Structure in Ionic Liquids

A Dissertation in Chemistry

By

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Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

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DECLARATIONS

Statement of Originality

I hereby certify that this Thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying subject to the provisions of the Copyright Act 1968.

Acknowledgement of Collaboration

I hereby certify that the work embodied in this Thesis has been done in collaboration with other researchers. I have included as part of the thesis a statement clearly outlining the extent of collaboration, with whom and under what auspices.

Thesis by Publication

I hereby certify that this Thesis is submitted in the form of a series of published papers of which I am a joint author. I have included as part of the thesis a written statement from each co-author; and endorsed by the Faculty Assistant Dean (Research Training), attesting to my contribution to the joint publications.

Robert Hayes

STATEMENT OF CONTRIBUTION

The following co-authors have provided statements attesting to my contribution to the publications included as part of the Thesis:

A/Prof Rob Atkin Professor Greg Warr Dr Silvia Imberti **Professor Frank Endres** Dr Natalia Borisenko Dr Grant Webber Professor Mark Rutland **Professor Roland Bennwitz** A/Prof Sherif El Abedin Dr Patrick Howlett Dr Deborah Wakeham Dr Florian Hausen Dr Luiz Gasparotto Dr Benedikt Huber Dr Marcel Drüchler Mr James Sweeney Mr Brendan Corr Mr Matt Tam

LIST OF SCIENTIFIC PUBLICATIONS

Seventeen publications were produced during my PhD candidature and are listed below.

- <u>**R. Hayes**</u>, G.G. Warr, R. Atkin
 "At the interface: solvation and designing ionic liquids" *Physical Chemistry Chemical Physics*, **2010**, 12, 1709
- <u>R. Hayes</u>, D. Wakeham, R. Atkin
 "Ionic Liquid Interfacial Structure (2)" in *Ionic Liquids UnCOILed: Critical Expert Overviews*; John Wiley & Sons, (2012)
- <u>**R. Hayes**</u>, S. Imberti, G.G. Warr, R. Atkin
 "Amphiphilicity determines nanostructure in protic ionic liquids" *Physical Chemistry Chemical Physics*, **2011**, 13, 3237 (* *journal cover*)
- <u>**R. Hayes**</u>, S. Imberti, G.G. Warr, R. Atkin
 "Pronounced Sponge-like Nanostructure in Propylammonium Nitrate" *Physical Chemistry Chemical Physics*, **2011**, 13, 13544
- <u>R. Hayes</u>, S. Imberti, G.G. Warr, R. Atkin "How water dissolves in Protic Ionic Liquids" *Angewandte Chemie International Edition*, 2012, 51 (30), 7468
- 6. <u>R. Hayes</u>, S. Imberti, G.G. Warr, R. Atkin
 "The Nature of Hydrogen Bonding in Protic Ionic Liquids" *Angewandte Chemie International Edition*, 2013, 52 (17), 4623-4627
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 "Effect of cation alkyl chain and anion type on protic ionic liquid nanostructure" To be submitted to *Physical Chemistry Chemical Physics*, 2013
- <u>R. Hayes</u>, N. Borisenko, M.K. Tam, P. C. Howlett, F. Endres, R. Atkin "Double Layer Structure of Ionic Liquids at the Au(111) Electrode Interface: An Atomic Force Microscopy Investigation" *Journal of Physical Chemistry C*, 2011, 115, 6855-6863
- <u>**R. Hayes**</u>, N. Borisenko, B. Corr, G.B. Webber, F. Endres, R. Atkin "Effect of dissolved LiCl on the ionic liquid - Au(111) electrical double layer structure" *Chemical Communications*, **2012**, 48, 10246
- D. Wakeham, <u>R. Hayes</u>, G.G. Warr, R. Atkin
 "Influence of temperature and molecular structure on ionic liquid solvation layers" *Journal of Physical Chemistry B*, 2009, 113, 5961

- <u>**R. Hayes**</u>, S. Zein El Abedin, R. Atkin
 "Pronounced structure in confined aprotic room-temperature ionic liquids" *Journal of Physical Chemistry B*, 2009, 113, 7049
- R. Atkin, S. Zein El Abedin, <u>R. Hayes</u>, L. Gasparotto, N. Borisenko, F. Endres "AFM & STM studies of (BMP)TFSA & (EMIm)TFSA surface interaction with Au(111)" *Journal of Physical Chemistry C*, 2009, 113, 13266
- R. Atkin, N. Borisenko, M. Drüschler, S.Z. El Abedin, F. Endres, <u>R. Haves</u>, B. Huber, B. Roling
 "An in situ STM / AFM and Impedance Spectroscopy study of the extremely pure [Py_{1,4}]FAP
 / Au(111) interface: potential dependent solvation layers and the herringbone reconstruction" *Physical Chemistry Chemical Physics*, **2011**, 13, 6849
- F. Endres, N. Borisenko, S. Zein El Abedin, <u>R. Hayes</u>, R. Atkin
 "The interface ionic liquid(s)/electrode(s): *in situ* STM and AFM measurements" *Faraday Discussions* 2012, 154, 221
- T. Carstens, <u>R. Hayes</u>, S.Z. El Abedin, B. Corr, G.B. Webber, N. Borisenko, R. Atkin, F. Endres "In situ STM, AFM and DTS study of the [HMIm]FAP / Au(111) interface" *Electrochimica Acta*, 2012, 82, 48
- 16. J. Sweeney,* F. Hausen,* <u>R. Hayes</u>,* G.B. Webber, F. Endres, M.W. Rutland, R. Bennewitz, R. Atkin (* *Equal contribution*)
 "Control of nano-scale friction on gold in an ionic liquid by a potential-dependent ionic lubricant layer" *Physical Review Letters*, **2012**, 109, 155502
- R. Atkin, N. Borisenko, M. Drüschler, F. Endres, <u>R. Hayes</u>, B. Huber, B. Roling
 "Structure and Dynamics of the Interfacial Layer between Ionic Liquids and Electrode
 Materials"
 Journal of Molecular Liquids, accepted, MOLLIQ-D-13-00252, 2013

LIST OF CONFERENCE ORAL PRESENTATIONS

- "The Smallest Sponge: Nanostructure in Ionic Liquids"
 27th Australian Colloid & Surface Science Student Conference (27th ACSSSC) Roseworthy, SA, Australia, February 1st-5th 2010
- "Amphiphilicity determines nanostructure in protic ionic liquids" UK Colloids 2011: An international Colloid & Surface Science Symposium London, United Kingdom, July 4-7th 2011
- "How does water dissolve in an ionic liquid?"
 28th Australian Colloid & Surface Science Student Conference (28th ACSSSC) Riverwood Downs, NSW, Australia February 6th-10th 2012
- "How does water dissolve in an ionic liquid?"
 International Association of Colloid & Interface Scientists (IACIS2012) Sendai, Japan May 13th-18th 2012,
- 5. "How Protic Ionic Liquids Hydrogen Bond"
 Ionic Liquids at interfaces & in confinement symposium
 University of Oxford, United Kingdom, 22nd March 2013
- 6. "How Protic Ionic Liquids dissolve in water"
 Liquid-Liquid Interfaces workshop, Durham Centre for Soft Matter University of Durham, United Kingdom, 27nd March 2013
- "How Protic Ionic Liquids Hydrogen Bond and dissolve in water"
 6th Congress on Ionic Liquids Alagrave, Portugal April 21-25th 2013
- "How water dissolves in protic ionic liquids" Australian Institute of Nuclear Science & Engineering Lucas Heights, NSW, Australia, 28th May 2013

LIST OF CONFERENCE POSTER PRESENTATIONS

- "How Protic Ionic Liquids Hydrogen Bond and dissolve in Water"
 6th biennial Australian Colloid & Interface Symposium Noosa, QLD, Australia February 3-7th 2013
- "How Protic Ionic Liquids Hydrogen Bond and dissolve in Water" 5th Congress on Ionic Liquids (COIL5) Alagrave, Portugal, April 21-25th 2013

GLOSSARY OF TERMS & SYMBOLS

Many important terms and symbols are examined in this Thesis and are listed below. Units are provided in brackets () where relevant.

Symbol (Unit)	Term
$\left[Py_{n,n} \right]^+$	1-alkyl-1-alkylpyrrolidinium cation (n = carbon chain length)
$[\mathbf{C}_n \min]^{T}$	1-alkyl- 3 -methylimidazolium cation (n = carbon chain length)
l_c (nm)	Alkyl chain length
$v_c (nm^3)_{10}$	Alkyl chain volume
A $(=10^{-10} \text{ m})$	Angstrom
AIL	Aprotic Ionic Liquid
AFM	Atomic Force Microscopy
ω (°)	Average Molecular Orientation
$S_N 2$	Bimolecular substitution reaction
$[Tf_2N]^{-}$ or $[TFSA]^{-}$	Bis(trifluoromethanesulfonyl)imide anion
T_b (°C)	Boiling Point
BASCN	Butylammonium Thiocyanate
CARS	Coherent anti-Stokes Raman scattering
<i>b</i> (m)	Coherent Scattering Length
COIL	Congress on Ionic Liquids
N _C	Coordination number
ξ (nm)	Correlation Length
CE	Counter Electrode
$CMC (mol.L^{-1})$	Critical Micelle Concentration
g	Critical Packing Parameter
r _D (nm)	Debye length
ρ (g.cm ⁻³ /atoms.Å ⁻³)	Density
DFT	Density Function Theory
DLVO	Derjaguin, Landau, Verwey Overbeek theory
D_2O	Deuterium Oxide
3	Dielectric Permittivity
DRS	Dielectric Relaxation Spectroscopy
D	Diffusion coefficient
DSSC	Dye Sensitized Solar cell
DLS	Dynamic Light Scattering
EDL	Electrical Double Layer
ESI-MS	Electrospray Ionization Mass Spectrometry
$e_0 (1.602 \text{ x} 10^{-19} \text{ C})$	Elemental Charge
EPSR	Empirical Potential Structure Refinement
EtAN	Ethanolammonium Nitrate
EAF	Ethylammonium Formate
EAHS	Ethylammonium Hydrogen Sulphate

EAN	Ethylammonium Nitrate
EASCN	Ethylammonium Thiocyanate
FAB-MS	Fast Atom Bombardment Mass Spectrometry
fs-IR	Femtosecond Infrared Spectroscopy
$[HCO_2]^{-1}$	Formate anion
FTIR	Fourier transfer Infrared spectroscopy
D_{8} -	Fully Deuterated contrast
T_{σ}° (°C)	Glass Transition Temperature
Au(111)	Gold (1.1.1) crystallographic surface
X	Halide Anion
HF	Hartree–Fock
$C (J.mol^{-1}.K^{-1})$	Heat Capacity (thermal)
$[PF_{6}]^{-}$	Hexafluorophosphate anion
HOPG	Highly Oriented Pyrolytic Graphite
$\langle r \rangle (nm^3)$	Hole (void) size
H-Bond	Hydrogen Bond
hbl (Å)	Hydrogen Bond Length
$\hat{\mathcal{A}}_{max}(^{\circ})$	Hydrogen Bond Angle
<i>H</i> -	Hydrogeneous contrast
[HSO ₄] ⁻	Hydrogen Sulphate anion
$\kappa (S \text{ cm}^{-1})$	Ionic Conductivity
II	Ionic Liquid
$L \pmod{L^{-1}}$	Ionic Strength
7:	Ion Valency
Lnhase	Lamellar phase
LAXS	Large Angle X-ray Scattering
	Lennard Iones potential
20/1:	Linear H-bond percentage
Li ⁺	Lithium cation
m/z	Mass to charge ratio
$T (^{\circ}C)$	Mass to charge ratio
$T_{\rm m}$ (C) $\sigma_{\rm D}$ (nm)	Molecular Diameter
MD	Molecular Dynamics
$M_{\rm (nm^3)}$	Molecular Volume
$MW (g mol^{-1})$	Molecular Weight
MC	Monte Carlo
$nm (=10^{-9} m)$	Nanometer
$nN (=10^{-9} N)$	Nanonewton
NIMROD	Near & Intermediate Range Order Diffractometer
NICISS	Neutral Impact Collision Ion Scattering Spectroscopy
ND	Neutron Diffraction
$[NO_2]^-$	Nitrate Anion
C:E:	Nonionic alkyl polyglycolether surfactant (i =glycol units i =ether units)
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser effect
NOESY	Nuclear Overhauser effect spectroscopy
OCP	Open Circuit Potential
OHD- RIKES	Ontical Heterodyne-Detected Raman-Induced Kerr effect spectroscopy
	option interesting betered runnan induced Ren effect spectroscopy

OKE	Optical Kerr-effect
D_n -	Partially Deuterated contrast ($n =$ number ¹ H atoms replaced by ² H)
π-π	Pi-Pi (interaction or force)
PAN	Propylammonium Nitrate
PIL	Protic Ionic Liquid
QENS	Quasi-Elastic Neutron Scattering
<i>d</i> (nm)	Quasi-periodic repeat distance
QRE	Quasi-reference Electrodes
g _{ij} (r)	Radial Distribution Function for atoms <i>i</i> and <i>j</i>
RE	Reference Electrode
n _D	Refractive Index
RMC	Reverse Monte Carlo
RTIL	Room Temperature Ionic Liquid
Al ₂ O ₃ (0001)	Sapphire surface
STM	Scanning Tunnelling Microscopy
Q (Å ⁻¹)	Scattering (wave) vector
Si	Silica surface
SANDALS	Small Angle Neutron Diffractometer for Amorphous & Liquid Systems
SANS	Small Angle Neutron Scattering
SAXS	Small Angle X-ray Scattering
SWAXS	Small & Wide Angle X-ray Scattering
SDF	Spatial Density Functions
L ₃ -phase	Sponge phase
S(Q)	Structure Factor
SFG	Sum Frequency Generation Spectroscopy
SFA	Surface Forces Apparatus
T (°C)	Temperature
$N_{n,n,n,n}^{+}$	Tetraalkylammonium cation ($n = carbon chain length$)
$P_{n,n,n,n}^{+}$	Tetraalkylphosphonium cation ($n = \text{carbon chain length}$)
BF ₄	Tetrafluoroborate anion
SCN	Thiocyanate anion
3D	Three dimensional
TOF	Time of Flight
[FAP] ⁻	Tris(pentafluoroethyl)trifluorophosphate anion
UV	Ultraviolet
P (Pa)	Vapour Pressure
η (Pa.s)	Viscosity
$V(J.C^{-1})$	Volt
V_{alkyl} (nm ³)	Volume of apolar groups
V_{polar} (nm ³)	Volume of polar groups
γ (N.m ⁻¹)	Surface tension
vdW	van der Waals (force or interaction)
WAXS	Wide Angle X-ray Scattering
WE	Working Electrode
XRD	X-ray Diffraction
XRR	X-ray Reflectivity

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PREFACE

"If you want to understand function, study structure!"^[1]

Francis H. Crick

Ionic Liquids (ILs) are a subset of molten salts distinguished by melting points below 373 K. ILs are unusual among solvents in that they are composed entirely of ions, with no neutral species present. Over the last decade or so, ILs have emerged as an attractive class of solvents for a range of chemical applications, mostly due to their 'green' characteristics and remarkable liquid properties. Understanding the ion arrangements in ILs is important as many of these applications and properties are related to their (bulk or interfacial) solvent structure.

Historically, ILs were considered structurally homogeneous solutions of freely dissociated ions or ion pairs. Whilst these concepts are adequate for molten salt melts, IL ions can participate in a range of attractive interactions (van der Waals, π - π , hydrogen bonding, or solvophobic) in addition to Coulombic forces. Notably too, ion-ion interactions in ILs are tuneable, because changes in anion/cation size, shape or functional groups alter the balance of inter-ionic forces. These features suggest different solvent structures may be present in ILs compared to molecular solvents or molten salts. Further, many IL ions (usually the cation) are amphiphilic with both charged and uncharged groups. This means that there is potential for self-assembly in a fashion similar to aqueous surfactant dispersions, microemulsions or liquid crystals, but on much smaller length scales. Recent experimental and theoretical research has tested this hypothesis for aprotic ILs. The results show that aprotic ILs are heterogeneous on the nanoscale, forming polar and apolar domains in the bulk liquid due to clustering of charged and uncharged molecular groups.

In this Thesis, the nature of *protic* IL structure in the bulk phase is examined using model fits to neutron diffraction data. It is shown that protic ILs are nanostructured solvents and that the solvent structure can be controllably varied. Secondly, aprotic IL structure at the Au(111) electrode interface are elucidated using atomic force microscopy. This provides fundamental insight to the IL electrical double layer structure that will underpin future IL-based electrochemical technologies.

THESIS OUTLINE

Chapter 1 reviews the relevant chemical literature. Sections 1 and 2 introduces ionic liquids (ILs) as both salts and solvents. Section 3 focusses on the bulk phase structure of ILs, after first surveying liquid structures of molecular solvents, self-assembled phases and molten salts for perspective. The morphology of the solid-IL interface is examined in Section 4, again with comparisons to similar interfaces. Section 5 links publications resulting from this Thesis to knowledge gaps in the literature.

Chapter 2 details the materials and methods used in this Thesis. Neutron diffraction, atomic force microscopy and empirical potential structure refinement are described. The fine details of experiment procedures can be found in the methods section of each publication.

The first of papers presented in Chapters 3-7 probe protic IL nanostructure in the bulk phase. Model fits to neutron diffraction data show that neat ILs form bicontinuous L_3 -sponge-like morphologies, with domains as small as 1 nm. The effect of electrostatic, H-bonding, solvophobic interactions and water dissolution is elucidated. A link to classical models for amphiphile self assembly is also drawn as the relative volumes of the polar and apolar moieties defines the packing geometry of the ions.

In Chapters 8 and 9, atomic force microscopy (AFM) is used to probe the structure of the IL-Au(111) electrical double layer via *in situ* electrochemical force measurements. The IL double layer is complex, and not consistent with the Stern-Gouy-Chapman model for aqueous electrolytes. AFM force versus separation profiles suggest a layered morphology forms at the interface, with a potential decay that oscillates between alternating planes of ion layers.

The key findings of this Thesis are discussed in broader context in Chapter 10, with future avenues of research suggested.

CHAPTER 1- INTRODUCTION

[Parts of this Chapter have been reproduced from R. Hayes, G. G. Warr, R. Atkin *Physical Chemistry Chemical Physics*, Vol 12, pages 1709-1723 (2010) and R. Hayes, D. Wakeham, R. Atkin "Ionic Liquid Interfacial Structure (2)" In *Ionic Liquids UnCOILed: Critical Expert Overviews*; John Wiley & Sons, (2012). Paragraphs that closely resemble, or taken directly from these reviews have been highlighted with "*" or "**" respectively]

1.1 Solvents, Solvent Mixtures, & Salts

1.1.1 Solvents

Much of chemistry is concerned with the study of reactions and processes in solution – that is, where liquids are used as *solvents*.^[2,3] The solvent is the liquid phase in which one or more *solutes* are dissolved in it to form a homogeneous *solution*.

Reaction kinetics, thermodynamics, yields and favoured products are influenced by the choice of solvent. These effects have long been recognized,^[4] and are closely related to the way solvent molecules arrange in the bulk or at interfaces, depending on whether the reaction is homogeneous or heterogeneous, respectively. However, most approaches to solvent selection are based on measurements of physical and chemical properties (e.g. boiling point, vapour pressure, heat capacity, viscosity, density)^[3,5] where solvents are treated as an unstructured media.^[6] The choice of solvent is determined from these properties, along with economic and environmental considerations.

Solvents are often classified from measurements of polarity. Solvent polarity is defined as the sum of all specific and non-specific intermolecular interactions in the solvent.^[2] Whilst this assumes the solvent is a homogeneous medium, polarity measurements are generally useful predictor of solvent chemistry, in accordance with the relation "like dissolves like." Water for instance, is a highly polar and thus is a poor solvent for non-polar compounds. Macroscopically, solvent polarity can be determined from liquid dielectric constants or

refractive indices. However these often fail to predict solvent effects at the molecular level. The most common approach to describe polarity across small dimensions is the dimensionless E_T^N value developed by Reichardt, normalised against values of tetramethylsilane ($E_T^N = 0.00$) and water ($E_T^N = 1.00$).^[7] This exploits the solvatochromatism of zwitterionic dyes dissolved in the solvent. Reichardt's scale is based on the position of the longest wavelength solvent intramolecular charge-transfer band, which is known to be a function of the polarity of the surrounding medium. This is shown in Figure 1 for a range of different solvents, including some ionic liquids.



Figure 1- Solvent classification via Reichardt's normalized solvent polarity scale. Ionic liquids span an enormous range of solvent polarities from ~0.35 to ~0.9, corresponding to values close to acetone to as high as ethanol. ([*Green Chemistry* 2005, 7, 339] Reproduced with permission of The Royal Society of Chemistry)

1.1.2 Solvent Mixtures & Solutions

Solvent mixtures are a useful way of modifying liquid polarity. Desired properties can be obtained by mixting two or more miscible liquids^[8] to obtain a more or less polar solvent. In principle, an infinite number of solvent mixtures can be prepared. However, use of solvent mixtures requires detailed knowledge of chemical and physical properties as a function of concentration. This is frequently unknown due to the lack of a predictive model that screens all possible cosolvents. Other more practical concerns are azeotrope or eutectic formation, which are accompanied by profound changes in solvent properties. Furthermore, solvent blends have a tendency to phase-separate, especially under extreme (temperature and pressure) conditions.

1.1.3 Crystalline Salts

Until recently, the salts most commonly used by chemists were crystalline solids at ambient conditions. Thus, salts could be employed as either solutes (e.g. in aqueous electrolytes, in the oceans, cellular biochemistry) or high-temperature molten liquids (e.g., nuclear reactors, energy storage). Both these functions are directly related to their crystalline structure. In common salts, the ions arrange into well-defined, 3-D network structures called *lattices*. Structural and theoretical models for lattices are well-described by the laws of crystallography and solid state physics. These essentially predict that a lattice is difficult to break down because ions are held together tightly in the arrangement, maximizing interactions between counter-ions (attractive electrostatic, energetically favourable) and minimizing that between co-ions (repulsive electrostatic interactions, energetically unfavourable). Thus, the lattice can only be disrupted if (1) the ions are dissolved in a solvent or (2) melting occurs.

Melting an ionic lattice requires considerable thermal energy input. This is because individual ions must be moved fast enough and far enough to escape the attractive well of its neighbours. This usually corresponds to temperatures in the hundreds of degrees Celsius, preventing the use of pure inorganic salts as solvents under standard laboratory conditions.

These concepts are illustrated by sodium chloride (NaCl). Sodium chloride is forms a rigid lattice structure of sodium cations (Na⁺) and chloride anions (Cl⁻) (c.f. Figure 2) of high internal energy (-787 kJ mol^{-1}).^[5] The small radii and neat, spherical shapes of the Na⁺ and Cl⁻ enables ions to close pack together as a simple cubic unit cell.^{*} This lattice melts at very high temperature (801°C) but can be easily dissolved in water^[9] (c.f Figure 2).



Figure 2- (left) Crystal lattice structure of NaCl (Na⁺ ions blue, Cl⁻ ions yellow) and (right) snapshot of intermediate state of Cl- ion solvation during NaCl dissolution in water from *ab initio* molecular dynamics simulations by Liu *et al*;^[9] Cl⁻ solvation is shown to be the rate determining step in lattice break down, leaving a Na⁺ protruding from the surface. (Reproduced with permission of the PCCP Owner Societies, *Phys. Chem. Chem. Phys.* 2011, *13*, 13162-13166)

^{*} Strictly speaking, NaCl should is not a simple cubic structure as this incorporates both ion types in the vertices of the unit cell. Formally, NaCl is two interpenetrating compact face centred cubes (fcc) of Na⁺ & Cl⁻ ions.

1.2 Ionic Liquids

1.2.1 Liquid Salts

In 1914, the German chemist Walden made a startling discovery: a pure salt (ethylammonium nitrate, EAN) that was liquid at ambient temperatures.^[10] Until then, it was never suspected that ions could form a liquid at room temperature unless diluted in a solvent; established theories of liquids dealt with uncharged molecules (water, benzene, ethanol) or atomic fluids (mercury, bromine) and Arrhenius had only recently proved the existence of ions in solution.^[11] EAN was strikingly similar to water in many respects as it was clear, colourless, odourless, with solid-like density (1.21 g.cm⁻³) and reasonably high viscosity. However, Walden's key finding was its electrically conductivity, a property intrinsic to all liquids that contain mobile ions.^[12] EAN's conductivity was consistent with a (near) pure solution of anions and cations. This conclusion was based on Walden's earlier studies of aqueous electrolytes^[13] in which a relationship between viscosity η and molar conductivity) and ρ (density)] was proposed:

$$\Lambda \eta = \text{constant}$$
 Equation 1

EAN could be well-described as a solution of independently moving ions because a plot of log Λ versus log η^{-1} follows the ideal line with slope of unity (c.f Figure 3).



Figure 3- Walden plot of log Λ versus log η^{-1} . The slope of the ideal line is from 1 M aqueous KCl solution data at 25°C. Several classes of ILs can be defined including "good", "superionic", "poor" and "non-ionic". EAN is close to a good IL, thus can be considered a pure mixture of ions. (Reprinted with permission from *J. Am. Chem. Soc.*, **2003**, 125, 15411, Copyright 2003 American Chemical Society)

For these reasons, Walden is widely credited as conceiving the field of liquid salts despite earlier workers creating similar materials with melting points just above room temperature.^[14] The science of liquid salts or "ionic liquids" has progressed leaps and bounds since the days of Walden, and to some degree reflect progress in both solution and materials chemistry. In the last few decades, ionic liquids have moved from niche electrolytes^[15] to mainstream scientific appeal.^[16-18] This has been driven by green chemistry principles^[19-21] and often remarkable solvent properties.^[22-24] These features, combined with the relative ease in which ionic liquids can be prepared, handled and distilled^[25,26] under standard laboratory conditions, has seen several authors advocate ionic liquids as wholesale replacements for molecular solvents.^[27-29] Figure 4 shows the exponential increase in scientific interest in ionic liquids.*



Figure 4- ISI Web of Science search for hits with the phrase "ionic liquids" or "molten salts" between 1960 and 2013. Correct as of 5th July 2013.

1.2.2 What is an Ionic Liquid?

Ionic liquids (ILs) are a subset of molten salts with melting points (T_m) below 373 K. In Walden's original paper on EAN, he described a class materials as "water-free salts... which melt at relatively low temperatures, about up to 100°C".^[30] This definition was later reaffirmed and codified in a NATO workshop in Crete in 2000.^[31] Definitions are important and relevant as the field is still relatively young, and the term "ionic liquids" was originally coined in reference to silicate slags with $T_m > 1000$ K.^[32] Similar systems have been described in the literature with names including "fused salts", "pure liquid electrolyte", "liquid salt", "ionophore", "organic ionic melts" or "molten salt at room temperature".^[33,34] Although the term "ionic liquid" has widespread acceptance, the definition has recently attracted criticism as it is based on somewhat arbitrary physical property (melting point) for a critical point relevant to a molecular solvent (water).^[35] Some authors also distinguish between ILs ($T_m < 373$ K) and room temperature ionic liquids (RTILs) that melt below 298K. In this Thesis, the acronym "IL" is preferred and indicates a salt with $T_m < 373$ K.

