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Surface Structure of a "Non-Amphiphilic" Protic Ionic Liquid

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Dynamic aggregates form at the ethanolammonium nitrate surface to protect the polar regions from the gas phase.

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ABSTRACT

The nanostructure of the ethanolammonium nitrate (EtAN) – air surface has been investigated using x-ray reflectometry (XRR), vibrational sum frequency spectroscopy (VSFS) and neutral impact collision ion scattering spectroscopy (NICISS). The XRR data decays more rapidly than expected for a perfectly sharp interface, indicating a diffuse electron (scattering length) density profile. Modelling of the XRR using three different fitting routines produced consistent interfacial profiles that suggest the formation of interfacial EtAN clusters. Consistent with this, VSFS reveals that the EtAN surface is predominantly covered by $-CH_2$ - moieties, with the $-NH_3^+$ and -OH groups of the cation buried slightly deeper in the interface. The elemental profiles determined using NICISS also show enrichment of carbon relative to nitrogen and oxygen in the outermost surface layer, which is consistent with the surface cation orientation deduced from VSFS, and with the presence of EtAN aggregates at the liquid surface.

INTRODUCTION

Ionic liquids are attracting attention for a variety of applications including electrochemical processes,¹⁻³ catalytic reactions,⁴ chemical synthesis,⁴⁻⁵ particle stabilization,⁶⁻⁸ solid - liquid⁹⁻¹² and liquid - air¹³⁻¹⁴ interfacial phenomena, as solvents for surfactant self-assembly,¹⁵⁻²⁰ proteins,²¹⁻²³ and polymers,²⁴⁻²⁷ and for gas transfer and storage.²⁸⁻³² Many of these processes concern, or even depend upon, reactions occurring at interfaces and hence many studies have focused on elucidating structure at the ionic liquid – solid, – liquid, and – gas interface. However, the majority of work has investigated the influence of variation in cation alkyl chain, and/or type of anion, and less attention has been focused on hydroxyl functionalised ionic liquids. This is surprising given their potential use in CO₂ capture³³⁻³⁴ due to their ability to solubilise large volumes of CO₂, and their low volatility compared to more traditional aqueous

alkanolamines. Knowledge of interfacial structure is pivotal in applications such as gas absorption: ionic arrangement within the surface region facilitates the adsorption and transport of gas molecules from the atmosphere into the bulk liquid. In this paper we investigate the surface morphology of such a protic ionic liquid, ethanolammonium nitrate (EtAN).

The effect of variation in cation and anion species on the morphology of the interfacial layer, particularly for imidazolium ionic liquids, has been extensively studied using vibrational sum frequency spectroscopy (VSFS),³⁵⁻⁴⁰ neutron,⁴¹⁻⁴² and x-ray reflectometry (XRR),^{38, 40, 43-47} x-ray photoelectron spectroscopy,⁴⁸⁻⁵⁰ and metastable atom electron spectroscopy. In general, both the cation and anion reside at the surface. If either species incorporates an alkyl chain it will orient towards the gas phase, and if either ion has two alkyl groups, the longer chain will protrude into the air. As the alkyl chain length increases (usually above C = 8, although this depends on anion size) chain aggregation occurs, and a complete hydrocarbon monolayer can form, covering the cation and anion polar moieties.

X-ray reflectometry investigations of ethylammonium nitrate (EAN) and other similar protic ionic liquids have revealed surface-induced layering of the ions at the liquid – air interface.⁴⁶ The depth to which the layering persists into the bulk liquid depends on the hydrogen bonding capacity and amphiphilicity of the ions. Increasing the alkyl chain length from two (EAN) to three carbons (propylammonium nitrate, PAN) led to stronger segregation and orientation of the polar and non-polar regions. Conversely, when the hydrogen bonding capacity was reduced by changing the anion from nitrate (EAN) to formate (ethylammonium formate, EAF), the interfacial layering did not extend as far into the bulk liquid.

