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Surface Composition of Mixtures of Ethylammonium Nitrate, Ethanolammonium Nitrate and Water

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Abstract

Surface tensiometry of binary mixtures of ethylammonium nitrate (EAN), ethanolammonium nitrate (EtAN), and water reveals distinctive amphiphilic character for the ethylammonium cation, but not for ethanolammonium. Results also show that the surface film incorporates nitrate counterions, and that electrostatic and H–bondng interactions, rather than alkyl chain packing, determines the saturated adsorbed film structure and limiting molecular area.

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Introduction

The interfacial composition of liquid mixtures is elegantly described by the Gibbs isotherm.[1] The dependence of surface tension on composition has been used in this way since 1925 to examine molecular liquid mixtures,[2] electrolyte solutions,[3] and amphiphile adsorbed layers,[4] and has been verified by diverse techniques from microtoming[5] and radiography[6] to neutron reflectometry[7] and mass spectrometry.[8]

Ionic liquids (ILs) consist entirely of ions and have melting points below 100°C. They are excellent solvents for a wide variety of organic and inorganic solutes including water and other ILs.[9] In this paper we focus on protic ILs, synthesised by transfer of a proton from a Brønsted acid to a Brønsted base, which creates hydrogen bond donor and acceptor sites, and an extensive hydrogen bond network.[10] The oldest known and most extensively studied protic IL is ethylammonium nitrate (EAN)[11] whose melting point is 12°C. Its close relative ethanolammonium nitrate (EtAN)[12] is a very long-lived metastable liquid at room temperature, with an equilibrium melting point of 50°C.[13]

Recent scattering experiments[14-18] have shown that EAN and propylammonium nitrate (PAN) are amphiphilic, leading to solvophobic self-assembly into a bicontinuous nanostructure similar to a sponge phase or bicontinuous microemulsion. EtAN has a much less pronounced degree of nanostructure, and seems not to be amphiphilic.

Amphiphilicity goes hand-in-hand with adsorption and molecular orientation at surfaces. We recently showed by x-ray reflectometry (XRR) and vibrational sum frequency spectroscopy (VSFS)[19] that ethylammonium ions at the air-EAN interface are oriented with their alkyl chains directed out of the IL. Beneath the surface layer the IL is organized into an oriented bilayer-like structure that decays to the bulk sponge over several molecular dimensions. XRR and VSFS could not determine whether nitrate was incorporated into the surface layer of ions, or was

present as an anion layer immediately beneath a surface layer that consisted solely of cations. The analysis conducted here resolves this issue.

Alkyl groups also protrude into the air at the surface of aprotic ILs and subsurface layering has also been identified using a range of experimental techniques,[20-22] consistent with results from molecular simulations.[23]

Previous studies of the surfaces of IL-water mixtures are rare, and at least the cations of aprotic ILs are in general larger and more hydrophobic than their protic counterparts. E.g. 1-ethyl-3-methylimidazolium L-lactate.[24] Here we use surface tensiometry together with the Gibbs isotherm to examine the surfaces of binary mixtures of EAN, EtAN and water, each pair of which are mutually miscible at all compositions. Our results show that EAN does indeed behave as an amphiphile in both EtAN and aqueous solutions, whereas EtAN does not.

Materials and Methods

Ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN) were prepared by the slow addition of nitric acid (Merck) to ethylamine or ethanolamine (Aldrich) respectively. Equimolar amounts were mixed in an aqueous solution below 10°C.[25] Excess water was removed by rotary evaporation followed by nitrogen purging and heating at 105-110°C overnight. This led to water contents undetectable by Karl-Fischer titration.[26]

Surface tensions of the pure liquids and their mixtures were determined by the pendant drop method using a Dataphysics OCA20 optical tensiometer. A volume of liquid is suspended from a capillary and an image of the drop is captured by a charge coupled device (CCD) camera. The surface tension is calculated by fitting the Young-Laplace equation to the drop image using SCA20 software. Due to the hygroscopic nature of the ILs, a Petri dish containing the liquid was placed below the capillary to minimize water adsorption by the drop. The instrument was

thoroughly cleaned between samples to prevent contamination and accuracy was checked by measuring the surface tension of MilliQ water. All measurements were performed at room temperature.