ILs can be chemically distinguished from common molten salts ($T_m > 373$ K, §1.1.3) as bulky, sterically mismatched anion/cation pairings (1) dampen the Columbic attractions / repulsions between ions and (2) frustrate neat lattice packing arrangements. Electrostatic forces are reduced because the ions are larger and so the distance between charged centres is increased. Moreover, depending on the functional groups, the charge can be distributed over a large volume by resonance. Crystal packing is hindered via asymmetry in one or both ions. Together, these factors reduce the salt's lattice energy and thus destabilize the crystalline state so that melting occurs near or less than ambient.

A relatively large window of ion structures produce salts that are fluids at room temperature. Whilst there are no set rules to making an IL, in general this can be achieved by balancing ion-ion interactions and symmetry conditions as shown overleaf in Figure 5. For instance, the cation alkyl chain must be long enough ($\approx n > 3$) to reduce Columbic forces and disrupt lattice packing. However, alkyl chain cannot be too long ($\approx n < 12$) as this will increase salt m.p. despite the enhanced asymmetry; solvophobic interactions increase with length of non-polar groups as per linear alkanes. However, Davis *et al.* recently showed that low melting salts can form in very long chain (> C₁₆) cations by introducing a *cis* double bond "kink" on the alkyl group.^[36] This is similar to homeoviscous adaptation in cell membranes^[37] and highlights the complex array of packing and chemical factors that control IL melting point.



Figure 5- Melting point (T_m) as a function of cation alkyl chain length (n) for salts systems with (A) C_n-alkyl-3-methyl-imidazolium and (B) n-alkylammonium cations. n-alkane data (black crosses) is also shown for comparison. The trend in T_m is consistent across all salts: low n values $T_m > 100^{\circ}$ C; intermediate n values 50° C<T_m<100^{\circ}C then T_m < °C 25 and; large n values 50° C< T_m < 100^{\circ}C. Dashed lines indicate the boundaries between molten salts (T_m > 100^{\circ}C) ILs (T_m ≤ 100^{\circ}C) and RTILs (T_m ≤ 25°C). In (A) hexafluorophosphate (PF₆, red squares), tetrafluoroborate (BF₄, green triangles), bis(perfluoroethyl-sulfonyl)imide (tf₂N, purple diamonds) and chloride (Cl⁻, blue circles) data sourced from References.^[38-41] Nitrate (NO₃⁻, blue crosses), formate (HCO₂⁻, orange rectangles), hydrogen sulphate (HSO₄⁻, green triangles) and thiocyanate (SCN⁻, pink plusses) is sourced from unpublished data and Reference.^[22] Note, data points for zero carbon atoms in (B) corresponds to the NH₄[X] salt.

1.2.3 Ionic Liquid Classification

Classifying ILs is challenging. Suggestions in the literature vary from condensed (ionic crystal and liquid) phases of matter,^[42] to fragile glass-forming systems^[43] or the missing link between aqueous/organic solutions and high-temperature molten salts.^[44] There are also interesting analogies to be drawn with solvent mixtures^[8] as the anions and cations^[45] or ionic and non-ionic segments^[46] can be treated as discrete components in the liquid phase. The vast number of potential ILs^[20] complicates this discussion, as a diverse range of liquid chemistries and solvent polarities are possible.*

Similar to molecular solvents, ILs are usually classified on the basis of chemical structure. ILs can be broadly divided into protic^[22] and aprotic^[47] classes based on the well-established division between proton donating (protic) and non-proton-donating (aprotic) molecular solvents. This effectively means that ILs are classified on the mechanism of ion formation. Other subclasses are known, including chiral^[48] magnetic,^[49] fluorous^[50] or oligoether carboxylate^[51] which is significant as there are limited analogues in molecular solvents. Some chemical structures of common cations and anions used in ILs are shown in Figure 6.



Figure 6- Chemical structures of representative cations and anions used in protic and aprotic ionic liquids. The drawn cations (top row) from left to right include: ammonium, phosphonium, 1-methyl-3-alkylimidazolium, 1-pyridinnium (c) pyrrolidinium species. Anions include formate, trifluoro-acetate, nitrate, hydrogen sulphate bis(perfluoroethylsulfonyl)imide, (bottom row) halide, tetrafluoro-borate, tris(penta-fluoroethyl)trifluorophosphate, dicyanamide, and thiocyanate anions.

1.2.4 Protic Ionic Liquids-

Protic ILs (or PILs) are formed by a proton-transfer reaction between a Brønsted acid and a Brønsted base.^[22] Notably, protic ILs were discovered before their aprotic cousins with ethylammonium nitrate (EAN) (m.p. 12°C) discovered by the German chemist Walden in 1914 by combination of nitric acid and ethylamine.^[10] Even earlier than this, in 1888 Gabriel reported the synthesis of a salt with a m.p. of ~52 °C, ethanolammonium nitrate (EtAN) using nitric acid and ethanolamine.^[14] In doing so, it is possible to distinguish between a protic IL and substances like water (which can be made molten under extreme temperature [>1200°C] and pressures [> 50 GPa])^[32] as the proton-transfer in the ILs is stable and (near) complete at ambient conditions.

A key feature of the acid-base synthesis is that hydrogen bond donor and acceptor sites are created on the ions. This enables protic ILs to form 3-D hydrogen bond networks, which have been likened to water.^[52] As the proton transfer is a complex chemical equilibrium, a concentration of neutral species is expected. In reference to this, a widely cited paper by MacFarlane and Seddon has argued protic IL should only be considered a pure "ionic liquid" if the concentration of neutral species is less than 1%.^[12] However, predicting the concentration of neutral species is difficult as the PIL acid-base equilibria is not well described by aqueous pK_a values. Instead, classifications of "poor", "superionic", and "good" protic ILs are used from comparisons with ideal aqueous behaviour using Walden plots of molar conductivity *versus* fluidity.^[26] Whilst most protic ILs show "poor" ionicity,^[47,53] it is not clear whether this is due to incomplete proton transfer, ion aggregates / clusters, or the formation of a bulk nanostructure.^[22] Angell *et al.* have proposed ΔpK_a (= $pK_a(base) - pK_a(acid)$) values greater than 8 should be considered complete proton transfer, as these salts have near ideal Walden behaviour.

1.2.5 Aprotic Ionic Liquids-

Charge-transfer metathesis and quaternization reactions produce aprotic ILs, often consisting of organic imidazolium or pyrrolidinium-based cations.^[54,55] Aprotic ILs form inter- and intra-molecular hydrogen bonds, but usually not networks like protics.^[56] The earliest description of an aprotic IL can be found in a letter published by Braun in 1927,^[57] which noted a red oil by-product of an AlCl₃-catalyzed Friedel-Craft alkylation. Between the 1950s to late 1980s, aprotic ILs were niche electrochemical solvents,^[15] investigated by the USA Airforce as electrolytes for thermal batteries.^[15,33,58] However, acute moisture and oxygensensitivity issues cultivated a reputation for aprotic ILs to be very difficult to work with, and limited any foreseeable usage to closed electrochemical systems. It was only in 1992 and advent of air and water-stable anions^[59,60] (e.g. BF₄⁻, CH₃COO⁻, HSO₄⁻, NO₃⁻, PF₆⁻) that brought aprotic ILs (and arguably, ILs broadly) into wider acceptance in the chemistry community, so that applications outside electrochemistry began to be explored.^[61,62]

1.2.6 Ionic Liquids Solvent Properties-

ILs have interesting solvent behaviour due to their pure ionic composition. However, the structural diversity of ILs, which provides enormous avenues for scientific innovation, means that it is not possible to identify a general set of IL properties. In principle, the only solvent property common to ILs is ionic conductivity, because they contains mobile ions.^[12] Many papers in the literature claim that, non-volatility, non-flammability, high electrochemical / thermal stability, biodegradability, wide solubility ranges, or "green characteristics" are intrinsic to all ILs. Whilst some ILs fit these labels, it is possible to find counter examples with other combinations of properties. In general, ILs have solvent properties that resemble polar protic liquids, molten salts and bicontinuous microemulsions (c.f. Table 1). This is related to the nature of their liquid structure.

Property	EAN	BmimPF ₆	Water	Molten NaCl	Mercury
Appearance	Clear, colourless	Clear, colourless	Clear, colourless	Clear, colourless	Silver, lustre
T_m (°C)	12	11	0	801	-38.8
T _b (°C)	255	180	100	1413	356.7
ρ (g.cm ⁻³)	1.21	1.37	1.00	1.539	13.534
η (Pa.s)	32 x 10 ⁻⁴	31.2 x 10 ⁻⁴	8.95 x 10 ⁻⁴	12.5 x 10 ⁻⁴	1.526 x10 ⁻³
P (Pa)	Negligible	Negligible	3173	45.9	2.67
n _D	1.4524	1.411	1.332	1.408	-
D			3 x 10 ⁻⁵	Na ⁺ 1.53 x 10 ⁻⁴	
				Cl^{-} 0.83 x 10^{-4}	
γ_{LV} (mN/m)	39.3	43.8	72.86	111.8	486.5
κ (S.cm ⁻¹)	2.69 x 10 ⁻²	1.4 x 10 ⁻³	5.5 x 10 ⁻⁴	0.256	
$C (J.mol^{-1}.K^{-1})$	-	-	4.184	-	27.98

Table 1- Properties of EAN & BmimPF₆ compared to water, molten NaCl (at 850°C) and Hg₍₁₎.

Interestingly, there is growing evidence to suggest that ILs have widespread ability to support amphiphile self-assembly.^[63-66] In a recent review by Greaves and Drummond,^[67] it was concluded that ILs are the largest known class of self-assembly media for amphiphiles; prior to 2006, only sixteen solvents (fourteen molecular liquids, and two ILs) were known to do this. Currently, every IL screened in the literature (thirty seven protic ILs, eleven aprotic ILs) has been shown to promote amphiphile self-assembly in some fashion, limited only by surfactant solubility. Thus, it is possible that this is another common IL trait, due to the solvation environment in the bulk phase (c.f §1.3.5.iv)

One structural feature unique to protic ILs is labile protons. This is a consequence of proton transfer as protons can "hop" between via H-bond donor and H-bond acceptor sites, likely in a Grötthuss-like mechanism.^[68] This proton transfer influences liquid behaviour, and has been linked vapour pressure,^[53] conductivity,^[53] thermal stability,^[26] catalytic activity,^[22] protein stabilization^[22] and the use of as ILs explosives.^[69] Thus, understanding the nature of H-bonds in protic ILs may provide insight into their solvent behaviour (c.f Chapter 6).

1.2.7 Designer solvents

Much current IL research focuses on their 'designer' characteristics, namely, the capacity to tune key intermolecular forces that govern liquid behaviour. IL structure–property relationships arise from a delicate balance of long-range (Coulombic) and short-range (van der Waals, dipole–dipole, hydrogen bonding, solvophobic^[67,70]) interactions, programmed by the choice of anions and cations. Thus, as summarized in Figure 7, molecular control of liquid properties is possible depending on how the ions are functionalized or anion/cation are mixed and matched. Unlike conventional solvents, this enables important solvency parameters (polarity, viscosity, cohesive energy, etc.) to be changed at the chemist's discretion, as molecular structure determines the set of intermolecular forces expressed in solution. IL solvents can therefore be designed for a particular reaction or process similar to retrosynthetic methodologies in organic chemistry.^[71] This represents a significant departure from empirical approaches to solvent selection; in principle desirable physicochemical properties can be identified from which to work backwards to determine appropriate IL molecular structures.*



Figure 7- Current scientific paradigm in IL research. This is analogous to retrosynthetic methodologies in organic chemistry. (Reproduced from Reference [72])

1.3 The Bulk Structure of Liquids

Of the three forms of matter (solids, liquids and gases), the physical structure of liquids is the least well-understood. Structural elucidation of liquids is challenging because the interactions between solvent molecules are too strong to be rationalized using kinetic theory of gases but too weak to be explained by the laws of solid-state physics.^[2] In fact, most cohesive forces in liquids are comparable to kT; the opposing, randomizing energy due to thermal motion. Thus, the molecular organization in liquids is dynamic, unlike the fixed, regular and close-packed arrangement in solids. This means that liquid structure exists only over short distances and time scales because molecules diffuse rapidly and randomly through the bulk. Compared to gases, liquids denisity's are several orders of magnitude higher and are weakly compressible. This serves to restrict molecular motion and induce order in the liquid phase. For all these reasons, Tabor's famous description of liquids as the "Cinderella of modern physics"^[73] still holds true today; a unified theory of liquid structure has not been established as they have features common to both solids and gases.

It is in this context that the current understanding of IL bulk structure is reviewed. The bulk structure of protic ILs is addressed first as it is the focus of this Thesis, followed then by aprotic ILs for perspective. Prior to addressing ILs, some remarks will be made on molecular liquids, self-assembled phases (liquid crystals and microemulsions) and molten salts, as all these systems show a number of structural similarities to ILs. It is important to emphasize that the bulk structure is not static; IL ions^[74-77] undergo Brownian motion with short rotational and translational correlation times in the order of 0.1 to 10 picoseconds.^[2] This means that scientists are generally limited to techniques that probe the time-averaged structure in liquids, or infer structure via thermodynamic arguments.

1.3.1 Molecular Liquids

1.3.1.i Formalist approaches

Liquid structure cannot be accurately modelled using modern statistical mechanics. However, the qualitative behaviour of liquids^[78,79] can be approximated by the classical van der Waals' equation of state^[80] that was developed in 1873:

$$(P + a/v^2)(v - b) = kT$$
 Equation 2

where *P* is system pressure, *T* is temperature, *k* is Boltzman's constant and *v* is volume per molecule. The relation constants $a = 2\pi C/(n-3)\sigma^{n-3}$ and $b = \frac{2}{3}\pi\sigma^3$ which account for the attractive and repulsive forces (respectively) between molecules of radius σ .

In the van der Waals model, liquid structure is largely a consequence of repulsive forces between molecules, with attractive forces playing only a minor role. This is because at very small separations (i.e. during a molecular collision), the electron clouds of neighbouring atoms/molecules overlap, resulting in a strong repulsive electrostatic force. The packing of molecules in this arrangement is suggested to be random and (weakly) compressible, unlike the regular, ordered arrays in the solid state.^[81,82] Here, molecules are assumed to experience no intermolecular force until they touch, whereupon they act as infinitely hard spheres. Hence, molecular size and geometry are important because they define an excluded-volume that proximal molecules cannot encroach upon. As depicted in Figure 8, this creates short-range order in the liquid over a few molecular diameters (σ), oscillating between regions of enhanced and depleted density $\rho(r)$ as a function of distance r. Beyond the first peak, local structure decays rapidly and the bulk density (ρ_0) is reached after ~ 4 oscillations. Because close packing of molecules is retained in the liquid phase, the short range structure can resemble that in the corresponding solid. The upshot of this is that insight into liquid structure can be gained from understanding arrangements in the solid phase (and *vice versa*).



Figure 8- (A) Radial density distribution g(r) function and (B) pair potential w(r) for a liquid of with diameter σ . In (A), the local density $\rho(r)$ oscillates above and below the normalized bulk value ρ_0 with period σ , leading to changes in w(r). (Reproduced with permission from Science 220, 787-794 Copyright 1983 American Association for the Advancement of Science)

Although statistical mechanics suggests attractive forces contribute only weakly to structure, it predicts a key role other areas. For example, recent simulations have shown that ignoring attractive interactions leads to large errors in fluid dynamics.^[83,84] More importantly, attractive interactions provide the uniform background potential over long distances (a 'mean field'). This enables the system to build up a cohesive energy and thus stabilise the liquid phase; it is because liquid molecules exist in an attractive field with respect to all other molecules that they do not instantaneously evaporate into the gas phase upon melting.

The general form of statistical mechanical models treats the interaction potential w(r) as the sum of two power laws^[85] for both the attractive and repulsive components:

$$w(r) = -\frac{A}{r^n} + \frac{B}{r^m}$$
 Equation 3

The most famous of these is the Lennard-Jones^[86] potential (for n = 6 and m = 12):

w(r) =
$$-\frac{A}{r^6} + \frac{B}{r^{12}} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$
 Equation 4

where σ is the collision diameter and ϵ the well-depth (the optimum distance between any two molecules) of the potential w(r).

An important conceptual development was proposed by Weeks, Chandler and Anderson (WCA) in 1971.^[87] They addressed the problem of how to separate the (weak, long range) attractive from (strong, local) repulsive forces in the equilibrium structure of simple liquids.

WCA suggests best agreement between w(r) and liquid structure is obtained when (1) repulsive forces are considered for all distances up to the position of the first peak in the g(r) distribution and (2) attractive forces act thereafter. This is shown in Figure 8B.

Coordination numbers (N_C) provide a picture of liquid structure and are obtained from the integrating radial density distribution functions over a specific distance range. N_C informs on the number of *j* units in a spherical volume around *i* (*i* & *j* can be an atom or a molecule):

$$N_C = 4\pi c_j \rho \int_0^{r_{min}} r^2 g_{i,j}(r) dr \qquad \text{Equation 5}$$

and c_j is the concentration of j, ρ the atomic density. It is important to note that liquid N_C values are usually derived from averaging many local arrangements. Thus, N_C is somewhat insensitive to structure arising from local attractive interactions.^[88] To this end, it is necessary to examine structure from the molecule's perspective, in the coordination shells.

1.3.1.ii A molecule's view of liquid structure

Whilst difficult to treat in statistical mechanics, attractive interactions are very important in determining liquid structure. The nature and strength of intermolecular forces between molecules fine tune local arrangements in the bulk. Liquids may participate in a variety of attractive interactions ranging from the weak, non-specific and isotropic forces (e.g. van der Waals, dispersion forces) to strong, specific and anisotropic forces (e.g. H-bonding, dipole-dipole, electron pair donor/acceptor, hydro/solvophobic interactions). According to Hellman-Feynman theory, all these interactions can be described by simple electrostatics once the shape of the atom's electron clouds are determined from the Schrödinger equation.^[89] However, some interactions have an entropic contribution, leading to more complex, higher order solvent structures. It is important to note that cohesive forces will only induce a defined solvent structure when the magnitude of the interaction is greater that kT, i.e. if it is greater than the opposing, randomizing effect of thermal motion.
1.3.1.iii Short-range solvent structures

The majority of liquids display a favoured orientation and separation of nearest neighbour molecules. This holds for a range of simple atomic, diatomic and molecular liquids. For example, simple atomic liquids (Br,^[90,91] Hg^[92,93]) are well-described by van der Waals picture of hard spheres; the average separation reflects the balance of repulsive and attractive forces in the bulk. Diatomic $(H_2, {}^{[94]}D_2, {}^{[95]}N_2, {}^{[96]}O_2, {}^{[96]}halogens, {}^{[97]}HF^{[98]}$ etc.) or triatomic $(CO_2, [^{[99,100]}]$ etc.) are consistent with this too, but the structure is often more complex as geometric constrains and inhomogeneous electron density distributions can lead to stronger orientational correlations, often along the molecular bond axis. For larger molecular liquids the preferred orientations become even more pronounced. Figure 9A-F shows that solvents as diverse as acetone,^[101] tetrahydrofuran,^[102] or benzene,^[103] exhibit a preferred molecular arrangement in the first coordination shell (3.5 to \sim 7 Å). The probability lobe for acetone is symmetric and concentrated around the upper hemisphere of the plot, and consistent with aligned dipole-dipole interactions (9D). In tetrahydrofuran (9E), a "Y-shaped" conformation is favoured due to dispersion forces between molecules. π - π interactions are the strongest intermolecular force in benzene and induce a population of both "T-shaped" and ring-aligned structures in the bulk (9F). Beyond the first coordination shell (> \sim 7 Å), structure in all these liquids falls away rapidly, and a uniform spherical molecular probability is obtained. This shows that the interactions are relatively weak and short range. Thus, structure is present only across small distances in the bulk of most molecular solvents.



Figure 9- g(r) distribution functions (top row) and spatial density distributions (bottom row) for acetone, (A, D), tetrahydrofuran (B, E) and benzene (C, F). The g(r) data shows local density variation for the center of mass between adjacent molecules. The lobes in D-F depict most probable 3D arrangement in the first coordination shell. Ac is consistent with aligned dipoles. THF indicates a "Y-shaped" orientations due to dispersion forces. π - π interactions induce both as both "T-shaped" and ring-aligned structure in C₆H₆. (Reprinted with permission from *J. Chem. Phys.* 127, 174515 [Copyright 2007, American Institute of Physics] and *J. Am. Chem. Soc.*, 128, 5119 [Copyright 2006, American Chemical Society] and *J. Am. Chem. Soc.*, 2010, 132, 5735 [Copyright 2010, American Chemical Society])

1.3.1.iv Long-range solvent structures

Attractive interactions can also induce structure over longer length scales. The most important of these are hydrogen (H-) $bonds^{[104-106]}$ which can act cooperatively across several solvation shells. The classic example of this is liquid water^[107-110] (c.f. Figure 10A-C). The consensus scientific view^[110-112] is that strong directional H-bonds of the form H–O····H–OH enabling water to build up a 3-D tetrahedral network structure although some non-tetrahedral structure may be present.^[113]



Figure 10- EPSR spatial density distributions with lobes showing most probable 3-D molecular arrangements in (A) 1^{st} shell (nearest-neighbour) and (B) 1^{st} and 2^{nd} shells (top 12% & 25%) for water molecules relative to a central water molecule. (Reproduced with permission of the PCCP Owner Societies, *Phys. Chem. Chem. Phys.* 2003, 5, 1981-1991. B and C are unpublished Figures from ESPR fitting of neutron diffraction data presented in Reference [¹⁰⁹])

For comparison, the ice (I_h) lattice is shown in Figure 10D. In ice, each H₂O molecule is Hbonded to exactly four neighbouring molecules in an ideal tetrahedral arrangement, such that the solid can be effectively described as containing exactly one H atom between each O atom.^[106,114] When ice melts, the tetrahedral arrangement is retained but the average structure becomes more disordered. The average coordination number for the first peak in the g(r) data (Figure 10A) is now closer to five (4.7,^[115] 5.1,^[116] 5.2^[117]). This increase compared to the ideal tetrahedral N_C of 4 suggest bifurcated/distorted H-bonds,^[88,118] broken H-bonds,^[119] or other complex non-tetrahedral arrangements.^[120] The first peak in the water oxygen-oxygen g(r) is slightly larger than the average water molecule diameter. This means that water molecules do not sit as close as predicted by closely packing of hard spheres; H-bonds hold the molecules slightly further apart to maintain the tetrahedral arrangement.

Other protic liquids form well-defined solvent structure via H-bonds. Solvents as diverse as methanol,^[121] methylamine,^[121] ammonia,^[122] and glycerol^[123] as well as their mixtures with water^[124-126] are often highly associated in 3D H-bonded networks. In other liquids, where directional interactions are more restricted, H-bonding results in aggregate structures, such as chains of alcohols,^[121,127] dimers in formic acid,^[128] or cyclic hexamers in formamide.^[129,130] Unlike most solvents, the chemical structure of 1-octanol is amphiphilic, consisting of a polar hydroxyl group attached to a linear C₈-alkyl chain. This induces different, entropically-driven long range liquid structure via solvophobic^[2,70] interactions. The solvophobic interaction is akin to the hydrophobic effect in water^[131] but for a non-aqueous solvent. Several papers have emerged in the literature using computer simulations^[127,132] or thermodynamic arguments^[133] to suggest that 1-octanol is heterogeneous in the bulk. This is consistent with X-ray diffraction data^[134,135] for the pure solvent which has a peak at low q < 0.5 Å⁻¹, corresponding to a repeat length scale larger than the size of individual 1-octanol molecules from the Bragg equation. Such a peak is characteristic of long range structure in glasses, liquids^[136] and is important in the context of this Thesis because ILs show similar correlation length (§1.2.5.iv, §1.2.5.v, §1.2.6.iv and Chapters 3-7).

The bulk structure of 1-octanol is depicted in Figure 11A from molecular dynamic simulations of 512 molecules.^[132] Distinct yellow hydrocarbon regions and red –OH channels are evident. Figure 11B shows an example of the type of aggregate found in the bulk structure on a smaller scale. The structure is rationalised as follows. Polar groups are attracted to each other via H-bonding, with each –OH moiety H-bonded to two neighbouring units. This enables the alkyl chains to aggregate together via solvophobic interactions so that long thin clusters of alkyl chains can form. Whilst similar controversial^[111] suggestions of solvent

hetereogeneity have been made for pure water,^[137] the bulk structure of pure 1-octanol is widely accepted to be heterogeneous, although some authors still advocate a spherical^[133] or reverse^[134] micelle-type arrangements. Regardless of the exact structure, amphiphilicity provides a foundation of long range order in 1-octanol as per aqueous surfactant dispersions.^[138] When amphiphilicity is removed in the case of pure octane, a low q peak is absent in the X-ray diffraction spectra^[135] as simple alkane molecules space fill in the bulk; there no driving force is present for long-range structure. It is possible to induce solvent heterogeneity in water by mixing it with an amphiphilic solvent eg. methanol^[124,139] or other alcohols^[140] because the hydrophobic effect^[131] will drive molecular de-mixing so that the local structure of both liquids as close as possible to the pure liquids.



Figure 11- Equilibrium bulk structure of 1-octanol. (A) shows snapshot of the 3D simulation box of 512 1-octanol molecules. The solvent structure is hetereogeneous, with regions of yellow (hydrocarbon) and red (-OH groups). Locally the arrangement is described as consisting of long H-bonded clusters, such as that depicted in (B). Note –OH groups represented as space filling spheres for emphasis. (Reprinted with permission from *J. Am. Chem. Soc.*, 124, 15085 [Copyright 2003, American Chemical Society])

1.3.2 Complex Liquids & Self-assembled systems

1.3.2.i Liquid Crystals

Liquid crystals are a special, intermediate state of matter that retains structural characteristics of both crystalline solids and amorphous liquids.^[141-143] These differences are shown schematically in Figure 12. Solid crystals possess both positional and orientational order, such that molecules are constrained to occupy specific sites in a lattice and point their molecular axes in specific directions. In most fluids (c.f. §1.3.1), molecules diffuse randomly through their sample container as a result of Brownian motion and there is no preferred alignment of molecules. This means that crystalline substances show long-range order in the compared to the short-range, time-dependent structure in most typical liquid systems.



