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Structure of the Ethylammonium Nitrate Surface: An X-ray Reflectivity and Vibrational Sum Frequency Spectroscopy Study

Petru Niga¹, Deborah Wakeham², Andrew Nelson³, Gregory G. Warr⁴, Mark Rutland¹, Rob Atkin^{2*}

¹ Department of Chemistry, Surface and Corrosion Science, Royal Institute of Technology, Drottning Kristinas Väg 51, SE-100 44 Stockholm, Sweden

² Centre for Organic Electronics, The University of Newcastle, Callaghan, NSW 2308, Australia

³ Bragg Institute, Australian Nuclear Science and Technology Organisation, PMB 1, Menai NSW

2234, Australia

⁴ School of Chemistry, The University of Sydney, NSW, 2006, Australia

Abstract

X-ray reflectivity and vibrational sum frequency spectroscopy are used to probe the structure of the ethylammonium nitrate (EAN) – air interface. X-ray reflectivity reveals that the EAN – air interface is structured, and consists of alternating non-polar and charged layers that extend 31 Å into the bulk. Vibrational sum frequency spectroscopy reveals interfacial cations have their ethyl moieties oriented towards air, with the CH₃ C3 axis positioned approximately 36.5° from interface normal. This structure is invariant between $15 - 51^{\circ}$ C. On account of its molecular symmetry the orientation of the nitrate anion cannot be determined with certainty.

^{*} Author for correspondence. E-mail: rob.atkin@newcastle.edu.au

1. Introduction

Ionic liquids (ILs) consist entirely of ions and have melting points below 100°C. They are green solvents on account of their (often) low volatility,¹ and usually have excellent conductivity,² wide electrochemical windows,³ high thermal stability,³ large liquidous ranges,⁴ and the ability to dissolve a wide variety of organic and inorganic materials.² ILs are also referred to as "designer solvents" as their physical properties can be controlled through careful selection of the constituent ions.⁵⁻⁷ These properties have seen ILs attract increasing research interest for applications including electrolytes in batteries⁵ and solar cells,⁸ as surface coatings and lubricants,⁹ as media for catalytic reactions,^{10,11} as solvents for chemical synthesis,^{1,11,12} and in separation technologies.¹³ However, for ILs to achieve their considerable potential, it is necessary to better understand the interfacial organization of ions and how this affects surface properties. In this paper we investigate the surface of ethylammonium nitrate (EAN). EAN is a protic IL, synthesised by transfer of a proton from a Brønsted acid to a Brønsted base. This creates hydrogen bond donor and acceptor sites, leading to the formation of an extensive hydrogen bond network in EAN and many of its protic analogues.^{4,14}

Recent scattering experiments¹⁵⁻¹⁷ have shown that ILs are often nanostructured, which is the key to understanding how cation and anion structure influences conductivity, viscosity and solvation of dissolved molecules: changing structure of the cation or anion alters the liquid nanostructure, which in turn changes bulk properties. Small angle neutron scattering (SANS) has shown that even short chain protic ILs have ionic and non-ionic domains.¹⁷ Both EAN and propylammonium nitrate (PAN), exhibit a single broad SANS peak whose position depends on the size of the cation, corresponding to distances of 9.7 Å and 11.6 Å, respectively. These distances are consistent with the increase in molecular volume that occurs on changing from a C_2 to C_3 cation. In these protic ILs nanostructure results from electrostatic interactions and H- bonding between the ammonium cation and nitrate anion favouring the creation of ionic domains. This produces a solvophobic force¹⁸ that induces alkyl group clustering into apolar domains. The scattering peak is more intense for PAN than EAN, which suggests liquid order is more pronounced in PAN, on account of the longer alkyl group producing stronger solvophobic interactions. SANS was consistent with a locally lamellar structure of alternating polar-apolar layers. Both the peak width and data fit imply these layers were quite disordered, suggesting a sponge-like structure for the liquid.