There have been few studies on the interfacial region of ionic liquids with functionalized alkyl groups.⁵⁰⁻⁵² A recent molecular dynamics simulation⁵¹ investigating four imidazolium ionic liquids: a short (C_2) cation alkyl chain liquid, a long (C_8) cation alkyl chain liquid, and their

respective alkanol analogues, has shown that the presence of the OH moiety altered the surface structure. The alcohol group is repelled from the hydrophobic gas phase, so the alkyl chains orient along the surface rather than forming an upright layer analogous to a surfactant monolayer. This reduces the templating (ordering) effect of the interface which, combined with the reduced solvophobic interactions between alkyl chains, lowers the depth to which interfacial ordering extends into the bulk liquid. XPS⁵⁰ has shown that although hydroxyl functionalized alkyl chains are less attracted to the gas phase than non-functionalized ones, they still form a (thinner) layer above the imidazolium rings. Similar results have been obtained for oligo(ethylenegycol) functionalized cations.⁵²

The liquid – air surface of hydroxyl functionalized protic ionic liquids has not previously been investigated, but should share some features of the solid – liquid interface. Atomic force microscopy force profiles⁵³ of EtAN at a mica surface revealed layers 0.5 nm apart, consistent with the molecular dimensions of EtAN. Fewer layers were observed in the EtAN force profile than EAN, implying that addition of an alcohol moiety reduces the amphiphilicity of the cation and extent of structuring.

The morphology at ionic liquid interfaces is strongly correlated to the bulk liquid structure. Many ionic liquids exhibit nanostructure in the bulk,⁵⁴⁻⁶⁰ mediated by electrostatic forces between charged regions and amphiphilic self assembly of the alkyl chains. Neutron diffraction studies of the bulk structure of EAN and EtAN⁵⁹ have shown that both are structurally heterogeneous liquids, having consistent spacing between like ions of 10.1 Å and 8.2 Å, respectively. EAN forms a well-defined structure segregated into polar and non-polar regions arranged in a bicontinuous sponge-like morphology. The anions interact solely with the amino cation groups via electrostatics and hydrogen bonding, while the alkyl chains assemble through solvophobic interactions. However, the presence of the OH moiety in EtAN disrupts the

solvophobic attraction between the hydrocarbon chains, and the anion is now able to associate with both the cation headgroup and hydroxyl unit. This results in small ionic clusters within EtAN as opposed to the organised long range order of EAN. Similarly, x-ray scattering measurements⁵⁸ on bulk EAN and EtAN reveal that the inclusion of a hydroxyl group leads to a less structured liquid.

In this work we use x-ray reflectometry, vibrational sum frequency spectroscopy, and neutral impact collision ion scattering spectroscopy in combination to develop a detailed picture of the ionic arrangements at the EtAN – air interface. This is compared to other protic ionic liquids recently investigated.

EXPERIMENTAL SECTION

Materials: Ethanolammonium nitrate was prepared by the dropwise addition of a 70% nitric acid aqueous solution (Aldrich) to ethanolamine (Aldrich, purity greater than 99.5%). The solution was vigorously stirred and kept below 10°C. Excess water, which is expected to be the only significant 'impurity', was removed by rotary evaporation at 35°C followed by nitrogen purging and heating at 110°C for at least 12 hours. This led to a final water content of 0.06wt% as determined by Karl Fischer titration, and analysis using nuclear magnetic resonance spectroscopy revealed no other species. We therefore conclude that the IL purity was greater than 99.9%. The mass density of EtAN was determined using an *Anton Paar DMA5000* densitometer to be 1.38 g cm⁻³.

X-ray Reflectometry: X-ray reflectometry experiments were conducted the Australian Nuclear Science and Technology Organisation (ANSTO) Sydney, Australia, using a Panalytical X'Pert Pro reflectometer (Cu-K α X-rays, wavelength = 1.541 Å). The EtAN sample was placed in a Teflon trough inside an airtight sample cell. The chamber was continuously purged with a

flow of dry nitrogen. The specularly reflected monochromatic X-rays from the ionic liquid surface were measured as a function of incident angle, θ (θ range = 0.025 - 4°, 0.02° step size). Longitudinal off-specular scans were collected and subtracted from the specular reflectivity data to remove any contribution from the bulk liquid structure to the reflectivity profiles. Measurements were conducted at 26°C.

Vibrational Sum Frequency Spectroscopy: The VSFS spectrometer is a ND:YAG laser system (Eskpla PL2143A/20) which pumps an optical parametric generator/optical parametric amplifier (OPG/OPA, LaserVision, USA) to produce the fixed visible beam (wavelength = 532nm) and the tuneable infrared beam. The optics are enclosed in a perspex chamber which is constantly purged with dry nitrogen and are arranged in a copropagating geometry, overlapping the incident beams on the EtAN liquid surface, which is contained in a sealed glass/Teflon with calcium fluoride windows. The generated sum frequency is passed through a monochromator then detected by a photomultiplier tube. Finally, the signal is processed by an integrated boxcar and a Labview computer program. Spectra were recorded at 23°C. A more complete description of the setup is given in Tyrode *et al.*⁶¹

Neutral Impact Collision Ion Scattering Spectroscopy: The details of the NICISS apparatus are described in detail elsewhere.⁶² For the NICISS measurements shown here, helium ions with energy of 3 keV were used as projectiles. A liquid film is generated by immersing a rotating, flat metal disc into a reservoir containing the target liquid following the design described in reference.⁶² Due to the method of preparing the liquid surface the dose of the He ions for this investigation was kept at a few 10¹⁰ ions/cm². As a surface typically comprises ~10¹⁴ molecules/cm², damage of the surface and the influence of the impinging ions on the surface structure can be neglected.