Figure 12- Schematic illustration of bulk structure in a crystalline solid, liquid crystal (nematic phase) and liquid phase. The elliptical shapes represent a molecule in each system. ω is the average molecular orientation relative to a preferred direction τ (Reproduced with from Reference [¹⁴³], Copyright Princeton University Press 2002)

Molecules in liquid crystals undergo diffusion much like that in a conventional liquid, but still maintain some degree of orientational, and occasionally positional order.^[143] This is represented by ω in Figure 12, which defines the average molecular orientation relative to a

preferred direction τ in a simple (nematic) liquid crystal. The more orientational order present in the liquid crystal, the closer ω is to zero. Interestingly, the latent heats of melting reveal that a liquid crystal is more like a 'liquid' than a 'crystal', as it takes more energy to move from crystal phase \rightarrow liquid crystal than liquid crystal \rightarrow liquid.^[143]

The first report of a liquid crystal dates back to 1888 when the Austrian scientist Friedrich Reinitzer^[144] observed "double melting" in esters of cholesterol.[†] Whilst it not the purposes of this review to describe all possible liquid crystal arrangements, the key point is that molecular structure has a strong influence on self-assembled structure, summarized in Table 2.

Tumo	Bulk Morphology	Molecule Ture	Order Present	
I ype		Wolecule Type	Orientational	Positional
Nematic	Molecular axis in parallel orientation	Rod-like	Yes	No
Smectic	Layered structures	Disk-like	Yes	Yes, partial
Cubic	Micellar lattice units or Complicated interwoven networks.	Rod-like	Yes	Yes
Columnar	Rod-like structures with parallel arrangement of molecules.	Disk-like	Yes	Yes

Table 2 Summary of common liquid crystal phases.

The type and extent of liquid crystal ordering have been well-characterized using a variety of techniques (NMR, Raman/X-ray/neutron scattering)^[143] but perhaps the simplest and most widely used is polarizing microscopy, which exploits the optical bifringence of the these morphologies. For a liquid crystal to be bifringent, structure must be of the order of the size of the visible wavelength of light (>100 nm) to induce optical scattering.

Typically, an essential requirement for liquid crystal or mesomorphism is that the molecules are anisotropic in shape, like a rod or a disk. Concentrated amphiphilic surfactants dispersions can also exhibit mesomorphism. This arises because amphiphilic molecules

^{††} The double melting refers to two critical points: a (low temperature) change from a crystalline solid \rightarrow an opaque liquid (liquid crystal) and a (high temperature) change from opaque liquid \rightarrow optically clear liquid.

respond to the solvophobic effect and self-assemble into micellar, lamellar or hexagonalshaped aggregates in the bulk. Because self-assembly is sensitive to temperature (thermotropic) and solvent (lyotropic) effects, there are examples of liquid crystals that pass through more than one mesophase before reaching isotropic solution. The key point for this Thesis is that pure ILs with very long cation alkyl chains (> C_{14}) form smectic mesophases, similar to traditional liquid crystal dispersions.^[145] This suggests there is a potential for similar patterns of self-assembly in ILs with smaller non-polar groups (C_2 - C_8), but that the structure may not be as well-defined.

1.3.2.ii Microemulsions

Microemulsions are chemical mixtures of at least three components, water, oil and surfactant (amphiphile) of generally low viscosity which form a homogeneous liquid phase.^[146] Danielsson and Lindman formally defined them as "single optically isotropic and thermodynamically stable liquid solutions."^[147] These special colloidal dispersions, first identified in 1943 by Hoar and Schulman,^[148] have attracted a great deal of attention due to their ability to solubilise unusual combinations of materials.

At a microscopic level, the surfactant molecules adsorb at the oil/water interface and form an extended interfacial monolayer which separates the water and oil molecules. This in turn reduces the interfacial tension between the polar (water) and non-polar (oil) phases ($\gamma_{o/w}$) effectively to zero, thus permitting spontaneous, stable dispersion of two otherwise immiscible solvents. The internal surface area of this structure is very high, which can be exploited in many fields including oil recovery, drug delivery and catalysis.

Microemulsions exhibit great structural diversity depending on the relative concentrations of all three components, the structure of the surfactant molecule and external conditions (temperature, pressure etc.), all of which has been extensively reviewed elsewhere.^[146,149] Of

particular importance to this research is an expression developed by Isrealachivili *et al.* that relates surfactant molecular structure to interfacial topology in self-assembled systems.^[150,151] This critical packing parameter *g*, can predict changes in bulk structure from local film curvature. *g* values are usually addressed quantitatively in terms of geometric factors (c.f. Table 3) and is governed by the relative areas of the surfactant headgroup a_0 to the tail group v_c / l_c , where v_c and l_c are the alkyl chain volume and length respectively:

$$g = \frac{v_c}{a_o l_c}$$
 Equation 6

g	General surfactant type	Expected Aggregate Structure
< 0.33	Single-chain surfactants with large head groups	Spherical or ellipsoidal micelles
0.33-0.5	Single-chain surfactants with small head groups or ionic surfactants in large amounts of electrolyte	Cylindrical or rod-shaped micelles
0.5-1.0	Double-chain surfactants with large head groups and flexible chains	Vesicles and flexible bilayers
1.0	Double-chain surfactants with small head groups or rigid, immobile chains	Planar extended bilayers
> 1.0	Double-chain surfactants with small head groups, very large and bulky hydrophobic groups	Reversed or inverted micelles

Table 3- Expected aggregate characteristics in relation to surfactant critical packing parameter, g

The structural correlation in microemulsions is more pronounced than in molecular liquid systems, but generally less than liquid crystal phases. The oil and water regions are fairly well separated by the organized surfactant monolayer, resulting in intermediate or mesoscopic order. When the volume ratios of oil and water are near unity, bicontinuous morphologies are observed, and can be described as two interpenetrating networks of polar hydrophilic and nonpolar hydrophobic domains. Thermal fluctuations are present in this arrangement,^[152] and so the surfactant film should be treated as a flexible sheet rather than a rigid structure. For balanced bicontinuous microemulsions, the alternating arrangement of polar and apolar regions is propagated over longer distances in the liquid. This can be characterized by an order parameter correlation function, $\gamma(r)$:^[138]

$$\gamma(r) = \frac{d}{2\pi r} e^{-r/\xi} \sin\left(\frac{2\pi r}{d}\right)$$
 Equation 7

Here *d* is a quasiperiodic repeat distance between adjacent polar (or non-polar) domains (c.f. Figure 13), and ξ is a correlation length, describing the decay of that periodicity. Microemulsions may be distinguished from weakly-structured mixtures and dispersions by the presence of a scattering peak corresponding to the repeat distance *d* at low-Q in neutron or X-ray scattering experiments. This peak arises when $\xi \ge d^{[138,153]}$ and equates to the presence of an amphiphilic self-assembled structure. Indeed, bicontinuous structures can be distinguished from simple fluid mixtures by the presence a scattering peak, with bicontinuous microemulsions said to form when the surfactant is *sufficiently amphiphilic*.



Figure 13- Schematic and (inset) molecular view of a bicontinuous L_3 sponge phase morphology. The domain size d is shown and corresponds to the repeat lengthscale that can be detected by scattering techniques when the surfactant is sufficiently amphiphillic.

1.3.3 Molten Salts

Elucidating structure in classical molten salts ($T_m > 373$ K) is challenging as there are relatively few experimental probes that are stable at these operating conditions. The most commonly used approaches are X-ray and neutron diffraction,^[154] which can examine timeaveraged structure in these salts with atomic resolution. This is achieved by extracting ion-ion g(r) correlations from a one-dimensional Fourier transformation of the scattering data. In general, the g(r) functions can be obtained accurately in molten salt melts because it is a two component system containing spherical ions of known radius and polarizability.^[155,156] However, as noted by Bockris "diffraction data do not play the same stellar role in determining the structure of liquids salts as they do for solid salts".^[157] This is essentially because of the large 10-25% volume of fusion expansion upon melting, and yet the ion-ion distances become *smaller*, not bigger, than in the solid state. Thus, several new concepts need to be defined prior to analysis of diffraction data.

1.3.3.i Electroneutrality & Charge Screening

The interpretation of scattering data for molten salts is built upon on two important concepts, electroneutrality and charge screening. Electroneutrality is a consequence of molten salt's dual composition. Because the salts are an equimolar mixture of anions and cations, the sum of all positive and negative charges must be zero. This imposes constraints on ion structure both locally and macroscopically, by setting limits on relative ion concentrations in any given region. Moreover, electroneutrality is implicit in modelling the ionic atmosphere as a mean field; whilst populated with both anions and cations, the Columbic forces balance so that the whole system is uncharged. Formally:

$$\sum_{i=1}^{i} z_i \rho_i e_0 = 0 \qquad \qquad \text{Equation 8}$$

For ions of valency z_i and density ρ_i and e_0 is the elemental charge (1.602 x10⁻¹⁹ C). A direct consequence of electroneutrality is shielding of the Coulombic charge. From Debye-Hückel theory,^[158] molten salts are fluids of high ionic strength, *I*:

$$I = \frac{\sum_{i} z_{i}^{2} c_{i}}{2}$$
 Equation 9

where c_i is the concentration of *i* (mol.L⁻¹). Thus, the classical Coulomb potential $\phi_i (= \frac{z_i e}{4\pi \epsilon r})$ at a distance r from an isolated ion of charge $z_i e$ in a medium of permittivity ϵ does not apply: Instead, the ionic atmosphere causes the electrostatic potential to decay more sharply with distance and takes on the form of a shielded Coulomb potential:

$$\phi_i = \frac{Z_i}{r} e^{-r/r_D} \qquad \qquad \text{Equation 10}$$

Here, $r_D (=1/\kappa)$ is the Debye length, and is much smaller than the size of individual ions.

1.3.3.ii Structure by Scattering

Figure 14 below shows g(r) functions and hypernetted chain approximation fit of molten NaCl from neutron diffraction experiments at 1148 K.^[154,159] Charge ordering is evident in the $g_{Na+Cl}(r)$, $g_{Na+,Na+}(r)$, $g_{Cl-,Cl}(r)$ data. The structure can be explained by attractive and repulsive Coulombic forces and packing of spherical ions; it is not necessary to invoke repulsive van der Waals forces as for molecular liquids (§1.2.1.i). All three g(r) distributions have well-defined first peaks, followed by structure that decays sinusoidally over distance. This corresponds to regions of occupied and excluded ion density. As expected, the peak for average Na⁺...Cl⁻ separation [2.62 Å] is at smaller distance than the like ion-ion Na⁺...Na⁺ [4.04 Å] or Cl⁻...Cl⁻ [4.04 Å] correlations. A similar effect is seen in the distance of closest approach (r_L), corresponding to the first upturn in the g(r) data. This appears at 2.08 Å for the Na⁺...Cl⁻ g(r), compared to 2.70 Å and 2.83 Å for Na⁺...Na⁺ or Cl⁻...Cl⁻ respectively.

In Figure 14, the peak positions, and general shape of the $g_{Na+Cl}(r)$ is exactly out of phase with $g_{Na+,Na+}(r)$ or $g_{Cl-,Cl-}(r)$. This confirms an average oscillatory structure must exist around each ion in solution, beginning with the species of unlike charge in the first coordination shell, and then regions of successively alternating sign. The electrostatic potential mimics this structure to maintain electroneutrality. The potential switches between positive and negative values with distance until the bulk potential is reached.

Notably, the period of these oscillations is not consistent with the ion diameters (3.34 Å for Cl⁻, 2.32 Å for Na⁺). This is because the ions are not touching in an ideal close packed arrangement and that there is an appreciable volume between ions in solution, for reasons that become apparent in \$1.3.3.iii below. The structural effect of this is to reduce the N_c values in the first coordination shell compared to crystalline NaCl.^[159] Such behaviour is opposite to molecular liquids, where an *increase* in coordination number occurs upon melting, leading to a more structurally disorded system.



Figure 14- Radial distribution functions for molten NaCl at 1148 K. The y-axis is ion density and the x-axis is separation (Å). Cl⁻···Cl⁻ data is offset. g(r) data from neutron diffraction experiments^[154,160] is indicated by open circles. Black lines & black dots^[160] are fits this data. (Reprinted with permission from *J Chem. Phys.* 81, 3174 [Copyright 1984, American Institute of Physics])

The raw scattering data for some molten salts has a pre-peak or first sharp diffraction peak at ~1 Å^{-1.[136,161-163]} This is consistent with long range order, as the structure is much too large to be ascribed to scattering from single ions or ion pars. However, the origin of this peak is still unclear. Some evidence points to density fluctuations on ~1 nm length scales that are not captured by the g(r) correlations; these molten salts has local layered repeating ion structure that is stable for very small times.^[163]

Long-chain (C₆-C₁₈) alkylammonium molten salts that form thermotropic liquid crystal phases.^[164-166] Lamellar-like smectic phases were identified in the bulk, regardless of the nature of the anion (halides^[165,167-169], alkanesulfonates^[170], pyroglutamates^[171], naphthalenesulfonates,^[172] benzenesulfonates^[173]). Interestingly, there is also evidence of tetragonal symmetry in the lateral organization of alkyl chains within the layers, which likely 30

contributes to their high melting point, above 100°C.^[174] Surprisingly, H-bonding was shown to have a strong effect on the stability of their crystalline and liquid crystalline phases,^[175] yet the net structure was essentially invariant.

1.3.3.iii Hole Theory

Hole theory is the classical model used to describe structural and transport properties of molten salts, and attempts to reconcile the volume expansions upon fusion with scattering data and theoretical concepts. Developed by Fürth in $1941^{[176,177]}$ and later extended by Bockris,^[157,178-180] hole theory treats regions unoccupied by ion as a vacant space or a 'hole'. The radius of the averaged size of void (r), is related to liquid surface tension, γ :^[157]

$$4\pi \langle \mathbf{r} \rangle^2 = \frac{3.3kT}{\gamma}$$
 Equation 11

and the probability P of finding a hole of radius r is:

$$P = \frac{16}{15\sqrt{\pi}} a^{7/2} r^6 e^{-ar^2}$$
 Equation 12

where the constant $a = \frac{4\pi\gamma}{kT}$.

In the same way the properties of a gas are determined by the motion of molecules, hole theory proposes that the motion of the ions *and* voids govern molten salt behaviour. Ion self-diffusion is thus related to the probability of finding a hole adjacent to an ion that is of sufficient dimensions to permit movement. The average dimension of the holes in the molten salt (1.5-2.5 Å) is similar to typical ion sizes (1.0-2.6 Å). Hence, ions are mobile and can diffuse freely through the liquid. The picture that emerges is shown in

Figure 15A. The molten salt bulk structure is composed of randomly located and variably sized holes, in a continuum of ion pairs and free ions. This has been likened to "Swiss

Cheese^[157] because it is an interconnected network of voids and ions. The mechanism of hole formation is also presented in

Figure 15B. This is akin to creation of a vacancy in a crystal lattice or an expanding bubble in a liquid, and is linked to surface tension, γ .^[176,177] Assuming the latter case enables the work of hole formation W to be calculated:

$$W = 4\pi r^2 \gamma$$
 Equation 14

Hole theory provides good qualitative agreement with ion self-diffusion^[180] or viscosity^[181] measurements for molten salts. However, for ions of disparate sizes or ions with long linear functional groups (as is typically the case in ILs) the model provides reasonable correlation with bulk transport properties.^[181]



Figure 15- (A) the hole model for molten salt structure and (B) proposed mechanism of hole formation at times t_1 and t_2 . (Reprinted with permission from [¹⁵⁷], Copyright Plenum Press 1970)

1.3.4 The Bulk Structure of Ionic Liquids

This section surveys the bulk phase structure of ionic liquids. Historically, ILs were thought to be structurally homogeneous systems. Bernal's classic picture of liquids as homogeneous, coherent and essentially irregular^[82] systems strongly influenced thinking in the IL community. Most likely, researchers believed the IL bulk structure was similar to a highly concentrated salt solution or a molten salt melt, with Brownian motion propelling ions in a time-averaged uniform state of homogeneity. Recently however, the models used to describe ILs have suggested they are structured solvents, across supramolacular (ion pairs, ion clusters) or mesoscopic (H-bond networks, micelle-like and bicontinuous morphologies) length scales. Understanding this structure is key to unravelling their complex physical, chemical and dynamic behaviour. ILs are the ideal solvents to test the 'structured liquid' hypothesis^[182,183] as the amphiphilic nature of many ions provides a basis for ordering as per ionic surfactants; open to question is whether the long (electrostatic) and short (vdW, π - π , Hbonding, solvophobic) range interactions can induce strong ion-ion association or selfassembly. To date, almost every known physical chemistry technique has been used to investigate structure in ILs.^[184] This has yielded a wealth of sometimes conflicting data. The aim of this review is to describe the evolution of models used to describe IL bulk structure.



Figure 16- Different models for the bulk structure of Ionic Liquids from left to right shows: free ions + ion pairs + holes, ion clusters, 3-D H-bonded network and bicontinuous nanostructures. See text for details. (Reprinted with permission from References [136], [172], [158], [242])

1.3.5 Structure in Protic Ionic Liquids

1.3.5.i Crystal Lattice Structure

Knowledge of the crystal structure provides direct insight into the way that the IL melts.^[185] In practical terms, this will facilitate 'anti-crystal engineering',^[186] to extend the range of salts that can be used as IL solvents. IL crystal structures may provide clues to ion arrangements in the liquid phase, in the same way it can for molecular solvents.

Only one paper has examined the crystal lattice structure of a genuine protic IL cooled below its melting point.^[187] Recently, the crystal structure of ethylammonium nitrate (EAN, m.p. 12°C) was reported by Henderson *et al.*^[187] and compared to that previously reported for ethylammonium chloride (EAC, m.p. 110°C).^[188,189] EAN's unit cell is shown in Figure 17and is composed of two lamellar-like cations layers with alkyl chains segregated together and ammonium groups pointing 'up' or 'down'. Half anions are situated between ammonium groups to form an ionic domain. The remaining nitrate ions are interspersed between cation alkyl groups. Based on this crystal structure, a lamellar-like liquid morphology may be expected in pure EAN and other primary alkylammonium protic ILs.



Figure 17- Crystal structure of EAN at 260K. C is grey, H white, N blue & O red. (Reproduced with permission of the PCCP Owner Societies, *Phys. Chem. Chem. Phys.* 2012, 14, 16041-16046)

Unlike EAC, there is insufficient free space between ions for a solid 'rotator' crystalline phases to form. This is because ions are packed too tightly in the unit cell for cations to rotate freely. Thus, EAN exhibits a simple transition upon melting between crystalline and liquid phases; at 285 K the thermal energy is sufficient for ion rotations / vibrations etc to disrupt the overall lattice structure and the compound melts.

Unpublished calculations by the Atkin group have shown the volume expansion for $\text{EAN}_{(s)} \rightarrow \text{EAN}_{(l)}$ phases is 17%, based on atomic volumes calculated by Hofman.^[190] This suggests hole theory may be suitable for modelling EAN's bulk structure, provided there is a associated decrease in the ion-ion spacings. However, similar comparisons between the crystal^[191] and liquid^[77] structures of methylammonium nitrate (MAN, m.p. 110°C) showed a slight *increase* in the ion-ion spacings upon melting.

1.3.5.ii H-bond networks, free ions and ion pairs

Evans *et al.* first suggested structure in EAN from a study of gas solubilities in EAN as a function of temperature.^[192] The phase transfer of rare gases and hydrocarbons from cyclohexane to EAN was accompanied by negative enthalpy and entropy values, similar to water. This led the authors to postulate that proton donor and acceptor sites on the ions may form a three-dimensional hydrogen bonded network resembling water (c.f. Figure 18). This hypothesis explained Evans and co. workers previous detection of cationic and non-ionic surfactant micelles in EAN^[193,194] as solvent hydrogen bonding is thought to be essential for inducing the solvophobic interactions^[70] that drive amphiphilic self-assembly. Thus, the high critical micelle concentrations (CMCs) reported in EAN (~5 times corresponding aqueous systems) is related to the structure of cation, with the ethyl hydrocarbon chain conferring extra stability to the dissolved hydrophobic groups of surfactant unimers.



Figure 18- Evans *et al.*'s model of (A) EAN & (B) water's H-bond network structure (Reproduced with permission from *J. Am. Chem. Soc. 103*, 481, Copyright 1981, American Chemical Society).

Slightly different conclusions about EAN's bulk structure were inferred from revelations of critical behaviour in solvent mixtures of EAN and octanol.^[195] Weingärtner *et al.* derived ion pair association constants from conductivity measurements that were one to two order of magnitude larger than predicted by Bjerrum's theory^[196] for ion pairs in aqueous solution. This suggested that liquid EAN is a chemical equilibrium of both ion pairs and 'free' ions:

$$Ion pair \stackrel{dissociation}{\longleftrightarrow} free anion + free cation \qquad Equation 15$$

The key conclusion, however, was that ion pairs are much more favoured in the pure IL bulk than in corresponding solutions of aqueous electrolytes. This was attributed to likely anioncation hydrogen bonding. In solution, the above equilibrium was shifted towards the left as hydrogen bonds were thought to stabilise the ion pair by shielding the long-range Coulombic forces in solution. Interestingly, static and dynamic light scattering (DLS) experiments in a follow up paper showed a EAN-octanol phase transition, consistent with Ising-like behaviour.^[197] Unlike similar phenomena in aqueous electrolyte solutions, a simple mean-field model could not be used to describe the transition. Thus, the authors postulated the contribution of short-range solvophobic interactions that induced "solvophobic demixing" of EAN and octanol. This is important, as it hints possible alkyl chain aggregation in EAN, which was not conclusively revealed until the results in Chapter 3. Dielectric relaxation spectroscopy (DRS) has revealed the fraction of ion pairs in EAN.^[198] The measured relaxation profile could only be fitted by assuming ~8% of all ions exist as contact ion pairs (and 92% as free ions). The lifetimes of these ion pairs was found to be in the order of 10^{-10} s at 298K. This is close to values for anion-cation coupling in molten alkali metal nitrates NaNO₃ and KNO₃, but much larger than in dilute aqueous electrolytes.^[199] The enhanced ion pairing in EAN was attributed to anion-cation H-bonds. Assuming no neutral species, the authors estimated the equilibrium constant for Equation 15 at 142.9.

Whilst Evans *et al.* and Weingärtner *et al.*'s hypothesis was never seriously disputed, hydrogen bonding in protic ILs such as EAN was only conclusively demonstrated by Ludwig and co. workers.^[52] They measured far-IR spectra of EAN, PAN and DMAN (dimethylammonium nitrate) in the region (30-600 cm⁻¹) that excites H-bond bending, stretching and vibrational modes in molecular liquids, is shown below in Figure 19.



Figure 19- Low-frequency vibrational FTIR spectra of ethylammonium nitrate (EAN), propylammonium nitrate (PAN), and dimethylammonium nitrate (DMAN) at 353 K. (Reproduced with permission from *Angew. Chem. Int. Ed.* 48, 3184 Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

Density functional theory (DFT) calculations enabled the spectra to be deconvoluted and specific H-bond interactions assigned. Bands between 199 - 224 cm⁻¹ and between 134 - 159 cm⁻¹ were attributed to the respective asymmetric (v_{as}) and symmetric (v_s) stretching modes of the N–H····O hydrogen bonds. Vibrational bands around 60–78 cm⁻¹ could be assigned to the H-bond bending modes. In every case, the frequency difference between the asymmetric and symmetric stretches was approximately 65 cm⁻¹. This suggested the three ILs have

comparable hydrogen bonding strengths. The PIL peak positions and frequency differences were remarkably similar to far-IR spectra of pure water. This lead the authors to conclude the PIL H-bond networks, whilst unlikely to be tetrahedral, are structurally reminiscent of water, c.f. Figure 20.



Figure 20- Network structures of EAN and water via DFT calculations. Blue lines connect N atoms in the EAN whilst red lines connect O atoms in water. Both liquids possess a 3D H-bond network, but a tetrahedral network is only present for water. (Reproduced with permission from *Angew. Chem. Int. Ed.* 48, 3184 Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

Subsequent measurements by the same group^[200] have quantified the strength of H-bond interactions in PILs using DFT calculations.^[201] The energy per ion pair for trimethylammonium nitrate (one H-bond donor) was found to be ~49 kJ.mol⁻¹ higher than tetramethylammonium nitrate (no H-bond donors), attributed to the formation of a single anion-cation H-bond. Notably, this value is more than double that of H-bonds in water (~22 kJ.mol⁻¹) and suggests PIL H-bonds strength is between "moderate" and "strong" using established H-bonds scales.^[202]

Together, these papers provide evidence of H-bonds formation in the bulk, likely in a network structure. However, the overall effect of H-bonds is markedly different to molecular liquids; rather than increasing cohesive interactions and inducing a more rigid liquid, H-bonds appear to fluidize protic ILs by weakening electrostatic forces between ions or introducing defects in the Coulomb lattice.^[56] This favours higher order arrangements eg. ion pairs, ion clusters or bicontinuous structures.

1.3.5.iii Ion Clusters

The liquid state has often been modeled as time-dependent molecular clusters of finite size and number. In water, for example, the solvent structure has been described (to varying degrees of success) as "flickering clusters",^[203] linear molecular chains,^[204] or larger, unspecified units implied from suggestions it is a mixture of high and low-density forms.^[137] Recently, Kennedy and Drummond^[205] made a similar suggestion for PILs bulk structure. They noticed curiously large ion clusters from electrospray ionisation mass spectrometry (EI-MS) experiments. In the positive ion spectrum for pure PILs, many singly charged aggregates in the form $C_nA_{n-1}^+$ were observed (C = cation, A= anion), with the $C_8A_7^+$ mass/charge (m/z) peak dominant in EAN and PAN.

The negative ion EI-MS spectrum of the same PILs showed a different m/z aggregation pattern, but with no dominant univalent aggregates. From these results, the authors proposed the bulk structure of PILs such as EAN and PAN is a polydisperse mixture of aggregated ions, with the $C_8A_7^+$ cluster most prominent. This suggests a spherical clusters in the bulk that could account for their general "poor" ionic behaviour (c.f. Figure 3).^[43]

Ab initio quantum calculations by Ludwig supports these findings and showed that the $C_8A_7^+$ aggregate was thermodynamically favoured for EAN in the gas phase.^[206] The aggregate structure is presented in Figure 21, and was suggested to be the most stable species on enthalpic and entropic grounds because it formed the most compact H-bond network.