While the molecular organisation of the protic IL - air interface has not previously been investigated, the surface structure of aprotic ILs (formed by other means than proton transfer, and generally lacking an extended hydrogen bond network^{3,11}) has been studied using a range of techniques including x-ray reflectivity,^{19,20} neutron reflectivity,²¹ and vibrational sum frequency spectroscopy (VSFS).^{20,22-26} Broadly, the reflectivity experiments provide dimensional information about the interfacial ionic structure, while VSFS elucidates spatial ordering.

Neutron reflectivity experiments using 1-butyl-3-methylimidazolium tetrafluoroborate revealed interfacial structure extending approximately 40 Å into the liquid.²¹ Cation alkyl tailgroups and charged regions are segregated into a layered structure near the surface (alkyl chains form the uppermost layer) that persists for at least two tiers of ion pairs broadly consistent with, but more ordered than, the bulk IL.¹⁵ Two separate x-ray reflectivity studies have shown similar interfacial structures for the same IL. Jeon *et al.* reported two interfacial layers, each 4 -5 Å thick, in which the upper layer consisted of cation alkyl chains orientated towards the gas phase and the underlying layer was composed of both imidazolium rings and anions.²⁰ The fitted electron density of the upper layer was very low, as this layer was substantially penetrated by air. An earlier x-ray reflectivity study by Sloutskin *et al.* yielded the same structure, but in this case the data was fit without including any contribution from the alkyl chain layer.¹⁹

Molecular simulations also suggest surface layering of aprotic ILs. Classical molecular dynamics simulations of 1-butyl-3-methylimidazolium tetrafluoroborate using a modified version of the DL POLY program,²⁷ in which the intermolecular potentials include Lennard-Jones site potentials and electrostatic interactions between partial charges on each ion, displayed oscillations in atomic density normal to the interface, and the interface was concluded to be highly structured. The imidazolium rings were aligned just under the liquid surface interspersed with anions. Cation butyl chains were orientated towards the gas phase, while methyl groups pointed towards the bulk. A separate empirical potential molecular dynamics simulation²⁸ of 1butyl-3-methylimidazolium hexafluorophosphate found oscillations in the number density of cations and anions, the electron density, and the mass density in the vicinity of the surface. The cation and anion electron density peaks were out of phase, reducing the oscillation amplitude, which may explain the absence of significant oscillations in x-ray reflectivity data for this IL.¹⁹ Investigation of 1,3-dimethylimidazolium based ILs with various anions using polarizable potential models²⁹ also showed oscillatory interfacial density profiles. Analysis of the radial distribution functions showed the local molecular environment was influenced by the proximity of the surface.

VSFS studies have confirmed that the aprotic IL – air interfacial region consists of both cations and anions, with alkyl chains orientated into the gas phase. The VSFS spectrum of 1,3-dimethylimidazolium methylsulfate revealed C-H vibrational mode peaks from the N-CH₃ of the cation and the O-CH₃ of the anion, indicating both ions are positioned at the interface with their methyl groups facing away from the bulk liquid.^{24,26} A surface tension study of the same IL reported a decrease in surface tension from 65.1 mN.m⁻¹ to 41.8 mN.m⁻¹ as the anion alkyl chain length was systematically increased from one carbon to four.²⁶ Similarly, surface tension

decreased from 65.1mN.m⁻¹ to 44.1 mN.m⁻¹ when the cation alkyl chain length was increased from one carbon to four, confirming both ions are present in the interfacial layer.

VSFS has shown that interfacial cation orientation depends on the length and symmetry of the cationic alkyl chains. VSFS spectra for 1,3-dimethylimidazolium methylsulfate revealed C-H vibrational mode peaks attributed to N-CH₃ vibrations in the normal direction, which were absent in the 1-ethyl-3-methyl imidazolium methylsulfate and 1-butyl-3-methyl imidazolium methylsulfate spectra.²⁴ The presence of the N-CH₃ spectral feature for 1,3-dimethylimidazolium methylsulfate indicates the imidazolium ring is not parallel to the surface, whereas for the two longer alkyl chains, the N-CH₃ peak absence implies the ring is orientates within the interfacial plane. The same imidazolium ring orientation has been observed for 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium bromide.³⁰

Here we investigate the ionic arrangement of EAN at the air interface using x-ray reflectivity and vibrational sum frequency spectroscopy. The effect of temperature on the interfacial ionic orientation is also examined.