BACKGROUND THEORY

X-ray Reflectometry: A beam of x-rays is directed at the samples surface and the specularly reflected x-ray intensity is measured as a function of momentum transfer, Q_z :

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

where λ is the beam wavelength and θ the angle of incidence. Once the critical angle is exceeded the reflected intensity decreases rapidly as Q_z^{-4} for an infinitely sharp interface, known as a Fresnel surface. Any deviations from an infinitely sharp interface, such as roughness caused by capillary waves, or adsorption of material from the bulk, etc, affect the reflectivity. The measured reflectivity is a function of the scattering length density profile, and provides structural details perpendicular to the interface. The scattering length density, ρ , of a given species depends on its electron density and is given by:

$$\rho = \frac{\sum_{i} z_i r_e}{V_m}$$

where z_i is the atomic number of an element *i*, V_m is the molecular volume (0.16 nm³), and r_e is the Compton radius (2.817 × 10⁻¹⁵ m). The X-ray scattering length density (SLD) for EtAN is $1.25 \times 10^{-5} \text{ Å}^{-2}$.

Vibrational Sum Frequency Spectroscopy: VSFS is a second-order nonlinear optical technique capable of providing molecular information at interfaces. In this method, two laser beams, a fixed visible beam and a tuneable infra red beam, are overlapped on the samples surface which generates a third beam carrying interface information. The intensity of the generated beam is proportional to the incident lasers intensities (I_{VIS} and I_{IR}) and the square of the second-order nonlinear susceptibility, $\chi_{eff}^{(2)}$, as follows:

$$I_{SFG} \propto \left| \chi_{eff}^{(2)} \right|^2 I_{VIS} I_{IR}$$

 $\chi_{eff}^{(2)}$ is a third rank tensor with 27 elements, which can be determined by using different light polarisation combinations. In this work we use SSP, SPS, and PPP combinations, where P denotes light polarisation in the plane of incidence and S perpendicular to the plane of incidence, of the sum frequency, visible, and infra red beams, respectively.

Neutral Impact Collision Ion Scattering Spectroscopy: NICISS is used to obtain the elemental concentration depth profiles at surfaces up to a depth of about 20 nm and a resolution of a few Ångströms in the near-surface region.⁶² The target is bombarded with a pulsed beam of helium ions with a kinetic energy of several keV.⁶³ The energy of the ions backscattered from atoms in the target is determined by their time-of-flight from the target to the detector. The projectiles lose energy by two mechanisms: The first is the energy loss during backscattering and depends on the mass of the target atom. This energy loss is used to identify the element from which a projectile is backscattered. The second is a continuous energy loss on the trajectory through the bulk due to small angle scattering and electronic excitations of the molecules in the target, known as stopping power.⁶⁴ The second energy loss is proportional to the length of the trajectory of the projectile in the sample and is used to determine the depth of the atom from which a projectile is backscattered. In combination, these two energy loss mechanisms enable determination of the concentration depth profiles of numerous individual elements.

The absolute concentration of an element or another species is determined by combining the known bulk concentrations and the known cross sections for backscattering.

This method is not sensitive to the chemical environment of the backscattering element so NICISS cannot be used to determine bonding. Further, it is important to note that NICISS is not able to detect capillary waves when the ion beam incidence is close to surface normal. This is due to the nature of the method where the localized interaction of the projectiles with the constituents of the target results in the depth information.

The overall shape of the NICISS spectra is determined by the concentration depth profiles and the finite energy resolution of the method. The energy loss straggling (due to small angle scattering and electronic excitations), the distribution of inelastic energy losses during a backscattering event, the energy resolution, and the instrumental time to generate the pulsed ion beam determine the overall resolution in a NICISS spectrum.