An alternate explanation is that the aggregate structure is an artefact of the input parameters in *ab initio* calculations. For example, density functional theory calculations on gas phase clusters of EAN, PAN and butylammonium nitrate (BAN) show slightly different ion arrangements, with no stabilization of $C_8A_7^+$ aggregates.^[207] Likewise, femtosecond infrared spectroscopy (fs-IR) suggest the H-bond network in EAN is not compact as assumed by Ludwig, as the ammonium group can reorientate in large angle jumps.^[208]



Figure 21- Structure of the $C_8A_7^+$ aggregate (C = cation, A= anion) via *ab initio* quantum calculations C atoms are orange, H white, and N blue whilst anions are represented as red spheres. (Reproduced with permission from *J. Phys. Chem. B* 113, 15419 Copyright 2009, American Chemical Society)

The violent nature of fragmentation in a MS experiment may contribute to cluster detection. Thus, polydisperse aggregates in the EI-MS spectra may not be evidence for underlying structure in the PIL bulk. Notably, similar fast atom bombardment MS experiments of EAN yielded a very different aggregate distribution, with no evidence of $C_8A_7^+$ clusters.^[209,210] In the original EI-MS paper,^[205] the ion aggregates were conspicuously absent when EAN was dispersed in acetone. This finding cannot be reconciled with other data, (including by the same group),^[211,212] which indicate PIL solution structure is quite robust when mixed with molecular solvents; there is no reason to suggest bulk aggregate formation should be switched off when mixed with a non-H-bonding solvent.

Ion clusters were suggested by Wakeham *et al.*^[213,214] based on X-ray reflectivity (XRR), sum frequency spectroscopy (SFG) and neutral impact collision ion scattering spectroscopy (NICISS) experiments of the IL-air interface. The XRR spectra decayed more rapidly than expected for a perfectly smooth surface, indicating a rough, diffuse interface with significant gas interpenetration. The level of roughness could not be explained by liquid capillary

waves.^[215-217] The interfacial structure was postulated to be dotted with small, dynamic clusters of anions and cations in which the short alkyl moieties surround the charged core in a roughly spherical geometry. The SFG and NICISS data support these conclusions, as the hydrophobic alkyl groups were shown to interact exclusively with the air phase, shielding the charged groups subsurface. Such a structure is consistent with the clusters in Figure 21 based on the EI-MS data. This suggests that the enormous air-liquid surface area created upon ionizing solvent droplets in contributes to aggregate detection. Thus, it is possible that the EI-MS detects clustered structure at the IL air-liquid interface, rather than the bulk.

Separovic et al. have used nuclear magnetic resonance (NMR)^[218] experiments to show temporal ion aggregates in eleven protic ILs with ammonium based cations (dialkyl-, trialkyl-& alcohol-functionalised) paired to either dibuytlphosphate (BuO)₂PO₂, methansulfonate (MeSO⁻), sulfamic (OS⁻) acetate (AcO⁻) or formate (Fm⁻) anions. The pulsed gradient spin echo NMR data was obtained under high (500 MHz) and low (18.3 MHz) fields, and suggested strong ion association in the bulk, not consistent with a solution of free dissociated ions. As the exchange between ion states is faster than the probe resolution, it was not possible to distinguish between aggregation states with NMR. However, in every IL, selfdiffusion coefficients of anions and cations closely mirrored one another, despite large differences in ion sizes. Similar findings for ions dissolved in molecular liquids have been attributed to ion pairing.^[219] This suggests that, on average, the (anion + cation) move together through the IL bulk. Complementary NMR relaxation measurements indicated that ion association was more complicated than simple ion pairs, as long-range dynamic interactions were evident. For example, evidence of non-polar groups aggregating into clusters was observed for sufficiently amphiphilic ammonium cations. In Figure 22, the dynamic relaxation motions of all carbons (C_1-C_4) in the $[Bu_3N]^+$ cation are roughly equal Unlike other ILs studied, this indicates a rigid alkyl cation chain, likely due to aggregation of non-polar groups into clusters. The low field NMR data showed evidence of deviation from Stokes-Einstein behavior. This was related to formation of H-bonded aggregates with lifetimes shorter than characteristic timescales of ion diffusion. This is consistent with dynamic heterogeneity in colloidal^[220,221] or H-bonding^[221-223] liquids.



Figure 22- Relaxation times (T₂) of carbons C_x in the $(BuO)_2PO_2$ - anion when paired with four different cations. In $[Bu_3N][(BuO)_2PO_2^-]$, relaxation times are approximately equal, suggesting alkyl chain clusters. (Reproduced with permission from *J. Phys. Chem. B* 114, 11443 Copyright 2010, American Chemical Society).

A complementary rheology study Separovic *et al.* revealed many of the same protic ILs formed aggregates of dimensions larger than ion pairs. The ability for ILs to aggregate related to the capacity for cations to H-bond.^[224] These aggregates could be broken at high shear rates, and made smaller and less cohesive at higher temperature. The effect of water was also probed and showed that whilst the aggregate structure was likely invariant, but that the number of them decreased with increasing dilution.

1.3.5.iv Mesoscopic Nanostructures

Clear evidence of bicontinuous protic IL nanostructure was elucidated in two complementary small angle neutron scattering (SANS)^[225] and large angle X-ray scattering (LAXS)^[226] papers. In the first of these, by Atkin and Warr, a single SANS structure peak was measured for both EAN q= 0.66 Å⁻¹ and PAN q= 0.54 Å⁻¹ at 45°C (c.f. Figure 23A and Figure 23B). From the Bragg equation, the peaks at q= 0.66 Å⁻¹ and q= 0.54 Å⁻¹ corresponds to respective internal liquid Bragg spacings D ($=2\pi/q_{max}$) of 9.7 Å and 11.6 Å respectively, indicating repeat structure within the liquids on this length scale. This is significantly larger than the ethylammonium or propylammonium cations, nitrate anions or ion pair dimensions, and so cannot be attributed to scattering from single ions in these fluids. Rather, the distance is consistent with twice the calculated ion pair dimension (2 × 5.3 Å for EAN and 2 x 5.6 Å for PAN), which suggests that correlations between adjacent ion pairs are propagated through the ILs. The SANS data were fitted using the smectic model of Nallet *et al.*^[227] and are best described as locally alternating polar-apolar layers. This suggests these protic ILs are structurally heterogeneous, due to ion self-assembly. The results could not be fit to spherical aggregates of charged headgroups or alkyl tails from known scattering length densities.



Figure 23- SANS spectra for (A) pure partially deuterated EAN and (B) pure partially deuterated PAN at 45°C. The solid red lines shows smectic model fits from Nallet *et al.*^[227] (Reproduced with permission from *J. Phys. Chem. B*, 112, 4164, Copyright 2008, American Chemical Society)

Umebayashi *et al.*'s LAXS findings^[226] are consistent with the disordered lamellar structure of EAN presented by Atkin and Warr. Scattered X-ray intensities $I_{obs}(2\theta)$ were recorded over the 2 θ range 1.6–145°, corresponding to the scattering vectors Q (= $4\pi \sin \theta / \lambda$) between 0.25 – 16.86 Å⁻¹. The wider angles employed allowed intramolecular as well as intermolecular spacings to be probed. The location of the intermolecular structure peak (0.62 Å⁻¹) is consistent with Atkin and Warr's data (0.66 Å⁻¹). Molecular dynamics simulations of 256 ion pairs generated theoretical partial pair correlation functions for EAN, in reasonable agreement with the experimentally derived g(r) values.

Further indirect suggestions of a bicontinuous nanostructure in EAN and PAN have been reported from techniques that probe solvent dynamics, namely optical Kerr-effect (OKE) and dielectric relaxation spectroscopy (DRS).^[228] Because the alkylammonium cations have a permanent dipole and are weakly polarisable, it is sensitive to DRS. Conversely, OKE is suitable to study the nitrate species as it does not bear a permanent dipole and the negative charge is highly polarisable and anisotropic. Measured solvent relaxation could only be explained by a network of cooperative H-bonds between NH₃⁺ protons and nitrate oxygens. Ion dynamics were complex, and did not follow the Stokes-Einstein-Debye model for single molecules diffusing through a homogeneous solvent. This implies an inhomogeneous bulk structure for both liquids, with the alkyl chains aggregated together. The small deviation from non-Arrhenius behaviour suggested that the degree of aggregation of uncharged groups is low compared to other long chain (C₈ – C₁₂) aprotic ILs.

An ethyl moiety appears to be the smallest alkyl chain that induces mesoscopic structure. Recent *ab initio* MD simulations^[77] for methylammonium nitrate (MAN, m.p. 110 °C) revealed no evidence of methyl-methyl aggregation characteristic of a bicontinuous structure. This liquid was best described as a continuum of ions vibrating in long-lived ion pair cages.

1.3.5.v Micelle-like Nanostructure

Greaves *et al.*^[229] used small- and wide-angle X-ray scattering (SAXS and WAXS) to examine structure in a range of protic ILs with alkylammonium, dialkylammonium, trialkylammonium, and cyclic ammonium cations combined with organic or inorganic anions. The peaks in the scattering spectra were consistent with intermediate range order. The SAXS/WAXS data was interpreted as evidence for a globular, micelle-like nanostructure. This represents a slight departure from the bicontinuous model proposed by Atkin and Warr or Umebayashi *et al*; instead of interconnected polar/apolar domains, the ions were thought to form discrete hydrophobic cores surrounded by an intervening medium of charged polar regions (c.f. Figure 24A).



Figure 24- Greaves *et al.*'s schematic illustration of micelle-like nanostructure in (A) pure butylammonium nitrate (BAN) and (B) BAN + H_2O mixture. (Reproduced with permission from *J. Phys. Chem. B*, 115, 2055 Copyright 2011, American Chemical Society)

In general, two correlation lengths were evident in the SAXS/WAXS spectra; Peak 1 at low q $(< 1.0 \text{ Å}^{-1})$ and Peak 2 at higher q $(> 1.0 \text{ Å}^{-1})$. The correlation length of Peak 1 is consistent with bulk nanostructure. Peak 2 was ascribed to correlations between nearest neighbour cation alkyl chains in the hydrophobic regions of the micelle. Thus, changes in the position and intensity of Peaks 1 and 2 across different PILs enabled simple relationships between solvent nanostructure and ion types to be elucidated. It was found that Peak 1 moved to lower q (longer distances) and became sharper for longer cation alkyl chains, shown in Figure 25B. This is analogous to a swelling of the micelle units, increasing the distance between polar regions across the hydrophobic core. However, as shown in Figure 25B, Peak 1 was not detected at all when a hydroxyl moiety was attached to the cation alkyl chain. Similar results were also obtained for methoxy functionalised and sterically hindered ammonium cation centres. Both these results suggested bulk nanostructure is more pronounced with increasing cation amphiphilicity. The choice of anion also influenced Peak 1, with intensities in the order of nitrate > glycolate > formate, although the structural reason for this order could not be determined.



Figure 25- Effect of (A) cation alkyl chain length and (B) hydroxyl group addition on SWAXS data. In (A), spectra for ethylammonium nitrate (EAN), propylammonium nitrate (PAN), butylammonium nitrate (BAN), and pentylammonium nitrate (PeAN). Peak 1 is evident in EAN data in (B), but absent in the corresponding EOAN spectra. (Reproduced with permission from *J. Phys. Chem. B*, 114, 10022 Copyright 2010, American Chemical Society)

Monitoring Peak 2 as a function of temperature showed a 1 Å increase in the distance between alkyl chains upon heating from 25°C to 50°C. The shift in Peak 2 position as a function of cation alkyl chain length was between one and two times that predicted by the Tanford equation^[131] (c.f. Figure 26A). For each additional -CH₂- in the alkyl chain the size of the repeat spacing in the IL increased by 2.3 Å. This corresponds to a contribution of 1.15 Å from each alkyl chain since the intermediate range order is a measure over two cations. This suggests the alkyl chains are somewhat interdigitated or not fully extended in the micelle structure.

The Drummond group have since published numerous SAXS and WAXS spectra for protic ILs systems including neat PILs^[229], fluorous PILs,^[50] PIL solvent mixtures; PIL+PIL^[211], PIL+water (c.f. Figure 24B) ,^[212] PIL+ Bronstead acids or Bronstead bases,^[212] PIL+alcohol^[211] or PIL+alkane,^[211] and complex mixtures; PIL+C₁₂E_n surfactants^[230] [C₁₂E_n = non-ionic dodecyl poly(ethylene oxide)].



Figure 26- (A) SAXS / WAXS peak 1 position, for the ethyl-, propyl-, butyl-, and pentyl-ammonium formates and nitrates. The calculated comparison of 1 and 2 times the cation length L is included as dotted and solid lines, respectively. (B) shows raw SAXS / WAXS spectra for a series of pentyl-ammonium nitrate and water mixtures. (Reproduced with permission from *J. Phys. Chem. B*, 114, 10022, Copyright 2010 American Chemical Society and *J. Phys. Chem. B*, 115, 2055, Copyright 2011 American Chemical Society)

The SAXS / WAXS peak positions and intensities were systematically characterised as a function of ion structure or solvent / solute dissolution. This has lead to development of structure-property relationships for protic ILs based on solvation model of solutes incorporated into the IL solvent micelle. For example, the solubility of linear alkanes in the IL was shown to be related to calculated size of the micelle's non-polar domain; if the soluble alkyl chain lengths was smaller than the hydrophobic domain size, it was soluble. Alcohols displayed different behaviour as they were generally soluble in the PILs across all concentrations. Two scenarios were noted. If the alcohol alkyl chain was of comparable length to the non-polar domain, the hydrophobic and hydrophilic groups of the alcohol were incorporated into the solvent domains without changing the overall nanostructure. When the alcohol alkyl chain was long relative to the PIL cation, indicating a swollen non-polar domain of ions + alcohol aggregates was formed.

1.3.6 Structure in Aprotic Ionic Liquids

1.3.6.i H-bonds, Liquid Crystals and the Solid state

The liquid structure of aprotic ILs was initially inferred from the crystal structure of similar solid state analogues; the local ion arrangements in the liquid phase were assumed to be similar to the solid or liquid crystal state. Thus, melting was thought to induce a similar behaviour to molecular liquids, where a structured crystal phase decays into an isotropic liquid. Conclusions of early influential reviews by Welton "[ILs] are unlikely to have great differences in their structures and interionic interactions (compared to molten salts)"^[231] or Dupont "1,3- dialkylimidazolium [ILs] possess analogous structural patterns in both the solid and liquid phase... although significant randomness in organization is necessary to describe the structure of a liquid"^[232] are typical of this prevailing opinion.

1-alkyl-3-methylimidazolium ILs [C_nmim]X (where n = 12-18) have been shown to arrange into well-defined crystal lattices. The overall structure of these IL liquid crystal phases is best described as sheets of imidazolium rings and counter anions, separated by a domain of interdigitated alkyl chains. In many cases, the crystal lattice supported a H-bond network.^[233] The layer-layer separations in the crystalline phases range from 24-33 Å. This structure is strikingly similar to liquid crystalline alkylammonium and alkylpyridinium salts^[234,235] or the planar stacking of 1-ethyl-3-methylimidazolium ions in the earliest report of air- and water stable aprotic ILs.^[60,236] Notably, the anion strongly influenced the interlayer distance in the order CI⁻ (smallest separation) > Br⁻ > BF₄⁻ > OTf⁻ > TFT (largest separation) consistent with their relative ability to form a 3D H-bond network.^[39] Cation bilayer formation is observed in the crystalline and smectic liquid crystalline phases (c.f. Figure 27),^[41] supported by a network of H-bonds. Complementary NMR studies showed the H-bond network was largely anion dependent, as showed that the cation has limited H-bond donors (H2, H4 and H5 positions), that prefer to form in the plane of the imidazolium ring.^[237,238]



Figure 27- Unit cell of $[C_{12}mim]PF_6$ (m.p. 55°C). ([*Journal of Materials Chemistry*, 1998, 8, 2627-2636] Reproduced with permission of The Royal Society of Chemistry)

The conformation of the cation alkyl chains in the bilayer-like structures produced different crystal polymorphs. For instance, x-ray diffraction showed multiple polymorphs could be obtained from 1-butyl-3-methylimidazolium (C_4 mim⁺) cations paired with Cl⁻, Br⁻, Γ , [BF₄]⁻ or [PF₆]- anions.^[239] Monoclinic or orthorhombic crystals of C₄mim[X] ILs were possible, depending on whether the butyl group adopted a *trans-trans* or *gauch-trans* conformation. Complementary raman spectroscopy measurements revealed a equilibrium of both structures was present in the bulk, and that interconversion between the two may be responsible for the melting points < 100°C as it hinders crystallization.^[240,241]

Anions can also have different rotational conformations in the bulk crystal. X-ray diffraction showed the popular non-coordinating bis(trifluoromethanesulfonyl)imide anion (Tf₂N) in C_1 mim[Tf₂N] in adopts the *cis* conformer in the crystal phase.^[242] This crystal geometry is rationalised by bifurcated cation–anion C–H····O hydrogen-bonds. Interestingly, later neutron diffraction measurements by Hardacre *et al.* revealed the *trans* geometry is favoured in the bulk liquid,^[243] suggesting the *cis* form is more a result of ion close packing in the lattice.

1.3.6.ii Ion pairs or free ions

Ion pairs are the simplest repeating unit in ILs. Thus, it is tempting to depict local arrangements in terms of the likely ion pair structure. Sophisticated quantum mechanics

(QM) or density functional theory (DFT) calculations have been extensively used to this end, optimizing both electronic and molecular structure.^[244-247] For example, the Cl⁻ anion can sit above/below the plane of the C₄mim⁺ cation ring, to interact via Coulombic interactions (c.f. Figure 28). Positions in the plane of the ring, particularly in front of the C2 carbon, are also favoured due to anion-cation H-bonds. Interestingly, these H-bonds are relatively long (>2.5Å) and non-linear (<165°) relative to the ideal H-bond arrangement. Theoretical calculations suggest both conformations are present because reduced electrostatic attractions in the ion pair enables other H-bonding driven structures to form. IR spectroscopy data is consistent with this as a proportion of H-bonds conformers explains the lower than expected vibrational red shift in anion-cation interaction.^[248]



Figure 28- Coulombic (left) and H-bonded (right) anion-cation interaction from *ab initio* molecular orbital calculations. Coulombic interactions favour the anion to be located above or below the imidazolium ring whereas H-bonded anions interact with the H2 hydrogen. (Reproduced with permission from *J. Phys. Chem. B*, *115*, 14659, Copyright 2011 American Chemical Society)

There is conflicting experimental evidence for the existence of ion pairs in the IL bulk. Most studies suggest that the concept, while useful for electrolyte solutions, is not easily transferrable to neat ILs. Multinuclear NMR studies with $C_2 mim[X]$ ILs where (X= Cl⁻, Br⁻ and Γ) have suggested contact ion pairs form in the pure IL, in a quasi-molecular state stabilised by strong H-bonds.^[249] Likewise, a model for the bulk structure of $C_4 mim[I]$ based on ion pair formation was suggested from absorption spectroscopy.^[250] Indirect evidence was also inferred from transport properties of dialkylimidazolium ILs, related to the degree of charge localization on the anion.^[251]

However, the weight of scientific evidence is not consistent with a simple ion pair model for IL bulk structure. Dielectric spectroscopy data for a range of aprotic ILs (imidazolium^[252] pyrrolidinium,^[253,254] pyridinium,^[253] tetralakylammonium^[253] and triethylsulfonium^[253]) revealed no signatures of ion pair formation. This technique is highly sensitive to picosecond-to-nanosecond liquid dynamics, and so should be able to probe orientational relaxations of ion pairs or similar aggregates if they were present. Also, ion pairs were not detected in corresponding NMR measurements that investigate structure on microsecond-to-milliseconds.^[255] Thus, if they exist, the lifetimes of any potential ion pairs must be less than a few picoseconds.^[61]

These conclusions are in accordance with recent MD simulations that explored possible ion pair formation in imidizaolium ILs.^[256-258] For C₄mim[PF₆],^[256] The cation-anion interaction was best described using the concept of an *ion association* rather than an ion pair as each ion is not coupled to one counterion in the ionic atmosphere. Further simulations by Lynden-Bell^[258] showed the formation of anion+cation, anion+anion or cation+cation ion pairs is not important for describing bulk IL structure. These units are only weakly stabilised in pure ILs due to the small physical separation of ions in the bulk. This suggests that the origin of ion pair destabilization is to do with the overscreening of electrostatic charge in first solvation shell. As multiple co- and counter ions can inhabit this region, mutual attraction in a given ion pair is weak, so pairs readily dissociate into individual ions when they form.

Likewise, for most ILs, modelling the bulk as a continuum of anion/cation couples migrating together cannot be reconciled with their characteristically low vapour pressures. Properties such as vapour pressure are controlled by ionicity, as represented in a Walden plot of molar conductivity *versus* fluidity. In isolation, the ion pair unit is neutral and thus will not contribute to measured solvent conductivity. Therefore, ILs with high proportion of ion pairs or larger neutral aggregate structures (§1.3.6.iii) should be "poor" because the conductivity

will be less than expected from their viscosity. However, most common aprotics are "good" ILs with low vapour pressures.^[259] The classical explanation of this is that ions must be distributed in a relatively uniform manner in the bulk with each ion surrounded by a shell of opposite charge.^[47] An interesting counter example was recently reported by MacFarlane *et al.*^[260] who showed a novel class of phosphonium-based aprotic ILs with chloride or sulfonyl amide anions do not behave as "good" or "poor" ILs. Their position on the Walden plot is best described as a liquid ion pair compounds. Such strong ion-ion association represents an interesting intermediate state between molecular solvents and ILs.

Unlike the pure systems, many reports have suggested ILs form ion pair structures when dissolved in molecular liquids. Besides the body of work in IL+water mixtures,^[261-268] many other molecular solvents appear to support IL ion pairs. NMR measurements on C₂mim[X] ILs mixed with propionitrile indicate long lived anion-cation units.^[249] For the same ILs in non-polar solvents like trichloro- and dichloro-methane, π - π stacking between C₂mim⁺ cations becomes increasingly important, and anion-cation ion pair association is lost at the expense of cation-cation pairs. Contact and solvent separated anion-cation ion pairs were observed in ¹H-NOESY NMR studies of C₄mim[BPh₄] dissolved in DMSO and CDCl₃ respectively.^[269,270] Similar results have been obtained for slightly wet C₄mim[BF₄], and [C₄mim]BF₄ + DMSO mixtures.^[271] MD simulations of C₄mim[PF₆] with naphthalene^[272] and other aromatics^[273] showed anion-cation and cation-aromatic ion pairs across at a range of solute concentrations.

Elegant chemical confirmation of these results has been reported Welton & co workers.^[274] This group compared S_N2 reaction kinetics in ILs with IL+molecular solvent mixtures. The S_N2 reaction used incorporated an ionic electrophile, and thus the reaction mechanism relies upon ion pair formation in the bulk. Ion pairs were deduced to be present in IL+molecular solvent mixtures, leading to fast, non-linear partial-order kinetics. In contrast, slow, pseudo
first-order kinetics was observed from the same reaction in the neat ILs. This suggests the ion pairs concentration is insignificant compared to the population of free or networked ions. The absence of a charge-transfer peak in the UV absorption spectrum of ionic probes dissolved in the pure ILs is consistent with this, and points to time-averaged uniform ion association.

Thus, whilst transient as ion pairs may exist in pure ILs with lifetimes less than a few picoseconds, the bulk structure appears to be more complicated than a continuum of anion/cation couples in solution.

1.3.6.iii Ion Clusters

Similar to protic ILs (§ 1.2.5.iii) and molecular solvents, there have been some attempts to describe the bulk structure of aprotic ILs in terms of ion clusters. There is no set criteria to define an ion cluster; distinguishing between an ion pair and an ion cluster is arbitrary.^[255] Much of the early work was summarized in an influential review by Dupont, who postulated that ILs form a clustered supramolecular structure in order to maintain a 3D H-bond network.^[232] Thus, dissolving solutes in the bulk disrupts the H-bond network as per solutes in water, and may lead to selective solvation by the polar and non-polar groups (§ 1.3.6.iv). ESI-MS measurements fragment the bulk IL and analyse the mass/charge ratio of resulting ion assemblies.^[275-280] Strong conclusions are proposed in these papers, including a set of "magic" numbers for anion/cation interaction^[275] or empirical scales for ion association.^[276] In general, large [C_nmim]_a[A⁻]_b neutral aggregates were present for *a* and *b* values between 2-5. Even larger polymeric ion clusters have also been reported from fast atom bombardment mass spectrometry (FAB-MS) experiments.^[281] However, as outlined previously (§1.3.5.iii), MS studies are somewhat invasive and the ion clusters observed may provide more insight into the IL-gas interface rather that the bulk liquid structures.

Evidence for ion clusters has been provided by IR and raman spectroscopy experiments.^[236,282-286] These studies suggest small, fluctuating H-bonded aggregates are present in the bulk, often in a conformational equilibria with two or more rotational forms. *Ab initio* or DFT calculations of one or two cluster units accurately reproduced the measured IR and Raman spectra, thus identifying the absorption bands of different ion-ion interactions. Frequency shifts, due to stronger / weaker than expected associations, could be predicted and compared to similar studies for molecular solvents.^[287] The combination or IR / Raman spectroscopy and simulation data enables the mechanism by which H-bonds stretch and bend in ILs to be elucidated, the average ion binding energies in the bulk could be gauged for different species, and correlated to macroscopic physical properties.

NMR has also been used to suggest possible ion clusters in aprotic ILs.^[255] This technique was first employed by the Wilkes group, in series of classic papers on aluminium chloride based ILs.^[288,289] The reported ¹H and ¹³C chemical shifts suggested ion-ion interactions more complex than simple ion pair association. They proposed an IL model built upon oligomeric chains in which each ion interacts with two or more ions of opposite charge. Later publications by Hussey^[290] and Watanabe *et al.*,^[291] using more powerful instruments, questioned these conclusions because the expected signature signal splitting from single ions and/or ion aggregates was not observed. This meant that the rate of exchange between ions and their aggregates was faster than the probe timescale. Tokuda *et al.* have suggested one way around this by calculating the $\Lambda_{imp} / \Lambda_{NMR}$ ratio from NMR ionic self-diffusion coefficients as this may be used as quantitative evidence for ionic aggregates in ILs. This suggests that the NMR is likely unsuitable to probe cluster formation in the IL bulk, as the timescales of interest are much smaller than the instrument resolution; only time averaged ion solvation can be detected.

1.3.6.iv Mesoscopic nanostructures

One of the most intriguing suggestions to emerge in recent years is that liquids, in particular aprotic ionic liquids, are structurally hetereogeneous in the bulk, corresponding to domains of intermediate or mesoscopic range order.^[183] ILs are ideal solvents materials to test this hypothesis as the ions are often amphiphilic and can exhibit a range of solvent polarities.

The nature of the ion arrangements in aprotic ILs is a matter of debate. In many respects, the scientific literature parallels that described previously for protic ILs, where researchers formed two camps: sponge-like bicontinuous nanostructures (\$ 1.3.5.iv) or globular micelle-like nanostructures (\$ 1.3.5.v). There is also a third community that suggests the mesoscopic nanostructure is not justified and only smaller scale arrangements are present in aprotic ILs e.g. clusters, ion pairs, free ions. Whilst this Thesis concerns mesoscopic nanostructure in protic ILs, many more papers have been published on arrangements in aprotic ILs, and both types share a common structural origin for ion self-assembly. This discussion follows an approximately linear timeline of literature publications and surveys theoretical, experimental studies and complementary (simulation + experimental) approaches. The review is largely restricted to 1-alkyl-3-methylimidazolium [C_nmim]⁺ aprotic ILs, although important examples of structure in other ion systems are examined where relevant.