2. Materials and Methods

Ethylammonium nitrate (EAN) was prepared by the slow addition of nitric acid (Merck) to ethylamine (Aldrich). Equimolar amounts were mixed in an aqueous solution below 10°C.³¹ Excess water was removed by rotary evaporation followed by nitrogen purging and heating at 105-110°C overnight.³² This led to water contents undetectable by Karl-Fischer titration.

X-ray reflectivity measurements were conducted at the Australian Nuclear Science and Technology Organization (ANSTO), Sydney, Australia. A Panalytical X'Pert Pro Reflectometer operating with Cu K_{α} radiation ($\lambda = 1.541$ Å) was used. Reflectivity was measured over the 2 θ range 0.04 to 7.0° with a step size of 0.02. Each step was measured for 20 seconds. All measurements were performed in an enclosed sample cell, in a Teflon trough, under a nitrogen atmosphere.

The VSFS Spectrometer has been described previously³³ and will only be briefly outlined here. The system is composed of a Nd:YAG laser (1064 nm, 20 Hz, and 24 ps) from Ekspla which pumps a LaserVision Optical Parametric Generator/Optical Parametric Amplifier to produce the visible beam with a fixed wavelength of 532 nm and the tunable infrared beam in the range 1000 – 3400 cm⁻¹. The infrared and visible beams are overlapped in space and time over the sample surface in a co-propagating geometry. The generated sum frequency beam passes through a monochromator and is detected with a photomultipier tube. The signal is processed by a computer using a LabVIEW program. EAN was placed in a sealed glass/Teflon cell which is temperature controlled. A continuous flow of nitrogen was purged through the cell.

3. Background Theory and Data Analysis

X-ray reflectivity

In specular reflectivity techniques a beam of x-rays is directed at the interface at an incident angle, θ . The reflected beam intensity, *R*, is measured as a function of the change in momentum transfer, *Q*, normal to the surface. *Q* is defined as

$$Q = \frac{4\pi \sin\theta}{\lambda} \tag{1}$$

where λ is the wavelength of the beam. The reflected intensity is a function of the scattering length density profile perpendicular to the interface. The scattering length density, ρ , of a given species depends on its electron density, and is given by

$$\rho = \frac{\sum_{i} z_{i} r_{e}}{V_{m}} \tag{2}$$

where z_i is the atomic number of an element *i*, V_m is the molecular volume and r_e is the Compton radius. The x-ray scattering length densities for the species examined in this work are given in Table 1.

	$ ho_{x-ray}(x10^{-6} \text{\AA}^{-2})$	Volume (Å ³)	Length (Å)
CH ₃ CH ₂ NH ₃ NO ₃	11.0	150 ^a	5.3°
CH ₂ CH ₃	6.0	80^{b}	2.53 ^c
$NH_3 + NO_3$	16.8	69 ^a	2.8 ^c

Table1: Calculated X-ray scattering length densities (ρ), and molecular dimensions of EAN and the ionic and nonionic molecules of EAN.

a Calculated from the liquid density; b from ref³⁴; c calculated by taking the cube root of the molecular volume³⁵

The x-ray reflectivity data was modeled using the MOTOFIT³⁶ reflectivity analysis package, using the Abeles matrix method. Each model contains the following four variables as a minimum: instrumental scale factor, scattering length densities of the solvent and gas phase, and the sample background. The scattering length density profile of the interface is treated as a series of slabs, each of uniform scattering length density. During the fitting process the thickness and scattering length density of each slab is varied within physically reasonable ranges. In addition, a roughness may be associated with each interface between adjacent slabs.