A low-density gas jet of small molecules including the desired element(s) is generated at the same position in the NICISS apparatus as the solid sample in order to calibrate the zero of the depth scale.⁶⁵ Here nitrogen, oxygen, and diiodomethane were used. These spectra also allow determination of the energy distribution during backscattering and the time and energy resolution of the instrument. The spectrum of such a gas jet consists almost entirely of projectiles backscattered from individual atoms with no contribution from other energy-loss processes such as the stopping power in a bulk sample. Therefore the measured spectrum of a gas jet consists of a series of peaks due to each element present, each with a full-width-half-maximum (FWHM) due to the distribution of inelastic energy losses in the collision process. The energy loss straggling has been determined experimentally from the energy loss of helium projectiles passing through the gas phase. The distribution of inelastic energy losses during backscattering, and the energy loss straggling, limit the depth resolution and the depth range.⁶⁶ NICISS can resolve features in elemental profiles close to the surface of about 2 Å, even though the FWHM is significantly broader than this.

RESULTS AND DISCUSSION

X-ray Reflectometry: The x-ray reflectivity profile for the EtAN-gas interface is presented in Figure 1a. The data does not follow the $R \sim Q^{-4}$ Fresnel decay of a perfectly sharp surface; It decays faster, indicating a diffuse, rough or structured interface. Three different fitting procedures were used to model the reflectivity data using the *Motofit* reflectivity analysis package.⁶⁷ All three methods produce an electron density or scattering length density (SLD) profile, from which a reflectivity curve is calculated. This is compared to the experimentally acquired data, and model parameters are adjusted until good agreement is obtained. All three fitting procedures contained the following four parameters as a minimum: instrumental scale factor (used to scale the reflectivity below the critical edge to one), SLD of the bulk liquid and gas phases (latter set to 0), and the sample background.



Figure 1: A) X-ray reflectivity profile (displayed as R/R_F vs Q_z) for the EtAN - air interface. The solid line represents the modeled x-ray reflectivity fit using the slab routine. B) The SLD profile for the EtAN - air interface from the slab fit (dotted line), Chebyshev fit (dashed line), and slice fit (solid line) models.

The fitting routines have been described in detail previously,⁴⁶ hence are only briefly recapitulated here. The first is a slab fit method, which models the interface with a series of layers limited by known molecular dimensions. Each layer has a uniform SLD, and roughness is included between adjacent slabs. The model that required the least number of physically

reasonable layers was used as the final fit. The fit obtained using this method is shown as a solid line in Figure 1a, and the corresponding SLD profile is shown in Figure 1b.

The second method is a free-form model using first order Chebyshev polynomials which impose no constraints on the shape of the SLD profile. A number of Chebyshev nodes (which are not linearly spaced) are specified in the interfacial region, creating a polynomial describing the SLD profile. The polynomial is then sliced into subsections of uniform SLD, which is used to calculate to the theoretical reflectivity curve. Roughness is not included in this fitting procedure. The SLD profile is shown in Figure 1b and the fit to the experimental reflectivity data is shown in supporting information.

The final "slices" method combines features of the two previous procedures. In this approach the interface is divided into discrete slices, each 1 Å thick. Roughness is not included between layers. The number of slices is reduced to the minimum which still gives a physically reasonable model, and SLD values are constrained by known values. The SLD profiles for this fitting procedure are shown in Figure 1b, and the data fit is shown in the supporting information.

There is good correlation between the SLD profiles for the three fitting methods, giving confidence in the robustness of our fitting procedure and conclusions. The slab profile shows the SLD gradually increases with depth into the liquid, reaching a maximum value of $12.6 \times 10^{-6} \text{ Å}^{-2}$ at 12 Å. The SLD then decreases slightly to $12.2 \times 10^{-6} \text{ Å}^{-2}$ before climbing back to the bulk value of $12.5 \times 10^{-6} \text{ Å}^{-2}$ at a depth of 23 Å. The Chebyshev model differs slightly, in that its first SLD maximum has a lower value of $12.1 \times 10^{-6} \text{ Å}^{-2}$, which is lower than the bulk value. However, it does reach this first peak at a similar distance of 11 Å into the liquid. The Chebyshev model then follows a similar trend to the slab model, with the SLD decreasing slightly before gradually increasing to the bulk liquid value. Likewise, the slices model has a

gradual increase in SLD with liquid depth, reaching a maximum SLD at 11 Å. As for the other two models, the SLD decreases slightly, before rising to the bulk liquid value at 21 Å.

