.2	11.0 ± 1.0	6.2 ± 0.3	8.0 ± 1.0	1.6 ± 0.4	17.3 ± 8.1
75wt% EAN/ 25wt% H ₂ O	38.2 ± 1.0	4.3 ± 0.5	11.0 ± 1.0	6.5 ± 0.5	8.0 ± 1.0	1.5 ± 0.5	18.1 ± 11.1
25wt% EtAN/ 75wt% H ₂ O	43.8 ± 0.4	3.8 ± 0.2	11.0 ± 1.0	6.0 ± 0.7	8.5 ± 1.5	2.5 ± 0.5	29.1 ± 8.3
50wt% EtAN/ 50wt% H ₂ O	43.0 ± 1.0	3.9 ± 0.2	10.5 ± 1.0	6.4 ± 0.4	8.5 ± 1.5	2.0 ± 0.5	22.4 ± 8.9
75wt% EtAN/ 25wt% H ₂ O	41.5 ± 1.5	4.0 ± 0.3	11.0 ± 1.0	6.3 ± 0.5	9.0 ± 1.0	2.1 ± 0.4	26.8 ± 7.8
10wt% EAN/ 90wt% EtAN	41.6 ± 1.5	4.0 ± 0.3	10.5 ± 0.5	6.5 ± 0.5	9.0 ± 1.0	2.5 ± 0.2	40.5 ± 6.4
50wt% EAN/ 50wt% EtAN	36.5 ± 2.3	4.5 ± 0.5	11.5 ± 0.5	6.5 ± 0.5	8.5 ± 0.5	1.5 ± 0.2	19.5 ± 5.1
75wt% EAN/ 25wt% EtAN	38.5 ± 1.6	4.3 ± 0.5	11.5 ± 1.0	6.5 ± 0.5	8.0 ± 1.0	1.3 ± 0.3	15.3 ± 8.3

The adsorbed surfactant headgroup layer thickness and area per molecule vary in the pure solvents. In EAN, the headgroup layer is 7.4 ± 0.2 Å thick, whereas in water it is 10.5 ± 1.0 Å. Differences between adsorbed surfactant layers at the surface of EAN and water have been discussed previously.³⁶ In water, the headgroup is strongly hydrated, and the ethylene oxide chain extends into the bulk liquid. In EAN, the headgroups are less well solvated and form a more compact layer. In EtAN, the headgroup layer thickness, 9.0 ± 1.0 Å, is similar to water, which suggests the ethylene oxide groups are better solvated than in EAN. Based on

the fitted scattering length density and thickness, the average number of EtAN ion pairs solvating each E₄ chain is 1.1 ± 0.2 , significantly higher than the value of 0.7 ± 0.05 in EAN, suggesting attractive head group – cation interactions are stronger in EtAN. This may be attributed to the cation's additional hydroxyl- hydrogen bonding sites. In water, there are 7.0 ± 1.0 solvent molecules per headgroup,⁵⁸ which would seem to suggested a markedly different structure. However, the solvation *volumes* of EtAN ($1.1 \times 170 = 187 \text{ \AA}^3$) and water ($7.0 \times 30 = 210 \text{ \AA}^3$) are quite similar, and much larger than that of EAN ($0.7 \times 150 = 105 \text{ \AA}^3$), which is consistent with the observed layer thicknesses, and point to structurally similar layers in EtAN and water.

In the binary mixtures, the headgroup layer thickness is consistent, within error, at $8.5 \pm 0.5 \text{ \AA}$. This suggests that the adsorbed layer structure is independent of solvent composition, but the fitted scattering length density shows solvent penetration into the ethylene oxide layer varies (Table 3). In the EtAN/H₂O mixtures, the volume percentage solvent in headgroup layers is similar for all the mixtures, and consistent with the value obtained for pure EtAN but lower than that of pure water. This decrease must be due to incorporation of EtAN into the headgroup layer at the expense of water. The area's per molecule and surfactant surface excess values are consistent across all EtAN/H₂O compositions, and agree with values obtained using surface tension. This, combined similar values for the tail group and headgroup layer thickness and levels solvent penetration, suggests the adsorbed surfactant layer structure is similar in these mixtures. For EAN, addition of 25% and 50% water does not change the level of solvent penetration compared to pure EAN (within error). However, for 75% water the area per molecule is markedly increased, consistent with the ethylammonium cation acting as a co-surfactant. The same results are observed for the addition of EtAN to EAN, consistent with earlier suggestions that ethylammonium is more amphiphilic than ethanolammonium.⁷

The area per surfactant monomer adsorbed at the air interface is higher in EAN than in EtAN, water, or any of the binary solvent mixtures examined. The SLD of this layer is also lower than in any other solvent system, indicating that the chains are packed at only 70% of their liquid density. It is tempting to attribute this to cosurfactant-like behavior by the alkyl chain of the ethylammonium ion penetrating between the surfactant tail layer and pushing the head groups apart. However this would also necessarily occur in EAN/water and EAN/EtAN mixtures, which we do not observe. Rather, we attribute the lower adsorption densities to the high

solubility and correspondingly high CMC of this and other non-ionic surfactants in pure EAN. As noted previously,³² nonionic surfactants are much less amphiphilic in EAN than they are in water.

Conclusions

The adsorption of the non-ionic surfactant C₁₄E₄ in a series of mixed ionic liquid and ionic liquid – water solvents has been investigated using surface tensiometry and neutron reflectivity to elucidate the effect of solvent composition on the morphology of the adsorbed surfactant monolayer and surface properties.

Surface tensiometry showed CMCs are dependent on solvent composition. C₁₄E₄ is solvophobic in water and EtAN and a monolayer is formed at the air – liquid interface at low bulk surfactant concentrations. This is in contrast to EAN, where solvophobicity is weakened due to the large hydrocarbon regions formed by the ethylammonium cation alkyl chains which leads to high surfactant solubility. The CMC decreased with increased water content in EAN/water mixtures, due to a decrease in the volume fraction of the apolar regions that solubilise the surfactant alkyl chains and positive association between the solvent ions or molecules.

Neutron reflectivity revealed that the adsorbed surfactant structure is solvent dependent. The adsorbed surfactant hydrocarbon layer thickness did not change, within error, in all of the solvents examined, indicating that this layer is not affected by the solvent in these mixed systems. The most appreciable changes were the variations in the surfactant ethylene oxide layer thickness. This layer is thin and poorly solvated in pure EAN, but expanded and well solvated in pure water. EtAN is able to solvate the ethoxy units and hence the surfactant headgroup layer is similar to that of water. In EAN binary mixtures, the ethylene oxide layer contains less than 20% solvent in the 75wt% and 50wt% mixtures, resulting in densely packed surfactant layers. These results are attributed to solvent – solvent and solvent – surfactant interactions. In the pure liquid systems, the solvent ion or molecules interact with the surfactant. The headgroup ethoxy units only weakly interact with EAN which results in a thin compact headgroup layer adsorbed at the interface. Conversely, in EtAN and water, the headgroup region is larger.

This work has highlighted that by using ionic liquid mixtures and ionic liquid water solutions in conjunction with surfactants the surface modification can be fine tuned. It has also provided additional information on the interactions within ionic liquids, highlighting their complexity.

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