Vibrational Sum Frequency Spectroscopy

The theory regarding the VSFS technique is described in detail elsewhere.³⁷⁻³⁹ Briefly, this is a second order non linear optical technique capable of providing information about the molecules present at an interface. It involves two laser beams, a fixed visible beam and a tunable infrared beam, which are overlapped in space and time on the sample surface. A third beam is

generated due to nonlinear effects, which carries information about the interfacial molecules. The intensity of this laser beam is proportional to the intensities of the incoming beams I_{IR} and I_{Vis} and the square of the nonlinear susceptibility $\chi^{(2)}$ as follows:

$$I_{SFG} \propto \left| \chi_{eff}^{(2)} \right|^2 I_{IR} I_{Vis}$$
(3)

The elements of the nonlinear susceptibility $\chi^{(2)}$ tensor can be probed by employing several polarization combinations of the three laser beams used in the experiment. In this study we have used SSP, SPS and PPP polarizations combinations, where P refers to light polarization parallel to the plane of incidence and S refers to light polarized perpendicular to the plane of incidence, of the sum frequency, visible and infrared beams respectively. Moreover, by taking the ratio of certain elements of the tensor the orientation of a specific group can be determined, discussed in the orientation analysis section.

The features of the collected spectra were fitted with a Lorentzian profile described by the following equation using an IgorTM program:

$$I(\omega_{SF}) = \left| A_{NR} + \sum_{\nu} \frac{A_{\nu}}{\omega_{\nu} - \omega_{IR} - i\Gamma_{\nu}} \right|^2$$
(4)

where $I(\omega_{SF})$ is the intensity of the collected SF beam, A_{NR} refers to the nonresonant contribution to the SF signal, A_v is the amplitude of the v^{th} vibrational mode, ω_v is the wavelength of the v^{th} vibrational mode, ω_{IR} is the frequency of the IR beam, and Γ_n is the damping constant.

4. Results and Discussion

X-Ray Reflectivity of the Pure EAN – Air Interface.

The x-ray reflectivity profile of the pure EAN – air interface is presented in Figure 1. Once the critical angle is exceeded the reflected intensity decreases with increasing Q, but does not follow

the monotonic (R ~ Q^{-4}) behavior expected for an infinitely sharp Fresnel interface. The reflectivity signal decays at a faster rate, indicating that the surface is somewhat diffuse, and the bulk scattering length density is not reached until some distance from the Gibbs dividing plane. The interference fringe at Q = 0.13 - 0.33 Å⁻¹ can be used to estimate the depth to which the interfacial structure differs from that of the bulk liquid, τ , using $\tau = 2\pi/\Delta Q$. This suggests interfacial order extends ~31 Å into the bulk. This is much too large to be correlated with a single layer of EAN ion pairs, 5.3 Å (Table 1^{*}); interfacial ordering extends into the liquid for a distance corresponding to approximately six EAN ion pairs before decaying into the sponge-like bulk structure.¹⁷



Figure 1: X-ray reflectivity profile for the EAN – air interface at room temperature. The solid line is the fit to the data obtained using the parameters listed in Table 2. The inset shows the scattering length density profile.

It is therefore unsurprising that the x-ray reflectivity curve for the EAN-air interface could not be modeled as a single layer, so the number of layers was increased. In the fitting process,

^{*} This ion pair dimension is calculated by taking the cube root of the molecular volume, 150 Å³, determined from the liquid density, and makes the simplistic assumption of a cubic packing geometry.³⁵ However, this approach has proven to be an effective predictor of ion pair layer thicknesses at solid-liquid interfaces^{32,40} and in the bulk.¹⁷