The variation in SLD after the peak at 11 Å is minimal, ranging only \pm 0.3 x 10⁻⁶ Å ⁻² from the bulk value. This differs significantly from previously studied protic ionic liquids, in particular ethylammonium nitrate (EAN) and propylammonium nitrate (PAN), which exhibit multiple, pronounced oscillations about their bulk SLD values at the interface.⁴⁶ In these liquids, the undulating SLD arises from the alignment of the existing bulk nanostructure by the macroscopic interface, generating alternating layers of lower and higher electron density. However, EtAN does not have the same degree of bulk structure. Solvophobic aggregation of the alkyl chains, which is enhanced by Coulumbic interactions in EAN and PAN, are disrupted in EtAN by the presence of the hydroxyl moiety on the ethyl chain. The OH group enables the nitrate anion to associate with either the ammonium headgroup or the hydroxyl unit, reducing its amphiphilicty, and the liquid no longer segregates into polar and non-polar regions.

These interfacial SLD profiles are consistent with XPS experiments on imidazolium based ionic liquids with oligo(ethyleneglycol) functionalities in the cation which suggested the ionic composition near the surface mirrored that of the bulk liquid.⁵² Additionally, molecular dynamics simulations of alcohol functionalised imidazolium ionic liquids have shown that the inclusion of a terminal hydroxyl moiety in the cation alkyl chain inhibited multiple interfacial layers from forming.⁵¹

The three SLD profiles all indicate that EtAN has a diffuse interface, with an average density that grows from zero (gas) to its bulk liquid over a distance of 10 Å. This distance corresponds to two EtAN ion pairs, and is too large to be attributed to capillary wave roughness only, calculated to be 4.1 Å (see Supporting Information). Recently we investigated the surface structure of three protic ionic liquids, EAN, PAN, and EAF, and observed the same kind of

diffuse interface, but superimposed over a multilayered subphase structure.⁴⁶ We concluded that those protic ionic liquid surfaces were dotted with small (dynamic) clusters of cations and anions, in which the short alkyl moieties surrounded the charged core, segregating the charged centres from the non-polar gas phase.

We propose therefore that a similar phenomenon occurs at the EtAN surface. The EtAN SLD profile shows an oscillatory waveform superimposed on the curve in the z = 0 - 10 Å range, similar to those of the alkylammonium protic ionic liquids, and indicates the positions of high and low electron density within the surface aggregates.

Vibrational Sum Frequency Spectroscopy: The SSP and PPP VSFS spectra for the EtAN – gas interface are presented in Figure 2. The SPS polarisation spectra are not shown as there were no well-defined features detected (see Supporting Information). The data were fitted with a series of Lorentzian profiles described by:

$$I(\omega_{SF}) = \left| A_{NR} + \sum_{v} \frac{A_{v}}{\omega_{v} - \omega_{IR} - i\Gamma_{v}} \right|^{2}$$

where $I(\omega_{SF})$ is the intensity of the collected SF beam, A_{NR} is the non-resonant contribution to the SF signal, A_{ν} denotes the amplitude of the *v*th vibrational mode, ω_{ν} and ω_{IR} refer to the frequency of the *v*th vibrational mode and incoming IR beam respectively, and Γ_{ν} is the damping constant.

The data are best fitted using four peaks in the CH region at 2855, 2883, 2925, and 2970 cm⁻¹, shown as solid lines in Figure 2a. EtAN has two CH₂ groups which exist in chemically slightly different environments, N-CH₂-C and C-CH₂-O. The presence of the oxygen atom causes the C-H vibrational mode frequencies to shift by a few cm⁻¹ and results in a splitting of the spectral peaks.⁶⁸ Therefore, the symmetric stretching of the CH₂ adjacent to the NH₃ is assigned to the peak at 2855 cm⁻¹ and its Fermi resonance at 2925cm⁻¹.⁶⁹ The peak at 2883 cm⁻¹ is the symmetric stretching of the CH₂ adjacent to the OH and the 2970 cm⁻¹ peak is its Fermi

resonance.⁶⁹ The intensity for all four peaks is greatest in the SSP polarisation indicating highly ordered structures at the interfaces with an average orientation approaching the surface normal. It also suggests that the two CH₂ are not in a trans configuration which would tend to cause cancellation of the $\chi_{eff}^{(2)}$ terms and thus no VSFS signal. In order to absolutely pin down down the *direction (ie* pointing into or away from the bulk phase) of vibrational modes, phase measurements are usually required,⁷⁰ however the lack polarity of the hydrocarbon is generally considered sufficient to assign the preferrential ordering to the gaseous side of the interface.