Compton *et al.* made the first suggestion of a mesoscopic solvent structure in aprotic ILs.^[292] Diffusion coefficients of three electroactive solutes dissolved in aprotic ILs were measured as a function of water content. Large differences were observed for the diffusion of neutral and charged species when comparing 'wet' (up to 25.2 wt% water) IL samples. The authors concluded that binary IL-water mixtures "may not be regarded as homogeneous solvents, but have to be considered as nano-structured with polar and nonpolar regions." The research did not extend the research to 'dry' (i.e. no water) systems, and another six years elapsed before of mesoscopic structure was reexamined.

Mesoscopic structure was revealed in MD simulations for $[C_n \text{mim}]PF_6$ (n= 6,8,10,12) by Margulis.^[293] For the two longer chain ILs, structures reminiscent of reverse micelles were noted. The spherical anion attracted five or so cations such that the imidazolium heads solvate the negative charge and alkyl chains are expelled outwards, producing a structure of dynamic spherical-shaped aggregates with a polar interior and apolar exterior. This study also indicated long-lived, nm sized voids in the bulk. The presence of voids or cavities between molecules has often been associated with hetereogeniety in disordered phases^[294,295] and pure liquids,^[296] yet the implications for hole theory (§1.3.3.iii) were not explored. The void dimensions increased with length of the alkyl chain, which would not be predicted from Equation 11 given that γ_{LV} decreases with n.^[297,298] As the calculated holes size based on known γ_{LV} values for [C_nmim]PF₆^[298] are ~2-3 times larger than observed in the simulation, it is unlikely hole theory is applicable for describing the bulk structure of aprotic ILs.

By 2006, three independent molecular dynamics (MD) simulations suggested aprotic ILs arrange in mesoscopic nanostructures. The initial article by Wang and Voth,^[299] used a multiscale course-grained (MS-CG) computational approach to explore the effect of various cation alkyl chain lengths C_n , on 1-methyl-3- C_n -imidazolium nitrate type aprotics (for n=1-4,6,8). The atoms of unique cationic functional groups (imidazolium ring, methyl, methylene moieties) were represented as a series of connected, spherical 'sites' of defined volume, partial charge etc. The NO₃⁻ anion was treated in a similar manner, but could be modeled as a single site with a partial charge of -1. The simulations were run at 400 K and 700 K with 64, 400, and 800 ion pairs. The cation headgroups and anions are distributed relatively homogeneously in the bulk, but crucially, the tail groups aggregated together to form spatially heterogeneous domains. This effect was more pronounced for longer alkyl chains, suggesting ion amphiphilicity is an important factor in IL structure. For n=1-3, tail aggregation was only weakly apparent as electrostatic screening was thought to dominate.

Urahata and Ribeiro^[300] employed a united-atom model for imidazolium aprotics ILs and derived static structure factors at 323 K for 200 ion pairs. The simulations were consistent with intermediate range order, but the structural effect of different anions (F^- , CI^- , Br^- , PF_6^-) could not be not resolved. g(r) data related to cation tail aggregation was more pronounced for increasing alkyl chain, consistent with a more segregated structure.

Later MD simulations by Canongia Lopes *et al.*^[301] supported the basic picture of Wang and Voth^[299] and Urahata and Ribeiro,^[300] but with a few important differences. A more complex all-atom force field protocol enabled atomic resolution of ion arrangements in imidizaolium-based ILs. The charged domains in the liquid formed a continuous three-dimensional network of ionic channels. These regions coexisted with uncharged domains; for short alkyl groups (C₂) small, globular hydrocarbon 'islands' form within the (continuous) polar network. Increasing the alkyl chain length (C₆, C₈ and C₁₂) enabled the hydrocarbon globules to interconnect in a bicontinuous sponge-like nanostructure. The butyl side chain (C₄) denotes the transition between the two morphologies, as it is sufficiently amphiphilic to connect non-polar domains in the bulk. This is shown in Figure .



increasing arkyr chain length

Figure 29- Snapshots of the bulk structure of $[C_n mim][PF_6]$ ILs for *n*=2-12. Each box shows 700 IL ion pairs at equilibrium with polar domains (red, anion + cation imidazolium ring) and non-polar domains (green, cation alkyl chain) observed. Note, the box dimensions are not the same length due to differences in ion size and box density. (Adapted with permission from *J. Phys. Chem. B*, 110, 3330, Copyright 2006 American Chemical Society)

Recent simulations by the Canongia-Lopes group have shown that different bicontinuous nanostructures can be obtained by varying cation geometry from imidazolium (C_nmim^+) to trialkylmethylammonium ($N_{1,n,n,n}^+$) to tetraalkylphosphonium ($P_{n,n,n,n}^+$).^[302] Close comparison across all the simulations can be made as the [NTf_2^-] anion was kept constant. These studies emphasize the importance of the volume ratio of charged : uncharged groups (V_{alkyl} : V_{polar}) and the relative position of V_{alkyl} groups on the cation. V_{alkyl} : V_{polar} loosely defines a packing ratio in the bulk phase. In principle, larger V_{alkyl} : V_{polar} values are increasingly amphiphilic and enforces a stronger segregation of polar and apolar domains. The relative position of V_{alkyl} on the cation controls the number and position of anions around the cation, and thus influences the connectivity of the polar domains.

In $C_n mim^+$ salts, the alkyl groups point away from imidazolium headgroup in a trans-trans conformation between n=2 to n=8. The V_{alkyl} : V_{polar} ratio is therefore directly proportional to ion amphiphilicity, and facilitates neater segregation of the polar and apolar groups in the bulk. Thus, $[NTf_2^-]$ -based ILs arrange similar to corresponding $[PF_6^-]$ systems (Figure), transitioning from a globular to bicontinuous nanostructures. Notably, $[NTf_2^-]$ is slightly larger than the $[PF_6^-]$ and so a hexyl rather than a butyl alkyl chain marks the V_{alkyl} : V_{polar} ratio required for a bicontinuous apolar network.^[302] Also, the $C_n mim^+$ has potential for directional H-bonding interactions principally at the C2 but also from the C4 and C5 ring sites. This enhances the connectivity the polar domain as each $C_n mim^+$ ring can interact with multiple anions in the bulk.

The three long, symmetric alkyl groups in trialkylmethylammonium ILs (tributyl-, trihexylor trioctyl-) induces a reasonably well-defined layers of polar and apolar domains,^[303] consistent with earlier SAXS study that suggested disordered smectic-A phases in $[N_{1,n,n,n}^+][NTf_2^-]$ salts.^[304] A flatter, more layered structure is expected on geometric grounds in $[N_{1,n,n,n}^+]$ ILs as V_{alkyl} : V_{polar} is higher. However, cation solvation plays a key role in bulk organization. Anion arrangements around the $[N_{1,n,n,n}^+]$ are more restricted compared to imidazolium ILs; unlike $C_n mim^+$, the anions favour only one site, directly behind the $[N_{1,n,n,n}^+]$ methyl group, on electrostatic grounds. This means that on average fewer $[NTf_2^-]$ anions associate with each cation which reduces connectivity of polar domains. Hence, the increase in V_{alkyl} is not shared uniformly around the cation and the long alkyl chains are forced away from the polar domain and aggregate tail-to-tail in a lamellar-like structure.

MD simulations of tetraalkylphosphonium ILs $([P_{n,n,n,n}^+][NTf_2^-])$ reveal different structures compared to $[C_nmim][NTf_2^-]$ or $[N_{1,n,n,n}^+][NTf_2^-]$.^[302] Because each cation's P centre is uniformly surrounded by alkyl chains, increasing V_{alkyl} : V_{polar} makes the cation larger but not more amphiphilic, and poorly-defined thread-like network structures form. The anions sit between the alkyl chain threads, and are more likely to be paired up with a single cation.

Triolo and co. workers^[305] provided the first unequivocal experimental evidence for aprotic IL mesoscopic structure. X-ray diffraction (XRD) was used to examine the consequence of varying alkyl chain size (n) and anion in [1-methyl-3-C_n-imidazolium][X] aprotics ILs (where X is either Cl⁻ or BF₄⁻ and n = 3, 4, 6, 8, 10). The XRD spectra at 298 K exhibited a peak for aprotics ILs with $n \ge 4$, corresponding to a repeating spacing in the IL. The increased intensity and decreased q_{max} peak width with higher n values (c.f. Figure 30), suggests the level of nanoscopic structure is enhanced with longer alkyl chain lengths. An peak was not observed for the propyl (C₃) species. Altering the anion from the Cl⁻ to the larger, tetrahedral BF₄⁻ had no discernible effect on the diffraction spectra. This implies that the cation non-polar groups play the dominant role in aprotic IL bulk structure.

The effect of temperature on 1-methyl-3-octyl-imidazolium tetrafluoroborate ($[C_8mim][BF_4]$) between was examined 90-290 K, which covers the liquid and glass-states of this IL. In



Figure 29A, a clear temperature dependence is noted for the correlation peak at low-q, with the size of repeat length-scale increasing (lower q) with decreasing temperature. The size of repeat length-scale increases (lower q) with decreasing temperature, and has been confirmed for other pyrrolidinium-based ILs in systematic measurements be Santos *et. al.*^[306] This suggests a swelling effect occurs across liquid and glass temperature ranges; as temperature increases the polar-apolar domains become larger, thus leading to a lowering to density. These results compare well with the molecular dynamics simulations of Wang and Voth,^[299] who calculated a subtle thermal dependence of partial structure factors.



Figure 29- Evidence for solvent heterogeneity from temperature effects. (A) X-ray diffraction spectra in $[C_8mim][BF_4]$ in liquid and supercooled phases from 90 to 290 K. (B) plot of vibrational cooling

rate of excited S1 *trans*-stilbene against thermal diffusivity for several solvents. The molecular liquids shows a neat linear relationship, whilst the two aprotic ILs C_4 mim Tf₂N and C_2 mim Tf₂N do not fit to theory because of solvent heterogeneity (Adapted with permission from *J. Phys. Chem. B*, 111, 4641, Copyright 2007 American Chemical Society and reproduced with permission from *Acc. Chem. Res.* 40, 1174, Copyright 2007 American Chemical Society)

Interestingly, MD and X-ray scattering data for tetradecyltrihexylphosphonium $[NTf_2]^{-}$ was found to become *more structured* with increasing temperature. As the IL was heated between 150 K and 400 K, the bulk correlation peak became sharper, more pronounced, indicating a better defined bicontinuous nanostructure. This is somewhat counterintuitive other ILs, molten salts^[307] and liquid generally,^[182] become more disordered with increasing temperature. Subsequent analysis by Hettige *et al.*^[308] demonstrated to origin of this effect, by deconvoluting the opposing contribution of the polar and apolar groups towards the correlation peak as a function of temperature. In short, polar domains become more organised with higher temperatures, whereas the apolar groups are less structured. It was speculated that other IL systems may behave in a similar manner.

Hamaguchi *et al.* deduced aprotic IL heterogeneity from temperature changes.^[309] They developed a novel Raman spectroscopic technique to monitor the cooling rate of a photoexcited S1-*trans*-stilbene probe molecule. For molecular solvents,^[310] a linear relationship between *cis-trans* cooling rates (microscopic effect) and thermal diffusivity (macroscopic effect) is observed. A similar plot could not be produced for aprotic ILs,



suggesting the ILs are thermally inhomogeneous on the probe's length-scale (c.f.

Figure 29B). The apolar groups used by Hamaguchi *et al.* (ethyl, butyl) are too small relative to the charged groups to form a well-defined mesoscopic nanostructure. This means that the Raman response is likely a consequence of simple charge ordering in the bulk, rather than a preferential solvation in a bicontinuous network. Subsequent coherent anti-Stokes Raman scattering (CARS) experiments by this group appear to indicate that ILs [C_nmim][PF₆] (n = 4, 6, 8) possess a mesoscopic structure, but the possible size range of 10-100 nm is too large to make any meaningful conclusions about ion arrangements.^[311]

Signals in optical heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES) have been used as evidence for an inhomogeneous IL nanostructure on very short time scales. Giraud *et al.* adduced this from the unusually large number of functions required to fit the OHD-RIKES spectra of ILs.^[312] However, as argued by Chiappe,^[313] in isolation this is not sufficient evidence for a mesoscopic bulk structure and is most likely reflective of strong ion-ion interactions and a high degree of ion association. Later papers by Xiao *et al.* showed that, unlike molecular solvents, the low frequency intermolecular region of the OHD-RIKES spectra (200 cm⁻¹) for binary mixtures of [C₅mim][Tf₂N] and [C₅mim]Br are additative sums of the pure ILs. This result is surprising as an additive intensity is usually indicative of ideal solution behaviour. The result was explained in the context of the

aforementioned MD studies by assuming partitioning of the IL mixture into local domains or "blocks" of the neat ILs in which the polar and non-polar groups are segregated from one another.^[314,315] Further indirect evidence was obtained from experiments with the pure components; whilst the bulk liquid densities are temperature *dependent*, OHD-RIKES spectra were temperature *independent*.^[316] This suggests inhomogenieties in the local densities of the bulk liquids, which could be explained by a mesoscopic solvent structure.

There have been a number of papers that propose mesoscopic structure in aprotic ILs from techniques that probe ion dynamics or relaxation.^[75,317-321] This is similar to implying bicontinuous structure from transient spatial fluctuations in dynamic regime of microemulsions and colloidal gels.^[322-324] In general, ILs show an unusually broad spectrum of "non-Arrhenius" ion dynamics. As there are no corresponding examples of molecular or complex liquids with similar viscosity, this is usually cited as further evidence towards the mesoscopic model of IL structure. However, care must be taken with this interpretation for ILs as dynamic heterogeneity is not exclusive to structurally heterogeneous systems.^[325] For example, supercooled water is structurally homogeneous solvent but displays the characteristic non-gaussian translation and rotational diffusion.^[326-328]

Subsequent XRD measurements were used to postulate a micellar-like morphology for bulk IL solvent structure.^[329] A micelle-like structure was adopted to explain the linear relationship between cation alkyl length and position of the bulk correlation peak. Systematic alteration of alkyl chain in 1-C_n-3-methylimidazolium hexafluorophosphate ILs from butyl (n=4) to hexyl (n=6) to octyl (n=8) resulted in 2.1 Å domain size increases for each additional CH₂ similar to the findings for protic ILs^[229] (c.f. Figure 26A). This is slightly less than twice the increase for non-ionic micelles in aqueous solution from the Tanford equation.^[131] The alkyl chains were suggested to be weakly interdigitated, due to packing efficiency of apolar groups in the hydrophobic core.

Triolo *et al.* have since moved slightly away from micellular arguments to account for the diffraction peak at low-q, consistent with recent trends in experimental^[225,330] and theoretical^[331] studies. Recent scattering studies by this group^[76,332-335] have proposed the sponge-like networks exist in the bulk, which connect when the cation alkyl chain length is greater than or equal to four $-CH_2$ - units long. Below this critical point, the structure is assumed to follow the globular nanostructures detailed by Canongia-Lopes.

Hardacre *et al.* have published a number of important articles that use neutron diffraction experiments and EPSR simulations to investigate aprotic IL bulk structure.^[336-338] H/D-isotopic substitution used is similar to that previously performed for molecular solvents^[101,102,109] and the results presented in this Thesis in Chapters 3-9. Neat C₂-imidazolium ILs was shown to follow a close-packed 'onion-skin' structure of alternating shells of cations and anions. This structure satisfies the range of attractive interactions between ions as well as local and bulk solvent electroneutrality. EPSR fitting resolved the local ion-ion distributions in these shells (c.f. Figure 30D-F). The structural arrangements in these models show significant charge ordering, which in some respects resembles the structure in the crystal state (c.f. Figure 27).^[336] The IL ions examined in these studies have short cation alkyl chains. This means that the volume ratio of the ionic and alkyl components is dominated by the charged segments or, put another way, that the cation is very weakly amphiphilic. Thus, it is not surprising that IL bulk structure is principally determined by electrostatics as the cations are not sufficiently amphiphilic to induce segregation.

Hardacre *et al.* recently examined a series of $[C_n mim][PF_6]$ aprotic ILs,^[339] using alkyl chains long enough to induce cation alkyl chain segregation (*n*=4, 6, 8). Several important conclusions were presented that challenge the mesoscopic model. H/D substitution of the 1methyl and 3-alky H atoms, showed a clear bulk correlation peak in all the IL solvents including $[C_4 mim][PF_6]$. This is important because such a peak is very hard to detect in SAXS or SANS experiments of fully protiated $[C_4 \text{mim}]^+$ ILs. The overall trend in diffraction spectra is the same as that reported by Triolo *et al.* for the same ILs; the peak at low-*Q* moves to longer distances, sharpens, and becomes more intense with increasing cation chain length. This indicates that the correlation is related to the increase in the nonpolar hydrocarbon volume contribution of the cations, at ~2 Å per methylene unit. However, the EPSR model was not consistent with a micelle-like structure. Firstly, the height and sharpness of the scattering on the peak is less than other features on the diffraction spectra, notably the intraionic peak between 0.8–2.0 Å⁻¹. This suggests the interionic correlation weakly contributes to the overall scattering profile. Secondly, the peak position is detected at longer length scales than predicted by previous MD simulations of ILs.

Based on these observations, Hardacre *et al.* concluded the peak at low Q is not a signature of solvent hetereogeniety, but instead is a result of changes in cation anisotropy with increasing amphiphilicity. Moreover, the "data does not demonstrate the presence of a nanostructure beyond an immediate correlation" between nearest neighbour ions. The picture developed is intermediate to that for $[C_1mim][PF_6]^{[338]}$ and long-chain liquid crystalline ILs (c.f. §1.2.6.i and Figure 27); the anions solvate the cation's charge-bearing imidazolium head via Coulombic attraction to form an ionic domain. The alkyl chains fill the void between adjacent ionic domains, and are loosely associated in a bilayer- or sponge-like structure. This is different to alkyl-chain dominated aggregation models for bulk nanostructure (eg. micelles).



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Figure 30- Nanostructure in C_n mim-based ionic liquids. Top Row (from left to right): Chemical structures of $[C_n \text{mim}]Cl$, $[C_n \text{mim}]PF_6$ and $[C_n \text{mim}]TSFA$ respectively. Middle Row: X-ray diffraction and small-wide angle X-ray scattering spectra by Triolo *et al.* for (A) $[C_n \text{mim}]Cl$, n = 3, 4, 6, 8, 10, (B) $[C_n \text{mim}][PF_6]$, $n = 4, 6, 8, \text{ and (C) } [C_n \text{mim}][TSFA] 2 \le n \le 10$ aprotic ILs at 298 K. Corresponding Empirical Potential Structure Refinement (EPSR) modelling by Hardacre *et al.* of the cation probability distribution around an $[C_n \text{mim}]^+$ cation in (D) $[C_1 \text{mim}]Cl$ (E) $[C_1 \text{mim}]PF_6$ and (F) $[C_1 \text{mim}][TSFA]$ (Reproduced with permission from *J. Phys. Chem. B*, 111, 4641, Copyright 2007 American Chemical Society and *Chem. Phys. Lett.* 457, 362 Copyright 2008 Elsevier and *Acc. Chem. Res.* 40, 1146, Copyright 2007 American Chemical Society and *J. Phys.: Conden. Mat.* 21(42), 424121, Copyright 2009 IOP Publishing)

Margulis and co-workers arrived at similar conclusions to Hardacre *et al.*^[339] from MD simulations of the bulk structure of $[C_6 mim][Cl]$, $[C_8 mim][PF_6]$ and $[C_{10} mim][PF_6]$ compared to the crystal structure of $[C_{10} mim][PF_6]$.^[340] The low-q feature in all the liquid phase was proposed to be of the same repeating unit found in the crystal phase, and arises due to cation anisotropy. Related MD simulations by this group have confirmed this picture for pyrrolidinium^[341] or ammonium-based^[342] aprotic ILs.

Whilst ion anisotropy may play a role in peak formation, the traditional interpretation of IL scattering data is still widely accepted. In X-ray scattering experiments, the polar domains are known to be the principle scattering units in the liquid phase. Thus, increasing the length of the cation's alkyl chain effectively lowers the concentration of scattering centres in real space with increasing alkyl chain length. This should reduce the peak intensity of the bulk feature with alkyl chain length, indicating a less well-ordered system. However, in every experimental computational study the reverse is observed; the peak becomes more pronounced with ion amphiphilicity. For neutrons scattering events the situation is more complicated, yet Hardacre et al's data^[339] is consistent with the expected bulk spacing of a sponge-like bicontinuous phase, which follow similar relationship between scattering peak and molecular amphiphilicity.^[138]

Recently, these arguments were revisited in detailed simulations of x-ray scattering data by Castner *et al.*^[306,343] and SWAXS measurements by Russina & Triolo.^[344] Castner *et al.* deconvoluted the total contribution of each ion-ion correlation to the structure peaks in similar ILs. The measured structure factor was shown to be a complex combination of many different cation-cation (head-head, head-tail, tail-tail), anion-anion and cation-anion correlations, any of which may possess a positive or negative scattering contribution at different length scales. In general, the lowest q feature could be attributed to real space distances between ions of the same charge, whilst the second peak is mostly due to ions of opposite charge. Subsequent features in the diffraction spectra (> 3 Å⁻¹) were shown to be intramolecular in nature. These results are consistent with experimental observations of Hardacre *et al.*, but arrive at the mesoscopic model for IL bulk structure because the uncharged cation alkyl tails are aggregated together.

Russina & Triolo recently provided new experimental evidence for the mesoscopic model by comparing the SAXS profiles of $[C_6mim][Tf_2N]$ and its ether-based counterpart

 $[C_1OC_2OC_1mim][Tf_2N]$.^[344] As these ILs are isoelectronic, the x-ray scattering for core electrons should be identical. However, a clear bulk structure peak at low q is evidence in the former IL but not the latter. This suggests the bulk structural arrangements in the ILs are different. Because the polyether chain is relatively polar, the driving force for segregation of uncharged groups is weak. Thus, only in the amphiphilic $[C_6mim][Tf_2N]$ is there a bicontinuous solvent structure. Recent nuclear Overhauser effect (NOE) 2D NMR^[345] and experiments support these conclusions for phosphonium and ammonium isoelectronic homologs. This data showed specific ion-ion correlations from cross peak scales intensity of ion groups. Thus, the emergence of a correlation peak at low Q denoting the appearance of mesoscopic bulk structure is related to a sufficiently amphiphilic ion, and leads to a bicontinuous arrangement of polar and apolar domains. Revelations of stronger domain segregation with symmetric imidazolium cations^[346-348] is consistent with this, as it induces a more amphiphilic cation.

¹²⁹Xe NMR spectroscopy has provided new evidence in support of the mesoscopic model, complemented by MD simulations.^[349] A range of popular imidazolium ILs with [Cl⁻], [PF₆⁻] and [NtF₂⁻] anions were studied, and the chemical shift of the ¹²⁹Xe signal used to study bulk structure. Surprisingly, Xe was found to be an effective probe of local ion arrangements, and can differentiate between different atom types within the polar and apolar domains, and show how these domains evolve with changes in IL structure. Similar experiments by other workers^[350] have shown the broad applicability of this technique to investigate IL structure, though the authors in the later study indicated that the bulk was "cage-like" rather than mesoscopic, with voids of empty space in the bulk.

X-ray photoelectron spectroscopy (XPS) experiments by the Licence group could probe the binding energies in the bicontinuous mesostructure of pyrrolidinium^[351] or amino-acid^[352] based ILs. Subsequent work by this group has shown how XPS can probe the mechanism of

organic reactions conducted in ILs.^[353] The electronic environment for each element in the ILs could be deconvoluted from the XPS spectra. Notably, the length of the cation alkyl chain was shown to have little effect on the electronic environment of the charged moieties. This means that the electrostatic interactions in the polar domain are largely unaffected by the changes in the apolar domain.

1.4 The Structure of Solid-Liquid Interfaces

[Reproduced in part from R. Hayes, D. Wakeham, R. Atkin "Ionic Liquid Interfacial Structure (2)" In *Ionic Liquids UnCOILed: Critical Expert Overviews*; John Wiley & Sons, (2012). Paragraphs that closely resemble, or taken directly from this review are highlighted with "**"]

When liquid molecules come into contact with a second (solid, liquid or gas) macroscopic phase an interface forms. The interface is the common physical boundary between the two bulk phases. The study of solid-liquid interfaces probably dates back to Leonardo da Vinci, who demonstrated capillary wetting behaviour in liquids confined within narrow tubes.^[354] Our understanding of liquid interfaces has since advanced tremendously, reflecting progress that has been made in both chemistry and physics. Today, liquid interfaces underpin many important chemical, physical and environmental processes. This research has touched upon our everyday lives in a many of ways including surface coatings, energy storage and food preparation, among other things.**

Structural resolution of fluid molecules at interfaces is challenging. However, compared to gas-liquid (g-l) and liquid-liquid (l-l) interfaces, the solid-liquid (s-l) interface is more amendable to experimental investigation. This is due to the rigidity and fixed interfacial properties of solid surfaces compared to the deformable and dynamic nature of g-l and l-l interfaces. As a result, interfacial structure can be described in greatest detail for solid substrates, especially for atomically smooth surfaces.**

1.4.1 Structure of the Solid-Molecular Liquid Interface

Molecular liquid interfaces are typically diffuse. The density profile and physical properties do not change sharply, but rather vary over a few molecular diameters from the values associated with one bulk phase to those of the other. At most solid substrates, surface roughness greater than the molecular dimensions results in physical properties varying smoothly in a fashion usually best described by an error function. The exception is for atomically smooth solid surfaces, which induce the liquid to pack into solvation layers on account of geometric packing constraints.^[89]**

Direct measurement of the solid-liquid interface commenced in early 1980s following the invention of the surface forces apparatus (SFA). A variety of molecular liquids, including octamethylcyclotetrasiloxane,^[355] n-octane,^[356] cyclohexane,^[356] ethylene glycol,^[357] and dilute aqueous solutions^[358] were found to exhibit oscillatory force profiles normal to the closing plane of two mica interfaces; the period of oscillation is approximately equal to the size of the solvent molecule with an amplitude that decreases with increasing separation (c.f. Figure 31). This suggests an oscillatory molecular density profile is present that extends a few molecular diameters from the interface.