the scattering length densities of each layer was bounded by those of the ethyl and ionic groups that make up EAN (see Table 1), except for the first layer which was allowed to contain air. The simplest model that adequately described the data with physically reasonable parameters consisted of five alternating layers of non-polar and charged regions (Table 2). The layer closest to the air (Layer 1) is 2.9 Å thick, with a scattering length density lower than any of the EAN components (2.1 x 10^{-6} Å⁻²), corresponding to ethyl moieties substantially penetrated by air. Layers 2 and 4 are both 4.5 Å thick and have much higher scattering length densities (8.7 x 10^{-6} and 9.8 x 10^{-6} Å⁻² respectively), which indicates an excess of electron rich material, i.e. the polar ammonium and nitrate groups. Between the two electron rich regions lies 6.6 Å thick layer 3, with a scattering length density of 6.8 x 10^{-6} Å⁻², again indicating ethyl groups. This value is slightly higher than the calculated scattering length density for ethyl moieties (Table 1), suggesting the presence of some polar groups within this region. This is to be expected as the interface between layers is not perfectly sharp. The layer adjacent to the bulk is 10.2 Å thick which is consistent with two unresolved layers of EAN ion pairs. The scattering length density of 8.9 x 10^{-6} Å⁻² is lower than EAN, which suggests there is a slight excess of ethyl chains contributing to this region. The roughness of the layers varies between 1.6 and 3.3 Å. For liquid interfaces, roughness is the combination of thermally excited capillary waves and the static distribution of ions.⁴¹ It provides an indication to the amount of penetration of one layer into the next. The roughness values obtained for the model in this work are well within the range commonly reported for liquid-air interfaces.²⁰ The consequent x-ray scattering length density profile, showing the extent of layering is shown as an inset in Figure 1

This behaviour is consistent with previously reported fits to $x-ray^{20}$ and neutron reflectivity²¹ data for aprotic ILs, which have also suggested segregation of interfacial alkyl chains and charged groups. Here also, the interfacial layers decay into its bulk sponge

morphology¹⁷ as distance from the surface increases The ethylammonium cations (EA⁺) in direct contact with the gas phase experience different forces to those in the bulk, in that they are thermodynamically driven to minimize surface free energy, so orientate with alkyl chains towards the gas phase in a surfactant-like fashion. Our VSFS studies, described in the next section, confirm the orientation of EA⁺ in the surface layer. The macroscopically planar liquid – air interface and the cations' preferred orientation propagates regular, near-surface layering in which decays into the bulk.

Layer Number	Composition	Thickness (Å)	SLD (x10 ⁻⁶ Å ⁻²)	Roughness (Å)
1	CH ₂ CH ₃	2.9	2.1	1.6
2	$NH_3 + NO_3$	4.5	8.7	2.0
3	CH ₂ CH ₃	6.6	6.8	3.3
4	$NH_3 + NO_3$	4.5	9.8	1.9
5	CH ₂ CH ₃	10.2	8.9	2

Table 2: Best-fit parameters to x-ray reflectivity results for the pure EAN - air interface.

This amphiphilic model of EAN consisting of polar (ionic) and nonpolar regions rather than as discrete cations and anions, is similar in spirit to our previous SANS fitting of the bulk liquid.¹⁷ The fitted layer thicknesses are consistent with both the SANS results and the molecular dimensions of EAN. In this model, half of the thickness of the polar layer 2 or 4 (4.5 Å) and half the thickness of nonpolar layer 3 (6.6 Å) corresponds to an EAN ion pair. This calculation gives an ion pair dimension of 5.5 Å for EAN, in excellent agreement with calculated molecular size. The same periodic layering has also been observed at solid – liquid interfaces and in bulk. AFM force profiles of EAN at a mica surface^{32,40} revealed a series of steps 5 Å apart corresponding to layers of EAN, and SANS studies¹⁷ found a Bragg spacing of 9.7 Å, consistent with two EAN ion pairs in a locally lamellar structure. Both SANS and the present reflectivity results clearly show supramolecular organization in bulk EAN and at macroscopic interfaces, and that the layering observed by AFM is not a phenomenon induced by confinement between the AFM tip and substrate.

These results are also strikingly similar to surface-induced sponge-to-lamellar transitions that occur in lyotropic systems.⁴²⁻⁴⁵ Here also a macroscopically planar solid or liquid interface induces layering which decays into a structured but isotropic bulk phase on the length scale of a few layers.