Surface excesses were derived from the gradient of surface tension versus ln(composition) using both finite difference and polynomial fits. Errors indicate the range obtained from different fitting approaches.

Results and Discussion

Figure 1 shows surface tension as a function of composition for the water-EtAN, water-EAN and EtAN-EAN binary mixtures at 22°C. The surface tensions of EtAN (72.1 mN m^{-1}) and water (72.3 mN m^{-1}) are very similar, and much higher than that of EAN (48.5 mN m^{-1}). Figure 1 shows that EAN is effective at reducing the surface tension of both water and EtAN, but that the surface tension of EtAN/water mixtures changes very little with composition.

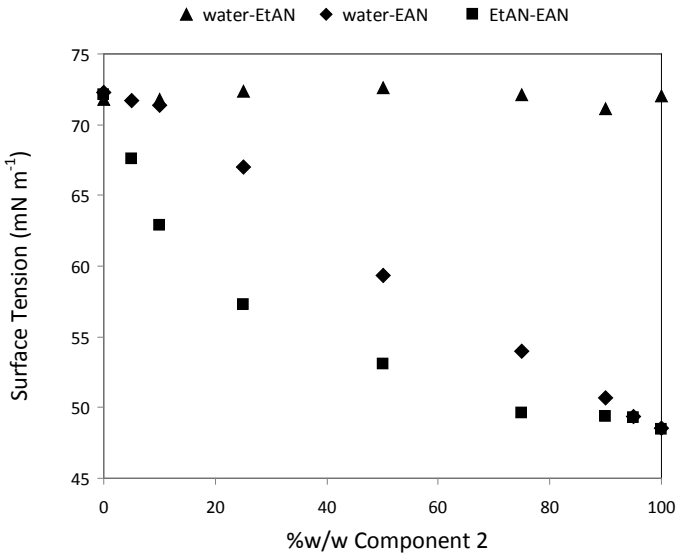

Figure 1. Surface tension as a function of composition for binary mixtures of EAN, EtAN and H_2O.

In molecular liquid mixtures the preferred application of the Gibbs isotherm is to use the partial vapour pressures of the components as the composition variable, as this avoids the effects of non-ideal mixing. This is impractical in IL systems as their vapour pressures are too low, and likely to be complicated by non-idealities like ion-pairing or clustering, even if measurable.[27] We therefore use the liquid compositions to determine the surface excesses.

The surface excess of EA^+ (or EtA^+) relative to H_2O (the Gibbs convention, $\Gamma_{EA^+}^{(H_2O)}$, where $\Gamma_{H_2O}^{(H_2O)} = 0$, and the superscripts are implicit from now on) is governed by the electroneutrality condition of EAN,

$$-d\gamma = \Gamma_{EA^+} RTd \ln x_{EA^+} + \Gamma_{NO_3^-} RTd \ln x_{NO_3^-} = 2RTd \ln x_{EA^+}$$

In EtAN/EAN mixtures, the nitrate content is the same at all compositions, so the surface excess of EA^+ relative to EtA^+ is

$$-d\gamma = \Gamma_{EA^+} RTd \ln x_{EA^+}$$

As the ionic strength in EtAN-EAN mixtures is approximately constant at all compositions, we expect the effects of non-ideal mixing (activity coefficients) to be relatively small. In the EAN-water and EAN-EtAN systems the mole fraction of the ethylammonium cation varies between 0 and 0.5. Plotted in this way, the rate of decrease in surface tension of EtAN with added EAN, and hence the surface excess of EA^+, is a constant 2.55×10^{-6} mole m^{-2}. That is, even at only 5 wt% EAN, the surface of EtAN is already saturated with EA^+, and remains so up to pure EAN; open to question is the role of nitrate in the surface layer.