Figure 31- (A) Schematic structure of a simple liquid confined between two parallel walls. The order changes drastically with distance, resulting in oscillatory force. (B) measured oscillatory forces in 10^{-3} M KCl solution. The period of oscillation is 2.2 to 2.6 Å, approximately the size of the water molecule. (Adapted with permission from *Surface Science Reports*, *59*, 1, Copyright 2005 Elsevier and reproduced with permission from *Nature*, 379, 6562, Copyright 1996 Nature Publishing Group)

The resulting arrangement, confirmed by later computer simulations,^[359] and X-ray reflectivity (XRR)^[360] studies, has been termed 'solvation layers' and is characterized by discrete layering of liquid molecules adjacent to a flat solid. It is important to note that there is no fixed orientation of liquid molecules in this arrangement, in the same way molecular liquids do not possess a defined structure in the bulk. However, for polar molecules such as water, the influence of the second phase can induce orientation order in the layer of molecules in direct contact with the surface, and change from an oxygen-up to oxygen down as a function of applied voltage.^[361]

Solvation layers cannot be explained by continuum theories of van der Waals, or electrostatic forces. The aforementioned SFA studies as well as AFM measurements^[362,363] have suggested the associated 'solvation force' is mainly of geometric origin because the interface induces order in an otherwise unstructured liquid.^[89] Thus, it is not surprising that solvation layering is sensitive to surface roughness around the size of the solvent molecule. This is because surface defects lead to a more disordered organization of liquid molecules in the vicinity of the interface and hence less layering. However, solvation layering varies with molecular shape; large, approximately spherical molecules are most conducive to layered packing.*

For smaller molecules, molecular flexibility becomes an important factor in determining the interfacial arrangement. This is because flexible molecules and groups can space fill effectively without layering. For example, n-octane is a linear chain of methyl (-CH₂-) groups connected in a less rigid structure than cyclohexane. This leads to fewer and more compressible layers in n-octane as a result of the rotational flexibility of the alkyl chain.^[356] Other physical changes such as temperature effects (e.g. supercooling), have a negligible effect on the solvation force. This means that solvation layering in molecular liquids is not a consequence of surface-mediated 'pre-freezing' of the liquid.*

1.4.2 Electrical Double Layer structure of aqueous electrolytes

Due to its crucial role in electrochemistry, colloid stability and cellular processes, double layer forces have been extensively studied both theoretically and experimentally. The nature of the electrochemical double layer in aqueous systems is reasonably well-understood using mean field models.^[364-367] Briefly, these models demarcate the interfacial structure into inner and outer regions. The inner (Stern) layer is composed of counter-ions specifically adsorbed to the interface. The outer (diffuse) layer is the region over which the surface potential decays to the bulk value and is of thickness $1/\kappa$ from Equation 12. Counter and co-ions inhabit this region and are less strongly–associated with the interface compared to the inner layer. Together, the Stern and diffuse layers neutralise the surface charge of the electrode.

The structure of this interface has been verified and enhanced by *in situ* electrochemical AFM force measurements. The double layer structure adjacent to a wide range of substrates including conductors (gold^[368-373] platinum^[369] graphite^[372,374]) semiconductors^[375] and polymer^[376,377] surfaces has been characterised. The force-separation profiles obtained evolve with changes in pH, electrolyte type and concentration, and applied surface potential. An example of this is shown in Figure 32 for a gold surface (mean roughness of 2.65 nm/ μ m²).



Figure 32- AFM force curve for silica sphere approaching a gold electrode in an aqueous solution of 10-3 M KCl at 25 °C and pH 5.5 as a function of applied surface potential (vs SCE). (Reproduced with permission from *J. Phys. Chem. B*, 100, 18808, Copyright 1996 American Chemical Society)

Notably, the force profiles in all of these studies show no evidence of solvation layering. Tipsurface interactions are well-described by DLVO theory, with no need to invoke structural forces (V_S) from the Derjaguin^[378] approximation:

$$F/R_T = 2\pi(V_A + V_E + V_S)$$
 Equation 15

Where F is force, R_T is probe radius and $V_A \& V_E$ are the van der Waals and electrostatic energies respectively. Even at low electrolyte concentrations, repulsive DLVO forces are strong and screen any underlying structural forces from ordering of the solvent / ions. This is not surprising, as oscillatory forces are generally hard to detect with commercial AFM^[363] or SFA^[379] instruments. To compensate, AFMs can be modified with lock-in amplifiers or experiments conducted in tapping mode, both of which to reduce signal to noise ratios for solvation layers to be characterized.

1.4.3 The Solid-Ionic Liquid Interface

The molten salt–solid interface was being used to make important chemical discoveries more than 200 years ago, notably in Humphrey Davy's isolation of alkali and alkali earth elements via melt electrolysis.^[380] Despite this pedigree, IL-solid interfaces remain largely unexploited in chemical processes because the subtle molecular, bulk and surface specific effects which govern interfacial behaviour are yet to be elucidated.**

Close to a solid surface, ILs exhibit oscillatory density profiles consistent with ion pair (anion +cation) dimensions. Whilst this invites comparisons with molecular liquids^[89,381,382] or molten salt^[383-386] interfaces, IL arrangements should not be termed 'solvation layering' because it is of is of fundamentally different origin. As argued throughout this Thesis, ILs have the capacity to self-assemble, which provides additional impetus to ion structuring over and above simple geometric constraints (in molecular liquids) or charge ordering (in molten salts). Thus, ILs can build up well-defined nanostructures at interfaces, reminiscent of their bulk structure, through segregation of their charged and uncharged groups. Consequently, IL interfacial structure is better described as 'layered' or 'lamellar-like'. The solid surface plays a key role in determining the extent and strength of IL interfacial structure. Ion-surface

interactions induce additional degree of order as the surface serves to (1) flatten the preexisting nanostructure and (2) templates new arrangements in the first ion layer. This is because it controls the composition and packing arrangements of first layer of ions, which then orients ions in the second layer and so on.**

This Section will show that the solid-IL interface can be divided into three basic regions. The *interfacial layer* consists of the layer of ions in direct contact with the solid surface. The region through which the interfacial structure decays to the bulk structure is referred to as the *transition zone*, which typically extends two to five (or more) ion pair diameters into the bulk. The width of this zone reflects the rate of change between interfacial and bulk structure. The third zone is the *bulk liquid*, which frequently has a bicontinuous structure (c.f. § Section 3), but form globular structure for short chain aprotic ILs. For the purposes of these definitions it does not matter whether the bulk liquid is structured or not; the key point is that interactions between the surface and the IL lead to enrichment of one ion species at the interface, which templates an interfacial structure that decays through the transition zone to the bulk morphology. Ion self-assembly occurs throughout all three regions, which makes near surface structure much more complex than for molten salts or molecular liquids.**

Obtaining atomic resolution of interfacial arrangements in ILs is challenging. Some techniques are better able to resolve structure in either the interfacial layer, or the transition zone, but not both. Unsurprisingly, the most detailed knowledge is obtained when two or more techniques are applied to the same interface. In this instance, the diversity in the range of ILs available,^[20] which provides enormous avenues for scientific innovation, has meant that studies of the same interface using more than one technique have rarely been performed. This complicates analysis, as it is difficult to tease out the relative effects of different investigative techniques versus different IL species for interfacial structure.**

In this Section, current understanding of the IL-solid interface is examined for a range of solid substrates. The similarities and differences between the properties of these surfaces, and how this effects interfacial morphology, is described. This is geared towards the second arc of this Thesis in Chapters 8 & 9: determining the IL solvent structure at atomically smooth electrode surfaces as a function of applied potential. An improved understanding of the near-surface structure in ILs will optimization of established IL systems including charge transfer processes in electrochemistry,^[387] current generation and dye-morphology in dye sensitized solar cells,^[388] as well as nucleation rates and deposit morphology in electrodeposition.^[389] Whilst electrochemists have shown greater interest in aprotic ILs than protic ILs, this Section concerns how both IL classes arrange at a charged and uncharged surfaces.**

1.4.3.i Mica - IL Interfaces

The mica surface an atomically smooth crystalline substrate. Negatively charged surface sites are arranged precisely with the surface lattice, leading to a constant surface charge density of 0.48 charges per nm².^[390] The atomic smoothness of mica make data analysis relatively uncomplicated compared to other surfaces whilst the high, well-defined surface charge invites direct comparison to a charged metal electrode surface.**

The first investigation of IL interfacial structure (of any type) was at a mica interface using the SFA for the protic IL ethylammonium nitrate (EAN) in 1988.^[391] Four to five oscillations in the force profile were observed, with the period of 0.5-0.6 nm consistent with the predicted ion pair diameter, assuming a cubic packing geometry (c.f Figure 34A). This suggested that cations and anions were present in equal numbers within the layers. On the basis of absolute mica-mica separations, up to nine near surface (anion + cation) layers were inferred. As the force necessary to squeeze out a layer increases as the mica-mica separation decreases, it was suggested that IL interfacial structuring is more pronounced closer to the surface (and decays

out into the bulk). The authors speculated that alternating sublayers of anions and cations may be present, but this could not be resolved from force measurements.*

This initial study was not expanded upon for almost a quarter of a century, until the mica-IL interface was revisited for protic and aprotic ILs using AFM force curve measurements.^[392] AFM can probe both IL interfacial and transition zone structure adjacent to a wide variety of surfaces.^[330] AFM force curve data from five key systems: propylammonium nitrate (PAN), propylammonium formate (PAF), dimethylethylammonium formate (DMEAF), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide ([EMIm]TFSA), and 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl) amide ([Py_{1,4}]TFSA), are presented in Figure 33A-E. These systems illustrate the diversity of IL structuring adjacent to the mica surface, and allow mechanisms for controlling surface structure to be revealed. (EAN-mica interface is dealt with separately in Figure 34A-E). In every case, the AFM data is characterized by a series of repeating 'push-throughs' at discrete separations on tip approach (blue) and (sometimes) retraction (red), from the surface. The rupture force increases closer to the surface, indicating near-surface IL order is more pronounced closer to the substrate. The contrast between the oscillatory results obtained by Horn *et al.*^[391] and the step-wise AFM data is ascribed to the differences in the experimental methods.*

A typical force profile for the EAN-mica system is shown in Figure 34B and can be rationalised as follows. Beyond 4 nm, zero force is recorded as the tip experiences negligible resistance moving through the IL towards the mica. This is significant, as it shows that the AFM is insensitive to the bicontinuous sponge-like structure that exists in the bulk.^[225] At 4.1 nm the tip encounters the first outermost detectable layer and pushes against it. The force increases up to 0.1 nN then the tip ruptures the layer and 'jumps' 0.5 nm before encountering another layer 3.6 nm from the interface, and the process is repeated.**



Figure 34- The structure of the EAN-mica interface. (A) Oscillatory force profile from SFA measurements. (B) Stepwise AFM force-distance profile. 10 x 10 nm soft contact AFM deflection image of the EAN-mica interface for the Si_3N_4 tip in soft contact with the (C) innermost ion layer on mica at high force (>6 nN) (D) worm-like innermost ion layer on mica at low force (4-6 nN) and (E) sponge-like structure of first near surface (ion pair) layer (< 3nN). The three directions of the mica lattice are marked in red on (C) (Reproduced with permission from *J. Phys. Chem. B*, 92, 3531, Copyright 1988 American Chemical Society and *J. Phys. Chem. C* 111, 5162 Copyright 2007 American Chemical Society and with permission of the PCCP Owner Societies, *Phys. Chem. Chem. Phys.* 2013, 15, 3320-3328)

The jump interval in all cases in the force profile of Figure 34B is 0.5 nm. This is in excellent agreement with the diameter of the ion pair determined from the bulk density. Attractions between adsorbed EA^+ cations on the tip and substrate are responsible for the adhesion force measured upon retraction. Zero force is reached at a separation of 2 nm, corresponding to the

4th interfacial layer. The forces has a strong temperature dependence, with both the number of detectable layers and rupture force decreasing by half between 14°C to 30°C.^[393]**

Initial interpretation of this AFM force curve explained the solvent structure as follows. Because mica is highly negatively charged, electrostatics dictates that a cation layer is adsorbed to the surface, with the anion largely excluded. As such, a thinner innermost layer should be detected in the force profile. The EAN-mica system in Figure 34B does not show this and all step sizes are 0.5 nm. It is noted that one cation occupies an area greater than the size of a mica surface charge site (one per 0.48 nm²),^[394] so even at cation saturation coverage, the degree of substrate charge quenching cannot exceed 87%.^[391] Thus, the 'zero' distance on the force profile actually corresponds to the tip pushing up against, but not penetrating, a strongly-bound, compact cation layer. The first non-adsorbed layer detected in the transition zone consists of an ion pair; the cations are closer to the substrate and oriented with alkyl groups pointing towards the surface to maximize solvophobic interactions with surface-bound cations, similar to the alkyl chain clustering inferred in the bulk (§1.3.4).^[225] This is followed by a NO₃⁻ anion layer above the $-NH_4^+$ headgroup to quench the electrostatic charge, resulting in an overall substrate A-(AB)(BA)(AB) arrangement, just like in the bulk phase. Thus, the surface serves to align the bulk structure, which then decays through the transition zone. This is distinct from molecular liquids, in which the surface induces structure in an otherwise unstructured bulk, and there is no molecular arrangement.

This model was confirmed in recent, high-precision soft contact and frequency modulation AFM experiments by Elbourne *et al.*^[395] shown in Figure C-E. The key finding of this publication is that the lateral structure of the EAN-mica interface is not homogeneous; the capacity for ions self-assemble is maintained from the bulk, through the transition zone down to near-surface and adsorbed ions. Remarkably, at intermediate force, the adsorbed ions form rows of worm-like structure on the surface (Figure 34D). This self-assembled morphology

represents a compromise between several factors including (1) cohesive interactions in the A-(AB) layers (2) packing geometry of the ions (3) templating effect of the mica lattice and (4) electrostatic requirements of the surface and the ions. At higher force, weakly-bound ions are expelled from the layer and the worm-like morphology is lost (Figure 34C). The three directions of the underlying hexagonal lattice are evident, but features of the image are blurred as an electrostatically adsorbed layer of cations is present between tip and the surface in a flattened geometry. This compact ion arrangement is the origin of markedly lower friction coefficient of EAN confined at high force.^[396] Interestingly, Figure35E shows a soft contact image of the same interface at low force, at least one ion pair further out in the bulk. A lateral structure reminiscent of the bulk sponge-like morphology is detected. This provides striking visual confirmation of a phase change induced by the solid interface. Given the structural simplicity of this IL, these results are far reaching and suggest that many ILs will exhibit similar patterns of self-assembly at solid liquid interfaces.

Fewer and non-vertical steps are detected by AFM when the cation alkyl group is increased from ethyl to propyl in Figure 33A.^[392] The longer alkyl chain increases rotational freedom and thus PAN can pack more efficiently without layering. This demonstrates another key difference between bulk and interfacial IL structure; the SANS peak is more intense for PAN than EAN as the longer alkyl chain leads to stronger solvophobic interactions and hence better defined bulk order.^[76] However, the converse is sometimes true at surfaces, where a longer alkyl chain leads to reduced interfacial order due to molecular flexibility.**

Replacing the nitrate anion with formate decreases the level of interfacial structure,^[393] with only two ion pair layers noted in the force profile (c.f. Figure 33B). Ions in layers are less strongly bound together, and the AFM is able to detect anion and cation sublayers, identified by steps thinner than the ion pair dimension at 0.28, 0.60 nm, 0.83 and 1.17 nm. As zero separation corresponds to a layer of PA⁺ ions electrostatically adsorbed to mica with propyl

chains oriented towards the bulk, the closest measurable layer at 0.28 nm corresponds to second PA⁺ layer with alkyl tails orientated towards the mica surface, interacting solvophobically with adsorbed cations. The step between 0.28 and 0.60 nm therefore equates to a neutralising layer of HCOO⁻ anions, yielding a total thickness for the anion and cation layers of 0.6 nm, consistent with the ion pair diameter of PAF.^[393] The next two layers have similar thicknesses within the accuracy of the measurement.**

The results for DMEAF in Figure 33C demonstrate how IL interfacial layering can be largely prevented at a solid interface. This IL has only a single, thin layer at 0.45 nm. This is 21% smaller than predicted for the ion pair geometry,^[393] and provides strong evidence for a single layer of weakly surface-adsorbed cations adjacent to the mica surface, and no subsequent transition zone structure. In contrast to the primary ammonium cations described previously, the DMEA⁺ charge centre is sterically hindered, which prevents close approach of the cation to the substrate. This reduces the strength of electrostatic attractions, which allows the AFM tip to displace the cation layer and move into contact with the mica. The bulk structure of this IL has not been reported, but we would predict that long-range order is absent.**

The AFM force profiles for the two aprotic ILs [EMIm]TSFA and $[Py_{1,4}]TFSA$ presented (c.f. Figure 33D and Figure 33E) are particularly well-defined.^[397] At least five steps are noted on approach and retraction. The step-wise retraction indicates that the liquid layers spontaneously reform as the tip is moves away from the surface. The step widths are in excellent agreement with the predicted ion pair diameters (0.75 nm for [EMIm]TSFA and 0.79 nm for $[Py_{1,4}]TSFA$) and Bragg d-spacings from crystallographic data.^[398] The non-vertical nature of $[Py_{1,4}]TFSA's$ 'push-throughs' is as a result of molecular flexibility imparted by the butyl moiety, as per the PAN argument developed above. Interfacial forces are stronger for the $[Py_{1,4}]^+$ cation, from stronger solvophobic interactions.



Figure 33- Force versus distance profile for an AFM Si_3N_4 tip approaching (blue) and retracting from (red) for (A) EAN-mica system at (B) PAN-mica system (C) PAF-mica system (D) DMEAF-mica system (E) [EMIm][TSFA]-mica system (F) $[Py_{1,4}]$ TSFA-mica system (Reproduced with permission from *J. Phys. Chem. C* 111, 5162 Copyright 2007 American Chemical Society and *J. Phys. Chem. B* 113, 5961 Copyright 2009 American Chemical Society and *J. Phys. Chem. B* 113, 7049 Copyright 2009 American Chemical Society)

In recent years, SFA community have recommenced investigations of IL structure at the mica interface, lead by Perkin *et al.*^[399-404] and Israelachvili *et al.*^[379,405] and others.^[406,407] The main advantage of SFA over AFM is that the surface geometry and absolute separation is known in an SFA experiment. This has enabled the ion orientations in the confined films to be resolved from force profiles. For instance, a cross-over structural transition from

monolayer to bilayer-type arrangements was noted in pyrrolidinium-based ILs when the alkyl chain length increased from n = 8 to 10.^[403] This is similar to earlier interpretation of AFM data for EAN and PAN. At the IL-mica interface, Perkin *et al.*^[402] also detected quantized friction-load regimes using the SFA, consistent with AFM nanotribology experiments.^[396] This was traced to the oscillatory layering of ions; because a unique number of ion layers are confined between the mica walls, there is a different friction coefficient for each separation. Interestingly, several of the early SFA papers find no evidence of oscillatory layering.^[379,406,408] This is at odds with much of the recent experimental and theoretical research at the mica- and other solid-IL interfaces. Explainations for this vary, and are usually attributed to surface roughness, large Debye screening lengths (1-4 nm) or strong repulsive forces superimposed on the oscillatory forces.

Israelachvili *et al.*'s^[405] most recent publication has been quite controversial in the SFA^[409,410] and AFM^[411] community. This is because a weak potential-independent attractive force ranging from 3 and 30 nm was measured between the two surfaces (mica at constant charge, gold at constant potential). No corresponding long range repulsion was observed. Such long-range forces have not been detected by previous SFA or AFM studies of pure ILs, even with instruments of similar force resolution. Furthermore, DLVO fits of the decay length for the attractive force – an effective Debye length – predicted a negligible free ion concentration (0.003%) in the bulk. This led the authors to propose a radical, non-intuitive view of ILs; they are best described as dilute electrolyte solutions of ion pairs plus a small fraction are dissociated free ions. Whilst the long range forces in ILs may be real, it is likely the main conclusions of the paper are premature as it is inconsistent with the wider body of experimental and theoretical IL research. An alternate explaination suggests that the DVLO framework is inappropriate because ILs (1) are strongly dissociated^[274,412] and not a single

ion pair in the bulk (3) only a long range attractive force is detected; a long-range repulsive force was absent. We note that similar force behaviour (long-range attraction, short range repulsion) has been observed in confinement of a sponge (L₃) phase,^[414] related to the surface tension between L₃ and lamellar (L_{α}) phases. It is likely that a similar effect is operating here but on smaller dimensions, because the size of the sponge (L₃) phase in the IL is an order of magnitude lower.

Simulations of the mica-IL interface are scarce. The main theoretical hurdle is modelling sufficiently large slabs of the liquid and solid phases to provide insight into structure in both regions. Only one of the current simulations^[415] accounts for the exchange of potassium ions in the mica lattice. This is important because a freshly cleaved mica surface consists of negatively charged surface groups 0.52 nm apart in a nearly-hexagonal (tetragonal) lattice, about half of which are neutralised by K^+ ions.^[416] These may be dissolved into solution, or remain on the surface. From an experimental perspective, it is reasonable to assume that K^+ ions are expelled from the surface as the high concentration and surface active properties of IL ions will prevail. The bulk concentration of dissolved K^+ is negligible.^[401,417]

Classical MD simulations of a thin 4 nm film of $[C_4mim][Tf_2N]$ have shown oscillations in ion and charge density normal to the mica interface.^[418] The results qualitatively agree with the AFM & SFA investigations. More pronounced ion layering was obtained by Payal & Balasubramanian^[415] and Zhou et al.^[417] using atomistic MD simulations and a more realistic interaction potential. This is shown in Figure 34B & D.

For $[C_n mim][Tf_2N]$ ILs, Payal & Balasubramanian^[415] showed cations with ethyl- or butylsubstituents (n=2 or 4) arrange with their alkyl tail parallel to the surface. The hexyl- and octyl- ILs oriented the uncharged groups normal to the mica interface in bilayer-like arrangement. Zhou *et al.* 's study was also notable as the model was compared and evaluated against ion layering seen in high resolution X-ray interface scattering data.^[417] This provides unambiguous experimental evidence oscillatory arrangements at the mica interface are not an artefact of confinement between AFM tip or SFA walls; the layering observed in the MD simulations is present at a free surface.



Figure 34- Structure of the interfacial layer of [bmim][Tf2N] at the mica interface from AFM experiment (A,C) and MD simulations (B,D). A and B show the lateral structure of the cations adsorbed in the interfacial layer. C and D show the z profile along a side axis. Note colours in the simulation are C = black, H = white, N = blue, O = red, Si = yellow, K+ = purple. (Reproduced with permission from *ChemPhysChem* 13, 1764 Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim and the PCCP Owner Societies, *Phys. Chem. Chem. Phys.* 2013, 15, 3320-3328)

1.4.3.ii Sapphire-IL Interface

Like mica, the Al₂O₃(0001) (sapphire) is crystalline and atomically smooth (2-2.5 Å along the basal plane) but its surface charge density is lower. (An ideal sapphire surface neutral pH in water displays a surface charge of one site per 52.7 nm²,^[419] however, this value should be considerably lower because of the ionizing effect of the X-ray beam). High-energy X-ray

reflectivity experiments for aprotic ILs have revealed an interfacial structure similar to that suggested for mica in most respects.^[420,421] An electron density model for $[Py_{1,4}][FAP]$ is shown in Figure 35. Gaussian distributions are modelled for both the anions (blue) and cations (red) at the interface, and summing these distributions provides the variation in electron density with distance, which has a period of 0.8 nm, corresponding to the size of the ion pair. It was suggested that the cation is in contact with the negatively charged surface, leading to ABAB packing until the bulk structure is reached after approximately five ion pair layers. However, given that studies of bulk structure consistently report bilayered (sponge or aggregate) structures as a result of solvophobic interactions, it may be that an A(AB)(BA) arrangement is present.**



Figure 35- Cation (red), anion (blue), and total (black) electron densities obtained from the best fits to the X-ray reflectivity profile of 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate $[Py_{1,4}][FAP]$ at T = -15°C. (Reproduced with permission from Science 322, 424 Copyright 2008 American Association for the Advancement of Science)

1.3.3.iii Silica-IL Interface

The surface chemistry of silica is quite different to mica and sapphire. Silica is amorphous, not crystalline, and is substantially rougher; typical rms roughness values for silica are 1.3 nm over 5 x 5 μ m.^[422] This degree of surface roughness is sufficient to broaden molecular liquid

solvation layers^[89] (roughness an order of magnitude greater than this will eliminate solvation layers completely^[423]). Compared to mica, silica has a greatly reduced and variable surface charge, which arises from equilibrium between protonated/deprotonated hydroxyl groups. In water, an average net negative charge of one site per 20 nm² is typical.^[422] The corresponding values in ILs are expected to be considerably higher, but still much less than for mica.** The different surface properties of silica compared to mica result in different AFM force profiles. Whilst the basic stepwise form of the data remains, for silica the forces are smeared and non-vertical, due to surface roughness. In Figure 36A for the EAN-silica system,^[392] the thinness of the innermost step (0.25 nm) suggests it consists primarily of an electrostatically-

bound cation layer, similar to that shown in Figure C. As the silica is of lower surface charge density than mica, the adsorbed layer can be displaced with higher force.**



Figure 36- Force versus distance profile for an AFM Si_3N_4 tip approaching (blue) and retracting from (red) for (A) EAN-silica & (B) [EMIm]Ac-silica interface. (Reproduced with permission from *J. Phys. Chem. C* 111, 5162 Copyright 2007 American Chemical Society and with permission of the PCCP Owner Societies, *Faraday Discussions* 2013, 154, 155-169)

The data for 1-ethyl-3-methylimidazolium acetate ([EMIm][Ac] (Figure 36B) is similar to that obtained for this IL and a mica surface. This suggests an electrostatically bound interfacial layer of EMIm⁺ cations, followed by two ion pair layers. The spacing of the inner cation layer is consistent with the ethyl group being orientated approximately normal to the interface. The increased molecular volume and charge delocalization on EMIm⁺ compared to EA⁺ means that adsorption is weaker for the aprotic IL. The bulk structure for this IL^[424] is not as well-defined as other aprotics,^[339] and so we should expect fewer ion pair layers.** Sum frequency generation (SFG) spectroscopy has also been used to investigate the arrangement of aprotic ILs at the silica surface.^[425,426] These experiments reveal the cation is absorbed with the imidazolium ring slightly tilted towards the silica surface (between 16° and 32° from surface normal), tending to more parallel orientations with decreasing alkyl chain length. The orientation of the cation alkyl chain is nearly normal to the surface, and longer alkyl chains are more ordered and have fewer gauche defects.**

The structure suggested by these AFM and SFG experiments is consistent with recent allatom force field modelling performed Canongia-Lopes *et al.*^[427] Figure 36C shows the equilibrium configuration in two simulation boxes: (1) (Top) a 5 x 5 x 5 nm cube of 1-(2hydroxyethyl)-3-methylimidazolium tetrafluoroborate and (2) (Bottom) a 5 x 5 x 2.5 nm slab of hydrophilic silica glass. The boundary conditions for both boxes are established in the directions parallel to the glass and are separated in Figure 36C for visual interpretation (during the simulation the IL box stands directly over the glass slab). The intervening surfaces show the charge distribution across the 2-D silica interface.**

The presence of blue/cyan and red/orange areas indicates that positively and negatively charged surface regions (respectively) are present but, as expected, the overall surface charge is negative. Crucially, the simulation shows that anywhere there is a negative charge the
surface a cation is adsorbed (and vice versa), supporting the argument that the surface templates the composition of the interfacial layer. For very highly-charged surfaces like mica or an electrode under voltage, it is therefore reasonable to suggest that the interfacial layer is essentially entirely composed of oppositely charged ions. On less highly charged or variably charged surfaces (like the one modelled here) it is correct to say that the interfacial layer is enriched in one ion or the other, but in such cases the key effect of the surface in terms of transition zone structure is its smoothness; The smooth substrate flattens the bulk structure into ordered near surface layers. As experimental techniques (e.g. AFM, SFG, X-ray reflectivity) sample a large surface area, they are therefore sensitive to the average compositions.**

1.4.3.iv Graphite-IL Interface

Interest in the graphite-IL interface has been fuelled by the desire to understand solvation of nanotubes,^[428,429] graphene,^[430] C_{60} ,^[431] as well as more traditional applications like supercapicators^[432] where graphite can be used as a cheap electrode material.