Vibrational Sum Frequency Spectroscopy

EAN – air interface VSFS spectra recorded under different polarizations (SSP, PPP and SPS) are presented in Figure 2a. Spectral features are well defined and strong, which confirms EAN is ordered at the interface. X–ray reflectivity measurements revealed the topmost ethyl layer is substantially penetrated by air thus quite different to the subsurface region. It therefore is expected that the VSFS signal is generated from this noncentrosymmetric surface monolayer. All spectra were fitted using Equation 3, assuming four resonance modes at 2890, 2945, 2989 and 3114 cm⁻¹ which are assigned to symmetric CH mode of the CH₃ group (Figure 2b), a Fermi Resonance of the symmetric CH mode of the CH₃ group with the overtone of the methyl bending mode, antisymmetric CH₃ stretch (Figure 2b), and symmetric NH₃ stretch respectively.⁴⁶⁻⁴⁹ The peak positions and fitted widths for each feature were kept constant for all spectra during fitting.



Figure 2: a) SSP, PPP and SPS polarization spectra of the EAN – air interface in CH OH region. The spectra were normalized to the most intense feature present in the recorded set of measurements. b) Molecular models showing the symmetric and asymmetric vibrational modes for CH₃.

The structural orientation of interfacial ions can be elucidated by monitoring the appearance and relative intensities of vibrational modes under different polarization combinations.^{37,50,51} The SSP polarization combination probes only vibrational modes with dipole moments aligned normal to the interface, while the SPS polarization probes vibrational modes with dipole moments aligned *parallel* to the interface. The PPP polarization spectrum is more complex, containing more than one nonlinear susceptibility term $\chi^{(2)}$.³³ Thus, as clearly seen in Figure 2a, different polarizations can result in strikingly different spectra for the same interface.

The SSP spectrum of the EAN – air interface (Figure 2a) exhibits peaks assigned to the symmetric CH₃, the Fermi resonance of the symmetric CH₃, the asymmetric CH₃ and the asymmetric NH₃ vibrational modes. Consequently all recorded vibrations have a finite dipole moment projection aligned normal to the interface. The symmetric CH₂ (2855 cm⁻¹) is practically

absent from the SSP spectrum which suggests the projection of the dipole moment normal to the interface is very small and predominately lies along the interfacial plane.

The SPS spectrum, which probes the projection of the dipole moments in the plane of the surface, has a well defined asymmetric CH_3 peak at 2985 cm⁻¹, while the symmetric CH_3 and its Fermi Resonance are absent. The asymmetric CH_3 peak protrudes from a relatively small, broad band spanning 2800 – 3200 cm⁻¹. This overlaps the symmetric CH_2 , symmetric CH_3 and symmetric NH_3 region, thus it is difficult to distinguish the presence or absence of the symmetric CH_2 , symmetric CH_3 and symmetric NH_3 along the interface.

The PPP spectrum shows two clearly resolved vibrational modes: the Fermi resonance of the symmetric CH_3 and antisymmetric CH_3 at 2945 and 2989 cm⁻¹ respectively. This indicates these vibrational modes dipole projections lie at an angle between the normal and the plane of the interface.

All three spectra are dominated by CH₃ peaks. This suggests a prevalence of interfacial alkyl chains, as the sum frequency signal strength depends on the number of species present at the interface. This indicates the ethyl moiety is orientated towards the gas phase, confirming the interfacial structure deduced from x-ray reflectivity. The most striking difference between the SSP, PPP and SPS polarizations is the absent symmetric CH₃ band from the PPP and SPS spectra. This implies that the symmetric CH₃ vibration has a large dipole moment projection toward the interface normal, and hence the ethyl moieties are oriented in an upright position. This will be discussed in more depth in the orientation analysis section.

The position and orientation of the nitrate anion cannot be assigned using VSFS. Figure 3 shows featureless SSP, PPP and SPS spectra in the NO region (the broad feature in the SSP polarization at approximately 1100 cm⁻¹ most probably arises from the nonresonant background). The absence of NO vibrations is due to the planar symmetrical structure of nitrate, with no

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permanent dipole moment. If the nitrate ion was located in the surface layer with significant polarization (due, for example, to a steep gradient in dielectric constant) a VSFS signal would be produced, but clearly this is not the case. Thus, the orientation of the nitrate anion within the interfacial layer can not be resolved.