Our previous studies of the EAN-air interface showed that the ethyl moiety of EA^+ in the interface is oriented towards air at an average angle of only about 10° from the surface normal.[19] If a monolayer consisting only of EA^+ is assumed, this corresponds to a molecular area of 65Å^2 per EA^+, which is much larger than expected for a close-packed monolayer (22 Å^2) in such a high

ionic strength environment (pure EtAN = ~11.7 M). This suggests that nitrate ions are present in the surface layer, and that the saturation surface excess of EA^+ is not determined by ethyl chain packing, but instead by the arrangement of the charged ammonium and nitrate ions, dictated by electrostatic and H-bonding interactions as in bulk;[15,16] There is necessarily an equal surface excess of nitrate ions balancing the charge. This is also broadly consistent with the surface tension of EAN, which is much greater than either ethanol (22 mN m^{-1}) or alkanes which do present a close-packed alkane-like layer at the air interface.

The surface excess isotherms of EAN at the EtAN and water surfaces are shown in Figure 2. The shape of the EAN/water isotherm is very similar to ethanol/water mixtures,[2] but the magnitudes of the surface excess are considerably smaller.

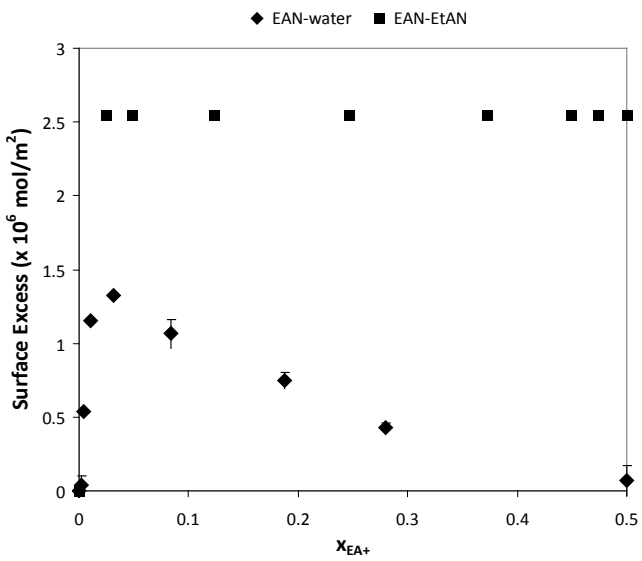

Figure 2. Surface excess of EAN on EtAN and water as a function of composition. Error bars denote range derived from different fits to surface tension data.

The surface excess of EA^+ increases more gradually in water than EtAN, reaching a maximum at 50% w/w EAN (x_{EA+} = 0.031) or approx. 1.7M, where the minimum average area

occupied per EA^+ is 126±4Å^2. At higher EAN content, the surface excess decreases, approaching zero in pure EAN.

As the solution becomes more enriched in EAN, there is less driving force for EA^+ to adsorb and the surface excess diminishes. Schofield and Rideal advanced essentially the same explanation to describe the corresponding ethanol-water isotherm.[2] More recently, the location of the maximum surface excess in alcohol-water mixtures has been correlated with changes in bulk structure.[28] Specifically the excess partial molar volumes of the alcohols were found to be minima at the same compositions as the molecular area, and this was inferred to correspond to a change in the H-bond network, and provides a molecular-level basis for the reduction in driving force. Partial molar volumes of EAN and water in their binary mixtures do not exhibit similar extrema, but do change in a complex way with composition.[29] The partial molar volume of EAN is almost constant above 0.4 mole fraction, decreasing monotonically at higher dilutions, whereas that of water exhibits three distinct regions. It is unsurprising then, given that the bulk structure of EAN is very different from that of water,[15] that the structure of EAN-water mixtures must change markedly with composition, and that this would also affect the surface adsorption behaviour.

In contrast with the strong adsorption of EAN, EtAN-water mixtures show negligible surface excess of either component at their mixed surfaces, further highlighting the amphiphilic character of EA^+.

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