Graphite is atomically smooth and interacts with ILs differently to the substrates considered previously. Because graphite is uncharged at open circuit potential solvophobic interactions with uncharged IL moieties dominate, similar to that for air-IL interfaces^[213] (and to date, experimental measurements have not been obtained under surface bias). This leads to significant differences in interfacial structure. In general, experimental measurements have not kept pace with interest in the structure of IL-graphite interface. To fill this void, many simulations have been performed,^[417,429,433-441] although the results differ widely in the literature. Recently, a consensus structure appears to be emerging that suggests layered ion arrangements close to the surface. This model can predict macroscopic capacitance quite accurately^[432,439-441] and are consistent with AFM studies.^[392]

The AFM force profiles for IL structure at the graphite interface are presented in Figure . 'Push-throughs' consistent with the ion pair dimensions are observed for EAN–graphite (Figure A) and [EMIm]Ac–graphite (Figure B),^[392] but they are superimposed on attractive van der Waals forces. A small final step is noted in both systems (and on retraction for EAN), which arises from the cation orientation; alkyl chains lying flat in the case of EAN, and the imidazolium ring aligned parallel to the surface for [EMIm]Ac–graphite. This favourable cation alignment leads to the formation of six to seven ion pair layers on graphite for [EMIm]Ac, substantially more than on silica or mica for the same IL where a perpendicular orientation of interfacial cations was preferred.**



Figure 39- Force versus distance profile for an AFM Si_3N_4 tip approaching (blue) and retracting from (red) for (A) EAN-graphite system at 21 °C & (B) [EMIm]Ac-graphite system at 21 °C. (Reproduced with permission from *J. Phys. Chem. C* 111, 5162 Copyright 2007 American Chemical Society)

1.4.3.v Gold- and other metal-IL Interface

Au(111) surfaces are excellent metallic electrodes and have been widely used in electrodeposition of elements from ILs.^[442] This hexagonally closed-packed crystalline surface is negatively charged at open circuit potential, although the precise value of the ocp in the presence of ILs is not known. Figure 37A and Figure 37B show force profiles for [EMIm]TFSA and [Py_{1,4}]TFSA adjacent to gold Au(111) surfaces.^[443]

The force profiles in Figure 37 are qualitatively similar to those obtained for the same aprotic ILs on mica (c.f. Figure 33A and Figure 33B), with a series of push-throughs on tip approach and retraction. However, unlike the mica systems, the width of the interfacial layer is much smaller than the ion pair dimension. Steps are visible at 0.65 nm and 0.60 nm for [EMIm]TFSA and [Py_{1,4}]TFSA respectively. As the surface is negatively charged, this result suggests the interfacial layer is rich in weakly bound cations that the AFM tip is able to penetrate and then move into contact with the gold substrate, similar to the results for silica. For [EMIm]TFSA, a 13% reduction in layer thickness is measured, suggesting electrostatic attractions induce the imidazolium ring of the cation to tilt towards the gold surface. The short ethyl group is expected to allow the aromatic ring on [EMIm]TFSA to be orientated substantially towards the substrate. A 25% reduction in step size is observed for the [Py_{1,4}]TFSA-Au(111) system. Strong electrostatic attractions, and the absence of an inflexible aromatic ring, must allow the [Py_{1,4}]⁺ cation to adopt a flatter surface conformation than [EMIm]TFSA, thus resulting in the reduced layer thickness.

This draws a nice parallel to recent SFG work by Baldelli^[444] and modelling by Lynden-Bell *et al.*,^[445] who could trace the change in cation conformation in the interfacial layer as a function of applied surface charge. IL–surface electrostatic interactions will influence the force required to push-through the layer of ions nearest to the substrate. The significantly higher force required to disrupt [Py_{1,4}]TFSA compared to [EMIm]TFSA is consistent with increased electrostatic interactions between the surface and the cation, which results from the positive charge being localized on one atom in the case of $[Py_{1,4}]^+$ and delocalized across an aromatic ring for [EMIm]⁺. Such effects provide a route to tuning interfacial properties.^[330]

The transition zone extent, and the force required to rupture interfacial layers is greater for $[Py_{1,4}]TFSA$ than for [EMIm]TFSA as per results on mica. This is attributed to differences in cohesive energy within layers. X-ray diffraction experiments for similar ILs^[305] have shown

the level of order increases with cation alkyl chain length. As $[Py_{1,4}]TFSA$ possesses a butyl group and [EMIm]TFSA an ethyl group, stronger solvophobic clustering occurs in the former IL, and hence it is more organized in the transition region.



Figure 37- Force versus distance profile for an AFM Si_3N_4 tip approaching (blue) and retracting from (red) for (A) [EMIm][TSFA]-Au(111) at 21°C (B) [Py_{1,4}]TSFA-Au(111) at 21°C (Reproduced with permission from *J. Phys. Chem. C* 113, 13266 Copyright 2009 American Chemical Society)

Scanning tunnelling microscopy (STM) has been an important tool to investigate structure IL-metal interface.^[443,446-454] Interesting changes in both the adsorbed ion layer and underlying metal surface have been characterized. Examples of this are shown in Figure 38A, with coil-like ion structures imaged at the Au(111) surface. Micelle-like structures on Au(100) are also seen in Ref [409]. Predicting structure in both the liquid and Au surface structures is difficult with STM, because the ion and Au arrangements are a complex function of IL chemical structure, crystal lattice plane, surface potential, temperature and tunnelling parameters. Further experiments are required to elucidate the origin of this behaviour.

In Figure 38B, the herringbone surface reconstruction of Au(111) is detected. A worm-like reconstruction of Au(100) has previously been imaged in Ref [409]. The pronounced structuring of the metal is important in the context of STM experiments, as to date, atomic resolution of the Au surface has not been obtained. This is likely due to strong IL ion adsorption to the metal interface, blurring surface features.^[455]

The lateral normal structure of ultrathin films of $[C_1 \text{mim}][\text{TSFA}]$ and $[C_8 \text{mim}][\text{TSFA}]$ vapour deposited on on Au(111)^[456] and Ni(111)^[457] has been determined. Ion adsorption, orientation, and growth was studied via angle-resolved X-ray photoelectron spectroscopy (ARXPS). In both liquids, anions and cations arrange in a checkerboard manner in the interfacial layer on Au(111). With increasing IL solvent deposited, layer-by-layer build-up is observed to thicknesses of 9 nm.^[458] For Ni(111), layer-by-layer growth is noted initially, and at submonolayer coverage, ion ILs begin to adopt a bilayer structure. At higher coverages on Ni(111) a transition to a checkerboard-type arrangement occurs.^[459]



Figure 38- In-situ STM images of (A) coil-like adsorbtion of [FAP]- anions on Au(111) surface in $[Py_{1,4}][FAP]$ (20 x 20 nm scan) (B) herringbone superstructure of Au(111) surface in $[Py_{1,4}]FAP$ at - 1.2 V (120 x 120 nm scan) Reproduced with permission from *ChemPhysChem 12*, 2565-2567 Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim and PCCP Owner Societies, *Phys. Chem. Chem. Phys.* 2011, *13*, 6849-6857

1.4.3.vi Solid and Liquid Phases co-existing?

Several recent AFM tapping-mode studies have suggested that IL liquid and solid phases coexist at the IL-mica interface at room temperature. Liu *et al.*^[460] and Bovio *et al.*^[461,462] diluted ILs in methanol (to ~0.5 wt%) and then probed the subsequent solid–liquid interface structure after methanol evaporation. Topographical images revealed solid islands 1–100 mm² in area and upwards of 50 nm thick and were supported by similar results from completmentary computer simulations. These studies are reminiscent of early AFM investigations of surfactant adsorbed layers, in which the equilibrium adsorbed layer structure^[463-465] was different to that observed by evaporative deposition.^[466]*

Interestingly, Yokota *et al.*^[467] showed inhomogeneous solid-like structures are present at the pure IL-mica and IL-HOPG interface. To our knowledge this is the only experimental report of solid-phase formation at pure IL–solid interface, including for macroscopic measurements. It is likely that the unusually rough mica and graphite surfaces, solvent impurities, lack of a sealed AFM fluid cell or some combination of these contributed to this behaviour.

Canongia-Lopes *et al.*^[468] recently addresses this controversy and showed that solid-like IL structure at the solid interfaces^[461,462] can be directly attributed to dissolving the IL salt in an alcohol. Films of pure $[C_8mim][BF_4]$ and mixtures of $[C_8mim][BF_4]$ +ethanol were depositied on silica and alumina surfaces and the topographical features analysed via AFM. No evidence of solid-like structures were observed in the pure $[C_8mim][BF_4]$ over time. In contrast, irregular fractal-type structures grew on the surface in the alcholol mixtures that one might expect from IL crystallization as the ethanol evaporated. Compementary MD simulations presented for the $[C_8mim][BF_4]$ -alumina interface are perfectly consistent with the model developed in this review, consisting of interfacial layer, transistion zone and bulk liquid.^[468] Other more recent studies casts doubt on coexistence of solid-like IL structure at solid-IL interfaces. Simulations of pure ILs confined in silica nanopores,^[469] in which there should be a stronger entropic driving force to crystallise, showed ILs remain liquid-like right up to the

interface because melting point decreases upon confinement.^[470] Likewise, solid state NMR measurements of $[C_4 mim]PF_6$ adjacent to a silica support^[471] revealed liquid-like behaviour close to the surface. As expected, ion mobility was slightly restricted because diffusion was hindered by the interface in the *z* direction.

1.4.3.vii Relationship between Bulk and Interfacial Ionic Liquid structure

Interfacial and bulk IL structure are intimately related. As the forces that generate bulk nanostructure are still present at the interface, the tendency to self-assemble is not diminished. However, interactions between the second phase (solid, liquid or air) and the IL ions have an organising effect, such that the interfacial structure is more pronounced than the bulk morphology, and features relating to cation surfactant-like properties are even more prominent. The bulk network of polar and non-polar domains is oriented and aligned by the presence of the interface. In general, a surface-induced sponge to lamellar phase change is observed at the interface. This transition has parallels in concentrated aqueous surfactant systems;^[472] a convoluted sponge morphology cannot be accommodated near a single boundary or confined between two macroscopic surfaces,^[414] instead a stacked bilayer architecture is favored.**

The neatness of this first order transition depends on factors such as surface roughness, temperature and deformability. However, the molecular factors such as cation amphiphilicity have the most significant influence, as demonstrated by EAN and EtAN. EAN forms seven or more layers at macroscopic solid interfaces each approximately 0.5 nm thick. EtAN forms at most two, and so decays into its bulk structure much faster than EAN because the hydroxyl group interferes with solvophobic contact between cation alkyl chains. A similar effect at the air-liquid interface have been reported.^[214,473]

Interestingly, the structure detected at the bulk phase and interfaces is different. Ion pairs are routinely observed at interfaces^[399,401,420,421] and yet their concentration in the bulk is essentially negligible, less than a few picoseconds.^[61,228,252-254] This can be explained as follows: in the bulk each ion has larger degree of freedom and interacts with multiple counterions,^[413] often within a polar domain. Thus, electroneutrality is maintained in the self-assembled structure by ions associating with several counterions. In contrast, interfacial ion arrangements are more lamellar-like, which promotes ions to pair up. This means that under confinement, electroneutrality is maintained by "squeezing out" an anion+cation unit, rather than a single ion. Future work should be directed at changing the nature of the interface such that one ion type is preferentially attracted to the surface. This may lead to single ion layers detected at the interface.

1.5 Chapter 1 Summary

1.5.1 Structure in Ionic Liquids

A key theme to emerge in this Chapter is that ILs are more complex than molecular solvents and thus their bulk and interfacial structures are markedly different. Recent advances in experimental methods have lead to unprecedented sensitivity in measuring IL bulk and interfacial structure, with the goal of these studies being to develop design rules for tailoring IL properties.^[474]

The bulk phase of ILs can be modelled with several different ways including, H-bond networks, hole theory, micelle-like and mesoscopic structures. Mounting experimental and theoretical evidences suggests ILs are structured on the nanoscale, with local domains of order or molecular phase segregation in the bulk corresponding to intermediate (mesoscopic) range order.^[334] This is explains the conspicuously well-regulated nanoscopic structure of polymers,^[475,476] particles;^[477] nanotubes;^[428] and micro/emulsions^[478,479] prepared in ILs. It is important to note that higher order self-assembled structures (H-bond networks, micelle-like and mesoscopic structures) are the most likely time-averaged bulk structure in protic and aprotic ILs. This is not the same as an instantaneous snapshot of the bulk liquid, in which ion pairs or small clusters and free ions may form.

As discussed in Section 3, bicontinuous IL structure, first predicted in molecular dynamics simulations^[299-301] and later confirmed by X-ray^[305] and neutron scattering^[225] studies is remarkable for two reasons. Firstly, virtually every other class of molecular solvent is structurally homogeneous (§1.3.1), i.e. lacks solvent structure beyond a preferred organization between adjacent molecules. In ILs, the ion arrangements are propagated over much greater distances as a result of strong clustering of like molecular groups. Secondly, the internal organization of polar and apolar domains raises interesting parallels to liquid crystals and microemulsions. In particular, there is strong resemblance to thermodynamically stable

bicontinuous microemulsions, however the length-scales in ILs are at least an order of magnitude smaller. Compared to liquid crystals, ILs macroscopically are not optically bifringent and so the morphology present must be disordered on the microscale.

The level of bulk liquid structure in ILs is largely dependent on how surfactant-like the IL is: more pronounced structure has been reported with increasing cation alkyl chain length and conversely, ILs lacking bulk order have been identified for short chain ($<C_4$) imidazolium salts. This means that it may be possible to apply relationships like the critical packing parameter (g) to IL ions. This could be used to predict the type and extent of intermediate range-order in ILs by considering the ratio of charged/uncharged or solvophilic/solvophobic molecular components on either ion. Whilst these relationships may not be applicable to all anion/cation combinations, its application, alongside evidence of a peak at low-Q in scattering experiments, should distinguish between weakly- and strongly-structured ILs in terms of amphiphilicity, and hence whether sponge-like ordering is present in the bulk. The order parameter correlation function described in § 1.3.2 for bicontinuous microemulsions is useful in this respect as it should now be possible to quantify these arguments. Because solvophobic alkyl chains are normally found on IL cations, IL amphiphilicity is largely a function of cation molecular structure. Experiments need to be conducted to elucidate the role of the anion in IL amphiphilicity.

For ILs that are weakly amphiphilic with short alkyl chains and large, charged molecular groups, the bulk structure is largely determined by Coulombic forces and ion packing effects. In this case, the bulk organization will closely resemble molten salts with alternating anion/cation three-dimensional shells that satisfies local and bulk electro-neutrality. This is because there is no driving force for apolar domain formation and the structure resembles the 'onion-skin' model suggested by Hardacre *et al.*^[336] At a critical point, when the IL ions are sufficiently amphiphilic, short-range solvophobic interactions become important. This

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enables uncharged alkyl chains to aggregate and a bicontinuous phase morphology in the bulk through the mutual attraction of polar and apolar groups.

In the same way that revelations of pronounced bulk liquid structure forced chemists to rethink the nature of bulk IL processes (eg. solvation and reactivity, thermodynamics and kinetic properties, rheology and transport behaviour), reports of well-defined interfacial ion organization will change our understanding of IL interfacial phenomena.**

In several respects, IL-solid interfaces are more structurally similar to absorbed surfactant layers. This may be expected, as many ILs are amphiphilic. The key concept developed in Section 4 is that IL interfaces consist of three separate but related zones: the *interfacial layer*, which refers to ions in direct contact with the other phase; the *bulk phase*, which refers to the bulk liquid region, which may be structured or unstructured depending on the length of the cation alkyl group; and the *transition zone*, which refers to the region over which the more pronounced interfacial layer structure decays to the bulk morphology. The properties, and therefore usefulness of ILs in interface dependent applications, will depend on the structure of the ions in all three regions.**

The interfacial layer consists of ions in direct contact with the second phase, and displays the greatest degree of organization, incliding in the lateral direction. The preferred ion orientation depends principally on the nature of the interface. For solid charged interfaces, ions are adsorbed electrostatically, and therefore will be organized to maximise the interaction between charged moieties and surface sites. High surface charge density will produce a monolayer of counter ions, while lower surface charges will produce an interfacial IL layer that is enriched in one ion or the other. As studies of charged surfaces have so far been limited to anionic substrates, cation monolayers have only ever been observed. Conversely, for uncharged and or hydrophobic solid interfaces, neutral segments (typically the hydrocarbon chain) arrange facing towards, or lying along, the interface to maximise

solvophobic interactions. This means that at hydrophobic interfaces, the interfacial layer is comprised of both cations and anions, with the relative population primarily determined by hydrophobicity. For short alkyl chain cations, Coulombic forces dominate and a mixed layer results. As the alkyl chains become longer, solvophobic interactions become more important than electrostatic ones.**

The transition zone refers to the region between the interfacial layer and the bulk liquid, through which the well defined interfacial structure decays to the less ordered morphology of the bulk liquid. For ILs with sponge-like bulk order, the transition that occurs is from a surface induced lamellar structure to the bulk sponge, analogous to the surface induced phase transitions that occur in aqueous surfactant systems. If the bulk order is not present, the interfacial structure decays to an amorphous fluid, but as this change still occurs over a discrete distance, the transition zone definition holds. The distance over which the transition zone extends is a function of the level of order induced by the surface and the strength of the bulk structure. Atomically smooth surfaces that interact strongly with the IL (either electrostatically or solvophobically) will lead to the most pronounced interfacial structure. The level of structure is decreased by surface roughness or reduced surface-IL interaction strength. In general, the transition zone is widest for strongly structured ILs with surfaces that are highly charged and atomically smooth. However, increasing the cation alkyl chain length also leads to increased molecular flexibility, which can decrease the extent of the transition zone. Experiments are required to determine which effect is of greater consequence.**

1.5.2 Overview of Chapters in this Thesis

To date, the vast potential offered by ILs as 'designer' solvent materials is unfulfilled because comprehensive knowledge of their structural arrangements has, unlike molecular solvents, yet to be ascertained. This is particularly evident for protic ILs which have generally received less attention that aprotic ILs, although the imbalance is slowly being addressed.^[22] The under-exploitation of ILs is illustrated by the fact that relatively few industrial chemical processes have successfully integrated them into their design methodology.^[480] Recent surveys have suggested industry decision makers rank ILs as very complex technology, and perceive a high risk associated with full-scale introduction.^[481]

In order to unlock the chemical (and economic) potential offered by ILs, significant investment of time and resources must be directed to elucidating the relationship between molecular structure, intermolecular interactions and physiochemical properties. In this Thesis we combine cutting-edge techniques such as Neutron Diffraction (ND) to examine bulk-IL structure and compare this to solid-IL interfacial morphology, probed using Atomic Force Microscopy (AFM). Building upon previous findings within our group,^[482] and others^[404] it is evident that bulk and surface morphologies in these liquids are closely related.

Most academic or industrial applications are expected to use ILs as solvents for bulk chemical processes or as functional additatives at interfaces. This means that it is important to characterize ion-ion and ion-interface interteractions that drive self-assembly, as well as understand their effects on the macroscopic properties. Thus, as summarised in the scheme presented in Figure 7, the goals of this work are to determine IL structure-property relationships. This will enable us to develop strategies for molecularly designing ILs likely to be suitable for a given application, depending on whether bulk solution or near-surface order is desirable. Moreover, the work will lead to intellectual breakthroughs in the understanding of IL solvent structure in order to create and optimise new nanostructured materials.

The bulk solution structure of the two oldest protic ILs is examined in Chapter 3. Neutron diffraction (SANDALS) data has been collected for ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN) and fitted using a reverse Monte Carlo based simulation called empirical potential structure refinement (EPSR). Robust models for the bulk solvent structure were developed by fitting three chemically identical, but isotopically different samples of each IL [fully hydrogeneous (H-), partially deuterated (d_3 -) and fully deuterated (d_8 -)] simulataneously. The SANDALS spectrum of d_3 -EAN has a well-defined pre-peaks or first sharp diffraction peak at low q consistent with long-range mesoscopic solvent structure. The EPSR model shows that this structure is of solvophobic origin, similar to a bicontinuous microemulsion or disordered L_3 -sponge phase, but with a domain size an order of magnitude smaller (10.1 Å). The alcohol (-OH) moiety in EtAN interferes with solvophobic association between cation alkyl chains resulting in small clusters of ions, rather than an extended network. Thus, this paper confirms the central hypothesis of this project: that the level of bulk PIL structure can be modified through simple changes in ion chemical structure.

Chapter 4 interrogates the bulk solvent arrangements in a related protic IL, propylammonium nitrate (PAN) using the same combination of SANDALS measurements and ESPSR data fitting. Until recently, the ion arrangements in PAN were a matter of some contention in the IL community. Apart from the most basic structural characteristics such as its "good" ionic composition and capacity to hydrogen bond, models developed for PAN's bulk structure differed widley in the literature, ranging from ion clusters to smectic arrangements and freely dissociated ions. This publication reports the bulk structure of PAN with atomic detail. The results show that PAN self-assembles into a quasi-periodic bicontinuous nanostructure reminiscent of an amphiphile L_3 -sponge phase. The nanostructure is longer (11.9 Å) and more pronounced than that previously determined for ethylammonium nitrate (EtAN) in Chapter 3 because of the extra methylene unit on the

cation alkyl chain. The model also shows unambiguous evidence of alkyl chain interdigitation, which suggests that packing arguments need to be considered in future studies of ionic liquid bulk structure.

How do protic ILs dissolve in water? This question is addressed in Chapter 5, and describes the bulk morphology of equal masses of water and the protic IL EAN. As EAN is completely miscible with water, this raises questions such as: how do EAN and water mix? Are the forces that lead to self-assembly in pure EAN (Chapter 3) sufficient to maintain a solvophobic nanostructure? What is the nature of ion solvation in such mixtures? SANDALS data for three isotopomers of EAN+H₂O were examined, d_3 -EAN+D₂O, d_8 -EAN+H₂O and d_8 -EAN+D₂O. Our results show that even at high salt content, EAN/water forms a pronounced, bicontinuous nanostructure. The local arrangement of water molecules and EAN ions in this solution is strikingly similar to the pure liquids because of self-assembly akin to surfactant mesophases but on much smaller length scales. This study paves the way for new, environmentally friendly nanostructured fluids that retain key solvent properties of ILs, but at lower overall cost.

In Chapter 6 we systematically examine how protic ILs hydrogen (H-) bond. Since the days of Latimer and Rodebush,^[107] much interest has been directed to understanding hydrogen (H-) bonding and its contribution to solvent structure. Despite their pure ionic composition, H-bonds are a hallmark of protic ILs as donor and acceptor groups are formed on the ions during synthesis via proton transfer. To date, there has been no systematic study of protic IL H-bonding; whilst H-bonds are ubiquitous in the bulk, its contribution to solvent (nano-)structure and macroscopic physical properties is difficult to deconvolute from other ion-ion interactions. The combination of neutron diffraction SANDALS data & EPSR simulation enables a highly detailed picture on PIL H-bonding to be developed, which cannot be achieved by other experimental / computational techniques. Information on the size,

direction, strength, and distribution of hydrogen bonds in several protic ILs is presented. There is significant variation in PIL hydrogen bond interactions ranging from short and linear to long and bi-/trifurcated. Strikingly, H-bond direction and strength can be related to macroscopic physical properties; shorter, more linear H-bonds produce solid-like ILs whereas weaker, bent H-bonds lead to a more fluid-like material.

Chapter 7 presents a comparative SANDALS and EPSR study of the bulk liquid nanostructure for several primary alkylammonium protic ILs. The results in this manuscript build upon and expands our recent publication in Chapter 6 where we examined the nature of hydrogen bonding in PILs. Models for six IL systems, each refined against multiple H/D contrasts are elucidated. We show that all the ILs self-assemble into L_3 -sponge-like bicontinuous nanostructures on account of their amphiphilic character. Here, the key role of partial volumes towards understanding IL nanostructure is documented. Thus, a link to classical models for amphiphile self assembly is drawn, similar to but distinct from the packing parameter g used in aqueous surfactant dispersion. This Chapter also reveals the relative contribution of electrostatic (attractive and repulsive), solvophobic and hydrogen bonding interactions towards these nanostructures.

IL electrochemical research is complicated by the absence of a comprehensive model for the structure of the electrified solid-IL interface and resulting potential distribution. Whilst well-described for aqueous systems, models for the IL electrical double layer still in their infancy. In Chapter 8, Atomic Force Microscopy is used to directly probe the near-surface structure of the Au(111) electrode interface for two aprotic ILs 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ($[Py_{1,4}]FAP$) and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ($[C_2mim]FAP$) for potentials between ±2.0 V (vs Pt electrode). The force-separation profiles suggest a multilayered morphology is present at the electrified Au(111)-IL interface, with more near surface ion layers detected at higher

potentials. This interfacial structure is not consistent with a double layer model in the Stern-Gouy-Chapman sense for aqueous electrolytes, as there is no diffuse layer. The structure is consistent with a capicitator-like double-layer model, with a very small separation distance between the planes of charge. Complementary STM data fo the same ILs at the Au(111) interface, is examined in Appendix 5 & 6. Likewise, *in situ* electrochemical control nanoscale friction has been demonstrated in Appendix 9 using the setup described in Chapter 8. This demonstrates the potential for (nano)tribotronics,^[483] where electric potentials control the lubricating properties of a self-replenishing boundary lubricant.

The effect of added LiCl on the IL electrical double layer structure is elucidated in Chapter 9. Interfacial layering is markedly weaker when small amounts of LiCl are dissolved in the IL 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate (C_6 mim FAP) for all potential between -2V and +2V (vs Pt). This means that models developed for pure IL electrical double layer may not be valid when solutes are present. The results in this Chapter should be read in conjunction with a corresponding study for pure [C_6 mim][FAP]-Au(111) interface in Appendix 7.