The intensity of the sum frequency signal depends upon a combination of both the surface density of the molecules, and their average orientation. This suggests that the two CH_2 's have a somewhat different orientation (both tilt and twist) relative to the surface since their intensities are different in both SSP and PPP polarizations. No well defined feature is detected in the SPS polarization over the entire spectral range (spectra not shown) suggesting that all the peaks observed in the other polarizations have a symmetric character.



Figure 2: VSFS spectra for the SSP and PPP polarisations of the EtAN – air interface in the A) CH, NH, and OH region, and B) the NO, CO region. Solid lines show the fits to the data

The broad band at $3100 - 3200 \text{ cm}^{-1}$ in Figure 2a is attributed to the symmetric stretching of the NH₃ vibration.⁷¹ It is present in both the SSP and PPP polarisation combinations, which will allow a detailed orientation analysis to be completed (see next section).

There are no features in the spectra which can be attributed to the cation's OH moiety (Figure 2a). OH vibrational modes occur in two wavenumber regions: $3600 - 3800 \text{ cm}^{-1}$ for free OH groups, and $3200 - 3500 \text{ cm}^{-1}$ for hydrogen bonded OH's.⁷²⁻⁷⁴ The absence of the OH signal can be due to one of two reasons. Firstly a completely random orientation of the OH bond directions. This is clearly not possible since the observation of signal from the other moieties necessarily implies a well defined average orientation of the molecule as a whole. The explanation is therefore constrained to the fact that the OH group has its axis in, or close to, the plane of the surface, since that is the only other condition which could lead to lack of signal. Thus there are no free OH groups projecting out of the EtAN surface.

The nitrate ion has a planar centro-symmetrical structure and the absence of a steep dielectric constant gradient, which makes it impossible to resolve using VSFS. Figure 2b shows the SSP and PPP VSFS spectra for the EtAN – gas interface in the NO region. There are no distinguishable features in either spectrum. The small slope in the in the SSP spectrum is most probably a contribution of the non-resonant background. Therefore, the orientation or position of the nitrate anion could not be determined.

Orientational Analysis: The average orientation of a specific group or bond can be determined from VSFS spectra under different polarisation combinations. Orientational analysis is a well established methodology and the theoretical approach and fitting routines are extensively documented.^{68, 75-78} Spectral peak intensity ratios of different polarisation modes are simulated as functions of tilt angle, θ (θ is the angle between the principal axis of the NH₃ and the surface normal), and twist angle, φ . The theoretical curves are then compared to the

experimentally obtained intensity ratios. To do this it is necessary to have information about the molecular hyperpolarizability tensor elements of the molecules. The VSFS beam intensity is proportional to the square of the effective second order nonlinear susceptibility, $\chi_{eff}^{(2)}$, which in turn depends on the Fresnel factors, the configuration of the three beams, the number of molecules present at the surface and the orientationally averaged molecular hyperpolarizability, β . The nonlinear susceptibility $\chi_{eff}^{(2)}$ is a 27 element tensor, however if the interface is isotropic in the plane of the surface this reduces the tensor to the following four nonvanishing components: $\chi_{yyz} = \chi_{xxz}$, $\chi_{yzy} = \chi_{xxx}$, $\chi_{zyy} = \chi_{zxx}$, and χ_{zzz} , where z is normal to the interface and x,y is the surface plane in the laboratory coordinate system. The laboratory coordinate system of the nonlinear susceptibility $\chi_{xyz}^{(2)}$ can be related to the molecular coordinate system (*abc*) of the molecular hyperpolarizability, β_{abc} using the Euler rotation transformation matrix.

The NH₃ group has C_{3v} symmetry,⁷¹ and the molecular coordinate system is assigned accordingly, as shown in Figure 3. This allows the theoretical curves which model the change in sum frequency signal as a function of tilt angle, θ , to be simulated, shown in Figure 4a. The theoretical curve shows the SSP polarisation intensity is always stronger than the SPS and PPP polarisations. Generally in VSFS, the SSP polarisation probes projections of the vibrational mode dipole moment in the direction normal to the interface, while SPS polarisation probes projections along the plane of the surface with an asymmetric character. The PPP polarisation is more complex, as it contains more hyperpolarizability terms. Despite the fact that there are a number of assumptions in this model some general conclusion can be extracted from these calculations. Therefore the strong SSP signal in the VSFS spectrum indicates that the principal NH₃ axis does not lie within the surface plane. Furthermore, the PPP polarisation signal is only present for tilt angles between 0 - 45°. As the VSFS spectrum has a NH₃ vibrational mode signal in the PPP polarisation, it can be concluded that the NH₃ principal axis must be within this angle range.