Figure 3: SSP, PPP and SPS polarization spectra of the EAN – air interface in NO region. The spectra were normalized to the most intense feature present in the recorded set of measurements.

Orientation analysis

The VSFS spectra at different polarization combinations allow the average orientation of a specific group or bond to be determined. Sharp, strong peaks are used as the molecular species and symmetry contributing to broad peaks cannot be well defined. The interfacial EAN methyl group is a suitable bond for calculation of an absolute orientation, θ , with respect to the surface normal as the antisymmetric CH₃ mode is present, and well defined, in both SSP and SPS polarization combinations (Figure 2a). Orientational analysis of VSFS spectra is a well established methodology and the theoretical approach and fitting routines are extensively documented elsewhere^{38,52-54}.

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: $\chi_{yyz} = \chi_{xxz}$, $\chi_{yzy} = \chi_{xzx}$, $\chi_{zyy} = \chi_{zxx}$, and χ_{zzz} , where z is normal to the interface and x,y is the surface plane in the laboratory coordinate system. The CH₃ group is assumed to be of C_{3v} symmetry⁵⁵ (Figure 4) and thus 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. For the asymmetric CH₃ stretching mode we obtain:⁵⁶

$$\chi_{yyz, as} = \chi_{xxz, as} = (-1/2) N_s \beta_{caa} (\langle \cos\theta \rangle - \langle \cos^3\theta \rangle)$$
(5a)

$$\chi_{yzy, as} = \chi_{zzx, as} = \chi_{zyy, as} = \chi_{zxx, as} = (1/2) N_s \beta_{caa} < \cos^3 \theta >$$
(5b)

where N_s is the surface density of the chemical group of interest and the operator $\langle \rangle$ denotes the assembly average over different molecular orientations.



Figure 4: Molecular model of tilt angle and the CH₃ C₃ axis

Orientation can be determined by comparing the ratio of elements of the nonlinear susceptibility $\chi_{eff}^{(2)}$ tensor (from the different VSFS polarizations) with theoretical estimates obtained for different molecular orientations. For the EAN antisymmetric CH₃ group this is the ratio $|\chi_{yyz,as}^{eff}|$ to $|\chi_{yyz,as}^{eff}|$, and the terms are defined by equations 5a and 5b respectively. This ratio results in the molecular hyperpolarizability β_{caa} terms cancelling, leaving a geometric term. To allow the ratio of the *measured intensities* to be related to this term, the *field correction factor* (which depends on the Fresnel factors and the angle of the beams), is accounted for. Thus, for fixed beam angles, uncertainty only arises from the interfacial refractive indices. The interfacial refractive indices are poorly defined and intermediate between bulk EAN and air, and this constitutes a source of ambiguity when defining the theoretical models. Here we have used the following refractive indices: $n_1(\omega_{SF}) = n_1(\omega_{Vis}) = n_1(\omega_{IR}) = 1$ for air; $n_2(\omega_{SF}) = n_2(\omega_{Vis}) = n_2(\omega_{IR})$

The relationship between the EAN antisymmetric CH₃ $|\chi_{yyc,as}^{eff}|$ to $|\chi_{yy,as}^{eff}|$ ratio and the orientation angle, θ is shown in Figure 5a, assuming all CH₃ groups have exactly the same orientation. The solid curve is the field correction factor average value for the theoretical intensity ratio and the dashed curves correspond to the same distribution using the minimum and maximum field correction factors. Independently varying the infrared and visible interfacial refractive indices between minimum and maximum values provides the range of possible field correction factors. The ratio of the experimentally determined amplitudes for the asymmetric CH₃ for the SSP to SPS polarizations is 0.61, corresponding to $\theta = 40^{\circ}$. From Figure 5a the uncertainty arising from the interfacial refractive indices is $\pm 6^{\circ}$, which indicates the uncertainty in the orientation angle introduced by the inaccuracy of the infrared and visible interfacial refractive indices is not significantly large.



Figure 5: Simulated curves for the relationship between the $|\chi_{yyz}^{eff}|_{,as}| : |\chi_{yzy}^{eff}|_{,as}|$ ratio and the orientation angle for a) δ distribution and, b)more realistic Gaussian distribution. The propagated error in the experimentally determined ratio is 0.13 and is shown as an error bar.

A more realistic model employs a Gaussian distribution of orientation angles, given by:

$$\langle f(\theta) \rangle = \frac{1}{\sigma\sqrt{2\pi}} \int_0^{\pi} f(\theta) \exp\left(-\frac{(\theta - \theta_0)^2}{2\sigma^2}\right) \sin\theta d\theta$$
 (6)

where θ_0 is the mean orientation angle, and $f(\theta)$ refers to the function $(\cos\theta \text{ or } \cos^2\theta)$ which is used in equations 5a and 5b. Figure 5b shows the $|\chi_{yyz,as}^{eff}|$ to $|\chi_{yzy,as}^{eff}|$ ratio as a function of orientation angle assuming a Gaussian distribution using the mean field correction factor. The solid curve corresponds to the theoretical simulated intensity ratio for a single orientation, while the dashed curves correspond to Gaussian distribution functions with different standard deviations, σ . The experimental values are shown with solid straight lines. The ratio of the absolute value of the CH₃ asymmetric fitted amplitude for the SSP to SPS polarizations for the EAN – air interface is 0.61, therefore when considering the Gaussian distribution, the spread in the orientation angle spans from $\theta = 32.5^{\circ}$, corresponding to a deviation of $\sigma = 40^{\circ}$, to $\theta = 40.7^{\circ}$, corresponding to a deviation of $\sigma = 10^{\circ}$.

Thus, the average orientation of the CH₃ group is between $\theta = 32.5^{\circ}$ and $\theta = 40.7^{\circ}$ suggesting the ethylammonium cation adopts an upright configuration at the EAN – air interface. However, there is a propagation error (0.13) associated with the experimentally determined intensity ratio (indicated by the error bar near the y-axis in Figure 5b) which increases the uncertainty in the orientational angle. Thus, the variation interval of the C3 axis of the CH₃ group would span from $\theta = 26.8^{\circ}$, corresponding to a deviation of $\sigma = 30^{\circ}$, to $\theta = 54.1^{\circ}$, corresponding to a deviation of $\sigma = 50^{\circ}$.

Temperature dependence

Previous AFM studies investigating the EAN structure at a mica surface have revealed interfacial order decreases with increasing temperature due to increased thermal motion of the ions.⁴⁰ Temperature dependent VSFS measurements of the EAN surface were completed to

determine whether corresponding effects can be detected at the liquid-air interface, and are shown in Figure 6. SSP polarization spectra were recorded at 51°C, 23°C and 15°C. The features in the SSP spectra were consistent over the entire temperature interval, suggesting no structural or orientational change.



Figure 6: VSFS spectra of the EAN – air interface taken under SSP polarization conditions at 15, 23, and 51°C.

4. Conclusions

X-ray reflectivity shows that the EAN – air interface is highly structured, consisting of an oriented amphiphilic monolayer of ethylammonium cations with their ethyl moieties facing the gas phase. Below this the liquid contains alternating layers of non-polar and charged regions with dimensions in good agreement with an EAN ion pair. Ordering gradually decays over 31 Å (6 EAN ion pairs) into the sponge like structure of the bulk liquid, similar to results obtained at the solid liquid interface. Using Vibrational Sum Frequency Spectroscopy reveals features characteristic of interfacial EAN. The VSFS spectra are dominated by strong, sharp CH₃ vibrational peaks, indicating the ethylammonium cation is oriented with the alkyl chains towards the gas phase, confirming the x-ray reflectivity model. Orientational analysis shows that the

ethylammonium cation sits at the surface in an upright conformation with the C_3 axis of the CH₃ at an angle of approximately 36.5°. VSFS shows that the orientation of surface cations is invariant between 15°C - 51°C.

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TOC Graphic



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