Figure 3: Molecular model for a C_{3v} symmetry NH₃ moiety. The molecular coordinates axes (*a*, *b*, *c*) and surface coordinates axes (*x*, *y*, *z*) are shown for reference. The *c* axis is along the C₂ principal axis of symmetry

The NH₃ group is free to rotate about its C₃ axis, and therefore a twist angle, φ , integrated over this angle within the theoretical model and orientation is only described by the tilt angle, θ . The relationship between the ratio of the effective nolinear susceptibility $\chi_{ssp}^{eff} / \chi_{ppp}^{eff}$ and the tilt angle, θ , is shown in Figure 4b. This model uses a depolarisation angle for the symmetric stretch NH₃ of ammonia of 0.03°,⁷⁹ which gives a hyperpolarizability ratio ($\beta aac/\beta ccc=\beta bbc/\beta ccc$) of 0.5. The experimentally determined ratio for the NH₃ symmetric stretch vibrational modes in the SSP and PPP spectra is added to the theoretical curve (shown as a solid line in Figure 4b), and shows the NH₃ principal axis has a tilt angle, θ , of approximately 25° to the surface normal. If the experimental error in the PPP spectrum was considered, the ratio would double and the tilt

angle would increase to approximately 40° for a delta distribution which assumes all the NH₃ moieties face the same direction.



Figure 4: A) Theoretical curve for the sum frequency intensity of the NH₃ symmetrical stretching vibrational mode in the SSP, SPS, and PPP polarisation combinations, and B) Theoretical curve for $\chi_{ssp}^{eff} / \chi_{ppp}^{eff}$ as a function of tilt angle, θ , for the NH₃ symmetric stretching vibrational mode

The same theoretical model was used to analyse the two methylene group orientations. The CH₂ vibration has C_{2v} symmetry,⁶⁸⁻⁶⁹ shown in Figure 5a, and therefore the nonlinear susceptibility theoretical equation is dependent on a twist angle, φ , as well as the tilt angle, θ . The CH₂ group is not able to freely rotate about its principal axis and hence the twist angle must become one of the variables. The theoretical changes in the sum frequency signal as a function of tilt angle, θ , for SSP, PPP, and SPS polarisations of a methylene group with twist angles, φ , of 1°, 40°, and 90° is shown Figure 5b. The curves show that for twist angles, φ , less than 40°, the tilt angle, θ , is closer to the surface normal for weaker SSP polarisation signals, and for twist angles, φ , greater than 40°, the tilt angle, θ , is closer to the surface normal for the surface normal for stronger SSP polarisation signals. The methylene adjacent to the NH₃ (2855 cm⁻¹) can only have a small twist angle, φ , in the range of 0 - 30°. This is due to the small tilt angle, θ , of the NH₃ principal axis, which imposes geometrical limitations on the twist angle, φ , of the symmetric stretching of the CH₂ moiety. Coupled with the facts that the two methylenes have a *cis* conformation and that the hydroxyl resides in the surface plane, this constrains the methylene adjacent to the hydroxyl to small twist angles. This means that the tilt angle of the CH_2 adjacent to the NH_3 (2855 cm⁻¹) is closer to the normal at the interface than the CH_2 next to oxygen (2883 cm⁻¹).



Figure 5: A) Molecular model for a C_{2v} symmetry methylene moiety. The molecular coordinates axes (*a*, *b*, *c*) and surface coordinates axes (*x*, *y*, *z*) are shown for reference. The *c* axis is along the C_2 principal axis of symmetry, and B) Theoretical curve for the change in sum frequency signal as a function of tilt angle, θ , with a twist angle, φ , of 1°, 40° , and 90°

The VSFS data suggests that the EtAN surface, is predominately covered by CH_2 groups, with the CH vibrations mostly aligned with the surface normal. The NH₃ group and OH moiety of the cation are positioned slightly below the methylene groups. The NH₃ principal axis is angled 25 - 40° from the surface normal, and the OH vibration sits within the surface plane (Figure 6). The position of the OH group is consistent with the aggregates implied by the x-ray reflectivity; the polar NH₃ and hydroxyl groups are protected from the hydrophobic gas environment by the methylene units.



Figure 6: Orientation of EtAN at the gas – liquid interface inferred from VSFS. See text for details.

Neutral Impact Collision Ion Scattering Spectroscopy: The concentration depth profiles of oxygen, nitrogen and carbon measured with NICISS are shown in Figure 7, each normalised by their bulk concentration. Thus a concentration of unity means is equal to the bulk concentration.

The nitrogen and oxygen profiles are virtually identical, however the carbon profile shows enrichment in the outermost layer. Note that the apparent diffuseness of the interface is the NICISS energy-resolution limit (*vide supra*). NICISS is sensitive to interfacial structure on the scale of individual collisions. These results are thus consistent with VSFS showing that the outermost layer of the EtAN surface is enriched in methylenes compared to $-NH_3^+$, -OH, and NO_3^- . It is also consistent with the VSFS results and the interpretation of the XRR profiles which requires that the ionic clusters have methylene groups oriented outwards towards the gas phase.



Figure 7: Concentration depth profiles of the elements oxygen, nitrogen and carbon measured with NICISS.

CONCLUSION

The free liquid surface of EtAN has been investigated using three complementary surface sensitive techniques, permitting a detailed description of the interfacial nanostructure to be made with confidence. The structure of the EtAN surface is similar in some respects to those of EAN, PAN and EAF, but also shows some important differences.⁴⁶

The XRR spectra for the EtAN – air surface decays too rapidly for a sharp interface, even after accounting for capillary-wave roughness. The simplest model (determined independently using three different routines) of the interface that fits the XRR results reveals that the electron density increases from 0 to the bulk value over a distance of ~11Å, a distance equal to approximately twice the EtAN ion pair dimension. The SLD profile in this increasing region, indicates that the ions are in a structured arrangement, consistent with the presence of (dynamic) interfacial EtAN aggregates, like those determined for EAN, PAN and EAF previously.⁴⁶

NICISS reveals that the outermost region of the surface is enriched in carbon, consistent with an excess of $-CH_2$ - groups at the interface compared to $-NH_3^+$, -OH and NO_3^- . Consistent with this, VSFS shows a surface excess of methylenes with their vibrations oriented almost normal to the surface. Thus the polar moieties $-NH_3^+$ and -OH are internalised to form, along

with NO₃⁻, the interior of the surface aggregate, which is coated by $-CH_2$ - moieties in contact with the gas phase. In EtAN the surface orientation of the hydrocarbon groups is quite different from EAN, where the $-CH_2CH_3$ groups protrude into the gas phase.⁴⁰ This difference in orientation is a consequence of the inclusion of the alcohol group.

For EAN, PAN and EAF, the surface aggregates form on top of a layered subphase,⁴⁶ which forms due to the macroscopic interface aligning the pre-existing bulk phase nanostructure. In EtAN, no subsurface layering is detected, which is consistent with results showing limited structure in the bulk liquid,⁵⁹ and few layers at the solid-liquid surfaces⁵³; EtAN's alcohol group disrupts solvophobic interactions between cation alkyl groups, resulting in much less pronounced nanostructure. Thus, these results at the air-liquid interface are consistent with ethanolammonium being a less amphiphilic cation than ethylammonium.

This study is a clear illustration of how the designer properties of ionic liquids can be exploited to control interfacial nanostructure. If a (relatively) unstructured interface is desired, the key is to incorporate polar functional groups into the alkyl chain to disrupt solvophobic interactions (achieved in this case via the inclusion of an alcohol group). This prevents the formation of a layered subsurface, which should facilitate more rapid adsorption and transport of species from the gas phase through the interfacial region into the bulk, desirable for applications such as carbon dioxide capture. To produce an even less structured surface, where the interfacial diffuseness can be described using roughness alone, requires further modification of the cation and the anion to prevent surface aggregate formation. This is the goal of subsequent work.

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SUPPORTING INFORMATION



Figure 1: X-ray reflectivity profile (displayed as R/R_F vs Q_z) for the EtAN - air interface. The solid line represents the modeled x-ray reflectivity fit using the Chebyshev routine.



Figure 2: X-ray reflectivity profile (displayed as R/R_F vs Q_z) for the EtAN - air interface. The solid line represents the modeled x-ray reflectivity fit using the slices routine.



Figure 3: VSFS spectra for the SSP, PPP, and SPS polarisations of the EtAN – air interface in the CH, NH, and OH region.

Equation 1: Capillary wave roughness of a liquid surface

$$\sigma^2 = \frac{k_B T}{2\pi\gamma} \ln\!\left(\frac{q_{\rm max}}{q_{\rm min}}\right)$$

where k_B is Boltzmann's constant, T is the temperature, γ is the surface tension of the liquid, q_{max}

= $(2\pi/D)$ and D is molecular diameter (0.54nm), and $q_{\min} = (2\pi/\lambda)\Delta\beta\sin\theta$ and $\Delta\beta$ is the

angular acceptance of the detector.