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CHAPTER 2

C2: Materials and Methods

This Chapter examies experimental procedures used in subsequent peer-reviewed papers. Sections 1, 2 & 3 are related to Chapters 3-7 whilst Section 4 is concerned with Chapters 8, 9.

2.1 Synthesis & Purification of Protic Ionic Liquids

The protic ILs examined via neutron diffraction are detailed in Table 5. This section describes the synthesis and purification methods used to prepare pure ILs for scattering experiments. The majority of ILs were created via acid-base neutralization reactions (§2.1.1). However, a multistep, reflux condensation was used in the synthesis of thiocyanate-based ILs to avoid use of thiocyanic acid (§2.1.2). Excess aqueous solvent was removed in each sample by a number of steps (§2.1.3). Chemically identical, but isotopically different IL contrasts were made by selectively replacing hydrogen with deuterium on the exchangeable (d_3 -ILs, §2.1.4) or exchangeable and non-exchangeable (d_8 -ILs and d_9 -ILs, §2.1.5,).

2.1.1 Acid-Base Neutralization

EAN, EAF, EAHS, EtAN and PAN were synthesied by equimolar combination of a Bronstead acid and Bronstead base. This involves dropwise addition of the acid to a chilled solution (<10°C) of the amine and distilled water (~50 wt% amine). During acid addition, the mixture was rapidly stirred to disperse heat generated. The hydrogeneous reagents used to prepare fully hydogeneous (H-PILs) are listed in Table 4.

2.1.2 Reflux Condensation

EASCN and BASCN were prepared as described by Poole et al. from gentle reflux (~75°C) of a solution of ethylamine (Alderich, 70 v/v%) or butylamine (Alderich 99.5 v/v%) and ammonium thiocyanate (BDH Chemicals, 98%). The solution was stirred over several hours until evolution of ammonia ceased. The solid product was purified by two or three hot recrystallizations in an ethanol + water mixtures, with increasingly lower ethanol content.

Reagent		Abbreviation	Supplier	MW (g.mol ⁻¹)	ρ (g.cm ⁻¹)	Purity (v/v%)
	Ethylamine	EA	Alderich	45.08	0.796	70
Bronstead	Ethanolamine	EtA	Sigma-Alderich	61.08	1.012	99
Bases	Propylamine	PA	Alderich	59.11	0.719	98
	Butylamine	BA	Alderich	73.14	0.740	99.5
Dronstand	Nitric	Ν	Sigma-Alderich	63.01	1.42	69
Acids	Sulphuric	HS	Sigma-Alderich	98.08	1.84	95
	Formic	F	Fulka Analytical	46.03	1.22	98
	<i>d</i> ₅ -ethylamine	d_5 -EA	CDN Isotopes	50.08	gas at STP	99
	d_4 -ethanolamine	d_4 -EtA	CDN Isotopes	65.08	NA	99
Other	RO water	H_2O	-	18	0.9994	99.9
Compounds	Deuterium oxide	D_2O	Sigma Aldrich	20	1.11	99
	ammonium thiocyanate	NH ₄ SCN	BDH Chemicals	76.12	1.30	98

Table 4- Chemical reagents used in synthesis of protic ILs.

2.1.3 Removal of aqueous solvent

Excess aqueous solvent was removed by a number of steps. Firstly, the samples were rotor evaporated for several hours at 40-50 °C. The resultant concentrated salt solution (H₂O content ~2% v/v%) was then purged for at least six hours with filtered N₂ gas. This was heated overnight in an oil bath at 110°C under a N₂ atmosphere, leading to water contents undetectable by Karl Fisher titration (H₂O content <0.01 v/v%). As EAF is known to thermally degrade, its samples were purified solely by rotor evaporation mostly at room temperature, with occasional ramping to 40°C.

Table 5- Properties and structure of protic ionic liquids examined via neutron diffraction. Molecular Weight (MW), Density (ρ), Melting Point (T_M), Glass Transition temperature (T_g), Ion Pair Diameter (D_m), Ion Pair Volume (V_{IL}), Alkyl Chain Volume (V_{alkyl}), Ionic Conductivity (κ), viscosity (η). Water is included for comparison. Atom colours are as follows: C is grey, N is blue, O is red, H is white. Data for the hydrogeneous (H-) contrasts are listed.

Liquid	Structure	Contrasts	MW (g.mol ⁻¹)	ρ (g.cm ⁻³)	T _m (°C)	Tg (°C)	D _m (nm)	V _{IL} (Å ³)	V _{alkyl} (Å ³)	к (mS/cm)	η (cP)	H ₂ O content	Thesis Chapter
Ethylammonium Nitrate (EAN)		H-EAN, d ₃ -EAN, d ₈ -EAN	108.1	1.21	13ª	-91.5	0.53	149 ^b	81.6	26.9 ^a	32	< 0.01	C3, C5, C6, C7, A1, A4
Ethylammonium Formate (EAF)		H-EAF d₃-EAF d ₈ -EAF	91.1	0.99	-15	-106	0.53	153	81.6	12.16	23	< 0.15	C6, C7, A1, A4
Ethylammonium Thiocyanate (EASCN)		H-EASCN d ₃ -EASCN	104.1	1.19	41	-84	0.53	145	81.6	-	-	< 0.01	C6, C7
Ethylammonium Hydrogen Sulphate (EAHS)		H-EAHS d ₃ -EAHS d ₈ -EAHS	143.0	1.42	40	-84	0.55	168	81.6	4.4	128	< 0.01	C6, C7
Ethanolammonium Nitrate (EtAN)		H-EtAN, d₄-EtAN, d ₈ -EtAN	124.0	1.26	52	-25	0.54	157	88	9.35	NA	< 0.01	C3, A1, A4
Propylammonium Nitrate (PAN)		H-PAN d ₃ -PAN	122.1	1.15	3	-	0.56	176	108.8	12.97	67	< 0.01	C4, C6, C7, A4
Butylammonium Thiocyanate (BASCN)		H-BASCN d ₃ -BASCN	132.1	1.01	20.5	-	0.60	216	136.1	-	97	< 0.01	C6, C7
Water (H ₂ O)		H ₂ O HOD D ₂ O	18.02	0.994	0	-137	0.31	-	-	-	1	_	C5

2.1.4 Partially deuterated $(d_3$ - or d_4 -) contrasts

The d₃-contrasts were prepared *in vitro* by selectively replacing hydrogen with deuterium on the exchangeable ammonium group protons. This was achieved by washing volumes of the corresponding pure H- sample several times in excess fresh deuterium oxide (D₂O, 99% Sigma Aldrich) where mol:mol ratio of D₂O:PIL in the mixture >3:1. Excess aqueous solvent was removed via rotor evaporation after each wash. Previous ¹H-NMR experiments reveal that, on average, 2.5 out of 3 amino hydrogens are replaced with deuterium per wash in D₂O.^[1] In these experiments, *d*₃-contrasts were washed at least three times in excess D₂O.

2.1.5 Fully deuterated (d_8 - or d_9 -) contrasts

The fully deuterated analogues d_8 -EAN, d_8 -EAF, d_9 -EAHS, d_8 -EtAN were prepared as per their partially deuterated contrasts but from special custom-made samples of deuterated reagents. Deuterated ethylamine and ethanolamine were sourced from CDN Isotopes and used as received. NMR and GC analysis by the manufacturer showed each possessed >99% isotopic H/D exchange and >99.5% chemical purity.

1,1,1,2,2- d_5 -ethylamine (CD₃CD₂NH₂, gas at STP) was used to synthesized fully deuterated analogues of the ethylammonium-based PILs. The gas was trapped in D₂O (99% Sigma Aldrich) on a Schenk line with liquid nitrogen.

1,1,2,2- d_4 -Ethanolamine was used to synthesise d_8 -EtAN. As it is a liquid at room temperature, preparation is much easier than for 1,1,1,2,2- d_5 -ethylamine, and the sample was initially mixed with D₂O (99% Sigma Aldrich) ready for acid addition.

Once deuterated amine + D_2O mixtures were isolated, fully deuterated analogues were subsequently prepared by reacting it with the appropriate concentrated acid. Pure samples were collected by removing excess aqueous solvent §2.1.3, and washing in excess D_2O as described for d_3 - contrasts §2.1.4.

2.1.6 Comments on purity and storage

Colloid science has a rich history of trace impurities (surface active or dissolved) that have been the cause of a number of sensational phenomena^[2,3] which were later refuted.^[4-6] The science of ILs is surely not immune to this; indeed IL solvents are well-known for their ability to simultaneously dissolve a polar and apolar compounds. An important example of this is water. Ideally ionic liquids have zero water content yet water is known to be the most common impurity in ILs^[7] and even nominally hydrophobic ILs absorb significant quantities of water when exposed to the atmosphere.^[8] There are numerous examples in the literature of dramatic changes in IL solvent properties when contaminated with water. The upshot of this is between experiments all ILs were sealed with parafilm and (when possible) stored in a desiccators, thus minimising sample exposure to the atmosphere.

All surfaces that come into contact with the IL sample for both the neutron diffraction and atomic force microscopy experiments were rigorously cleaned. Such surfaces include glassware, vials, lids, quick-fit joints, magnetic stirrer bugs, spatula's, *inter alia*. This was achieved by sequentially washing the surfaces in concentrated base solution (10 wt% NaOH), ethanol, acetone, dilute CTAB (or similar surfactant) solution. After this, the surface was rinsed seven times in RO water and left to dry.

2.2 Neutron Diffraction

2.2.1 Principles of Neutron Diffraction

A neutron is an electrically neutral, subatomic particle with mass 1.675×10^{-27} kg, spin number of $\frac{1}{2}$ and magnetic moment -1.913 nuclear magnetons. Neutrons are a stable constituent of all atomic nuclei except ¹H; so stable in fact that it was only in 1932 (well after the first reasonable models for the atom) that evidence for the neutron's existence was reported by Chadwick.^[9] Subsequent experiments by Halban & Preiswerk^[10] and Mitchell & Powers^[11] showed wave-like diffraction behaviour of neutrons. This was an important turning point in condensed matter research as diffraction was known to be a property of waves, not particles. Thus, neutrons must obey the wave-particle duality described by the de Broglie equation,^[12] as a wave of length (λ) and velocity (ν):

$$\lambda = \frac{h}{m_{N}.v}$$
 Equation 1

where m_n is the neutron mass (1.675 x 10⁻²⁷ kg) and *h* is Planck's constant (6.626 x 10⁻³⁴ J.s). Because diffraction occurs when the size of the spacing is equal to the probe wavelength, it was immediately recognised that neutrons could be used as a probe of atomic, or near-atomic length scales, depending on the velocity. This is the basis for a neutron diffraction experiment. However, several obstacles still existed, notably lack of reliable sources of neutrons, to develop a neutron beam of constant, high flux. In the latter half of the 20th century, this has been overcome with reactor- and synchrotron-based neutron sources. Here, classification according to their wavelength provided in Table 6 below:

Neutron Type	Wavelength, λ (Å)	Energy, E (meV)	Temperature, T (K)	Velocity, v (m.s ⁻¹)
Epithermal	0.29	1000	12 000	14 000
Thermal	1.8	25	290	2 200
Cold	10	1	12	440

Table 6- Classification of neutrons according to wavelength.

2.2.2 Scattering Theory

In principle, there are four main interactions of neutrons with matter: via the strong nuclear, weak nuclear, electromagnetic and gravitational forces. The strong nuclear interaction is the most important dominance of make controlled sources of neutron radiation an indispensible probe of condensed matter research. As neutrons are uncharged and long lived (~1000s as a free particle), they can strongly penetrate bulk matter without significantly perturbing the macroscopic or microscopic features of the system.

Since the pioneering work of the Braggs,^[13] it can be shown that when the probe wavelength is comparable with the interatomic spacings in a material, the scattered radiation generate an interference pattern that is characteristic of the underlying structure:

$$n\lambda = 2d \sin\theta$$
 Equation 2

Here, d and Q are the lattice spacings in Å and Å⁻¹ respectively and θ the diffraction angle. Like the wavelength (1), the non-relativistic neutron energy depends on its velocity:

$$E_k = \frac{1}{2}m_N v^2 = \frac{h^2}{2m_N \lambda^2}$$
 Equation 3

so it is possible then to select a neutron wavelength corresponding to structural features of interest. Combining Equation 2 and 3, we can show:

$$4Q = \frac{h}{m_N v \sin \theta} = \frac{T_f m_N \sin \theta}{hL}$$
 Equation 4

where *L* is the distance between the detector and moderator (11.016m in SANDALS instrument), and T_f is the time of flight. Hence, neutrons that are scattered from unique atomic planes arrive at the detector at the same time. The spatial distribution in a material is thus a function of several parameters, with the signal intensity as a function of time and diffraction angle, $I(T_f, \theta)$, corrected for deadtime,[‡] across specific wavelength spreads gives an indication of the structure.

^{\ddagger}Dead time: lag between the moment the ¹n collides with the detector and the time the detector notices this event.

Whereas X-rays are influenced by virtue of the charge in atom's electrons, neutrons interact with individual nuclei via the strong nuclear force. Consequently, the strength of neutron scattering events is not correlated with atomic number, but with a parameter called the scattering length (b) of the nucleus, that varies erratically with the mass (c.f Table 7). The upshot of this is that neutrons can distinguish one isotope of the same element from another and are sensitive even to light atoms such as hydrogen. This can be exploited for contrast variation, in which different molecular regions are systematically highlighted as the neutron "sees" (strongly interacts) with some nuclei and not with others.

Nuclei	$b (10^{-12} \text{ cm})$	Nuclei	$b (10^{-12} \text{ cm})$
$^{1}\mathrm{H}$	-0.3741	¹⁹ F	0.5650
2 H	0.6671	²³ Na	0.3580
12 C	0.6646	³¹ P	0.5131
14 N	0.9370	32 S	0.2847
¹⁶ O	0.5803	Cl	0.9577

Table 7- Selected atomic coherent scattering lengths, sourced from King^[14]

The scattering can always be mathematically divided into a *coherent* and an *incoherent* part. Coherent scattering depends on correlations between the positions and motion of the same nucleus and different individual nuclei as a function of time. This is subject to interference effects and can be thought of as the scattering the system would give if all the scattering lengths were equal to $\langle b \rangle$ (=b average). Incoherent scattering is related only to correlation between the positions of the same nucleus at different times. Thus, incoherent scattering arises from the deviations of the scattering lengths from the mean system value.

It is also possible to differentiate between *elastic* and *inelastic* scattering. Elastic scattering refers to neutron-nuclei collision events that result in changes in the direction of neutron momentum. Alternatively, energy may be lost or gained in the event (recoil of the whole nucleus or excitation of internal degrees of freedom) and when this occurs it is termed inelastic scattering.

2.2.3 Small Angle Neutron Diffractometer for Amorphous & Liquid Samples

SANDALS is a time of flight (TOF) diffractometer located at ISIS research facility, Rutherford Appleton Laboratories, United Kingdom (c.f. Figure 1).^[15] An intense, pulsed beam of neutrons is generated via a nuclear reaction (called spallation) from collisions between a proton beam accelerated to 800 MeV and a tungsten target. The large inelastic cross section of hydrogen atoms in a liquid methane moderator was used to slow the ejected neutrons to useful velocities for condensed matter research.

Neutron diffraction data were collected over the Q range 0.05 to 50 Å⁻¹, which corresponds to an incident neutron wavelength (λ) varying between 0.05 to 4.5 Å. Banks of Zinc Sulphide scintillator detectors between 0.75 and 4.0 m from the sample provided continuous angular monitoring of diffracted neutrons over the 20 range 3.8° to 39°.



Figure 1 Schematic representation of the (A) SANDALS instrument and (B) flat plate Ti-Zr sample can used to hold the ILs in the beam centre.

The ILs were loaded into specially designed 1mm wide flat plate curvetts, known as cans as shown in Figure 1B. The can is made of a Titanium-Zirconium alloy (67.5% Ti and 32.5% Zr) of known atom density of 0.0541 atoms/Å³ and wall thickness of 1 mm. It provides a
chemically inert, null[§] scattering environment in which to analyze the liquids. Prior to loading, the diffraction measurements over the Q range were made on the empty cans, empty instrument and a vanadium standard sample for the purposes of data normalization. The IL were sealed in the cans using a PTFE O-ring. These were then simultaneously mounted on an automatic sample changer for real-time control of the can position and assayed sample.

The experiments were conducted at 298K or 338K under vacuum. The sample chamber was left to equilibrate for 10 minutes prior to measurements taken. The temperature was maintained to $\pm 0.1^{\circ}$ by a Julabo FP50 temperature controller, circulating 8 litres of 50/50 v/v% ethylene glycol-water mixture within the automatic sample changer. The weight of the (can + IL) for each sample was measured before and after measurement to ensure no IL evaporation in the vacuum chamber. The net run time for each system was at least 8 hours.

2.2.3 Data Analysis and Normalization

The data analysis was carried out using a collection of FORTRAN programs available under the graphic interface GUDRUN and described in the ATLAS manual.^[16] This program applies the standard corrections for neutron scattering data: normalisation to the incident flux, absorption and multiple scattering corrections, Ti-Zr can subtraction. Gudrun then normalises the data to absolute units by dividing the measured differential cross section by a vanadium standard of known thickness. Finally, calibration for single atom scattering, particularly inelastic scattering of hydrogen inelasticity corrections, are applied.^[17] the equation for the background subtraction in q-space is:

$$I(q) = \sum_{i} A_{i} \exp\left(-Q/\gamma_{i}^{n}\right)$$
 Equation 5

 $^{^{\$}}$ Titanium has a coherent scattering length of -3.44 fm and Zirconium +7.16 fm. If these two elements are alloyed in the mass ratio Ti:Zr=7.16:3.44 i.e. 2.1:1 then the total coherent scattering length should equal zero. This provides a transparent container for neutron diffraction experiments.

Where A is the amplitude, γ is the decay constant and n is the scaling constant in the GUDRUN tabs. A, γ and n parameters used for various IL samples are listed in Table 8 below. Also present are values for the slightly more involved top-hat correction, developed by Soper.^[17]

	Stretche	Stretched Exponential Parameters						
IL System	Amplitude	Decay const.	Scaling Const.					
H-EAN	8.0	3.0	0.75	0.3				
d_3 -EAN	8.0	3.0	0.9	0.3				
d_8 -EAN	0.0	0.0	1.0	0.3				
H-EtAN	8.0	3.0	1.1	0.3				
d_4 -EtAN	4.5	3.0	0.9	0.3				
d_8 -EtAN	0.0	0.0	1.0	0.3				
H-PAN	5.0	3.0	0.9	0.3				
d_3 -PAN	10.0	3.0	0.9	0.3				

Table 8- Calibration for single atom scattering function parameters for the IL systems as performed in
 GUDRUN software

Once the data was normalized and inelastic corrections made the fitting process with Empirical Potential Structure Refinement (EPSR) could commence.

2.3 Empirical Potential Structure Refinement

2.3.1 Overview

Empirical Potential Structure Refinement (EPSR) is a special Monte Carlo simulation for disordered materials. Compared to traditional computational simulations of the liquid state, the EPSR algorithm is written to build a model of the system consistent with physicochemical properties (eg. liquid density, molecular structure) and available structural data (in this case neutron diffraction spectra).

In the following section an explanation of the conditions used to define Monte Carlo simulations generally, and EPSR specifically, is given. The account is not intended to be comprehensive, and the reader is directed to the official guide^[18] for further reference.

2.3.2 "That's all very well in practice, but will it ever work in theory?"^[19]

Repeatedly solving Schrödinger's equation, even approximately, for large numbers of molecules is enormously difficult, due to the large processing power required for the full treatment of electronic structure. Instead, simulations use approximate models for the forces between molecules, which can handle upwards millions of mutually interacting atoms.

A Monte Carlo algorithm, such as that in EPSR, converges to a solution by assembling a 3D box of molecules; whereby the number of particles and the pressure and temperature of the system are constrained. Within this framework, the atoms and molecules can be moved relative to one another via translations, rotations and torsional operations which may raise or lower the total potential energy (U) of the system. This process is based on the determination of a series of random numbers, so that a move results in a small change in the (x,y,z) coordinates of the atom or molecule. For instance:

$$\begin{split} x_{final} &= x_{initial} + (Random number \ between \pm 1) imes Step \ Size \\ y_{final} &= y_{initial} + (Random number \ between \pm 1) imes Step \ Size \\ z_{final} &= z_{initial} + (Random number \ between \pm 1) imes Step \ Size \end{split}$$

where $(x_{initial}, y_{initial}, z_{initial})$ and $(x_{final}, y_{final}, z_{final})$ are the initial and final Cartesian coordinates respectively and the Step Size is a quantity fixed at the start of the process.

Whether a particular move is accepted or rejected is governed by the Metropolis condition.^[20] This examines changes in the potential energy of the system:

$$\Delta U = U_{final} - U_{initial}$$
Equation 6

If the change lowers the total system energy, $\Delta U < 0$, the move is always accepted. If this raises the total system energy, $\Delta U > 0$, the move is rejected. (Strictly speaking, EPSR imposes a probability condition for changes resulting in $\Delta U > 0$ defined by:

$$\exp\left[\frac{-\Delta U}{k_BT}\right] > Random number between 0 and 1$$
 Equation 7

where k_B is the Boltzmann constant (1.3806 x 10⁻²³ J.K⁻¹) and *T* the system temperature. This is to ensure the system proceeds along a Markov chain^[21] over a long period of time visiting a large volume of the available phase space.)^[18]

Thus, the value and development of the total system energy is fundamental to the modelling process. In EPSR, this is broken into two terms, the reference potential energy, U_{Ref} , and the empirical potential (EP), U_{Ep} :

$$U = U_{Ref} + U_{Ep}$$
 Equation 8

The reference potential assumes the standard form by considering the total Lennard-Jones interaction potentials plus a truncated Coulombic^[22] charge:

$$U_{ref} = \frac{1}{2} \sum_{i,j \neq i} \sum_{\alpha,\beta} \left(4\varepsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i}\beta_j} \right)^n - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha_i}\beta_j} \right)^6 \right] + \frac{q_{\alpha}q_{\beta}}{4\pi\varepsilon_0 r_{\alpha_i}\beta_j} \right)$$
Equation 9

Here α,β represent types of atoms i,j respectively. $\epsilon_{\alpha\beta}$ (in KJ.mol⁻¹) and $\sigma_{\alpha\beta}$ (in Å) define the well depth and range parameter for Lorentz-Berthelot mixing rules for atomic interactions:

$$\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha}\varepsilon_{\beta}}$$
 Equation 10 and

$$\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_{\alpha} + \sigma_{\beta})$$
 Equation 11

 q_{α} and q_{β} are the Coulombic point charges on the atoms, $r_{\alpha_i\beta_j}$ is the distance of separation, π assumes its normal value (3.1415...), ε_0 is the permittivity of free space 8.854 x10⁻¹² F.m⁻¹, n

is set to 12 consistent with the Mie potential, ε_{α} and ε_{β} are the respective dimer binding energies for two α atoms or two β atoms ideally separated, σ_{α} and σ_{β} are the distances at which the interaction energy between two α atoms or two β atoms is zero.

These intramolecular and intermolecular forces in the reference potential are calculated as though each molecule is at the centre of the box with an effective radius of interaction called the minimum image convention.^[21] Periodic boundary conditions are also utilized so as to not penalise moves which approach the box wall. This means that if an atom is induced to leave the box, rather than bouncing off a hard wall, it moves back in from the opposite face. No correction is made for long range forces greater than half the box dimension.

The empirical potential is generated using a series of power exponential functions:

$$U_{Ep}(r) = k_B T \sum_i C_i p_{n_i}(r, \sigma_r)$$
 Equation 12

where
$$p_n(r,\sigma) = \frac{1}{4\pi\rho\sigma^3(n+2)!} \left(\frac{r}{\sigma}\right)^n exp\left[-\frac{r}{\sigma}\right]$$
 Equation 13

Here, ρ is the atomic number density of the material and C_i are real coefficients that can be estimated from the diffraction data via a 3D Fourier transform of the p_n function into Q space. σ_r is a width function defined by the user, used to guide the atomic and molecular moves in directions that yield the closest representation of the diffraction data. This approach has been very successful in representing true differences between simulation and diffraction data, provided that artefacts associated with statistical noise, truncation effects and systematic errors are eliminated.^[18,21]

2.3.3 The Fitting Procedure

A reasonable molecular skeleton for the ions can be developed from *ab initio* molecular orbital calculations in Spartan 08®^[23] software (c.f. Table 9 & Table 10). Makeshift ions were built in the editor window imported into the computational engine. This entailed assembling the constituent atoms in the blank workspace and connecting chemical bonds appropriately. Each three-dimensional (3-D) geometry drawn was sequentially optimized (bond lengths, angles & atom point charges etc.) at the 3-21G* basis set and Hartree-Fock (HF) theory level.

Table 9- Lennard-Jones and Coulombic charge parameters for EPSR modelling of PIL cations. Atom point charges were determined from Spartan 08 modelling at the 3-21G* basis set and Hartree–Fock (HF) theory level. ε is in kJ.mol⁻¹, σ is in Å and q is in Coulombs

Ethylammonium		Ethanolammoniun			Propylammonium				Butylammonium						
Atom	3	σ	q	Atom	3	σ	q	Atom	3	σ	q	Atom	3	σ	q
C_1	0.276	3.50	+0.263	C ₁	0.276	3.50	+0.091	C ₁	0.276	3.50	+0.108	C ₁	0.276	3.50	-0.055
C_2	0.276	3.50	-0.411	C_2	0.276	3.50	+0.315	C_2	0.276	3.50	-0.037	C_2	0.276	3.50	+0.037
Ν	0.711	3.25	-0.529	Ν	0.711	3.25	-0.589	C ₃	0.276	3.50	-0.653	C ₃	0.276	3.50	-0.049
H_1	0.126	2.50	+0.069	O_1	0.879	2.96	-0.753	Ν	0.711	3.25	-0.734	C_4	0.276	3.50	-0.130
H_2	0.126	2.50	+0.147	H_1	0.126	2.50	+0.124	H_1	0.126	2.50	+0.118	Ν	0.711	3.25	+0.586
$H_{\rm N}$	0.126	2.50	+0.366	H_2	0.126	2.50	+0.020	H_2	0.126	2.50	+0.095	H_1	0.126	2.50	+0.026
				H_N	0.126	2.50	+0.382	H_3	0.126	2.50	+0.209	H_2	0.126	2.50	+0.029
				Ho	0.126	2.50	+0.502	H_{N}	0.126	2.50	+0.421	H_3	0.126	2.50	+0.030
												H_4	0.126	2.50	+0.039
												$H_{\rm N}$	0.126	2.50	+0.108

Table 10- Lennard-Jones and Coulombic charge parameters for EPSR modelling of PIL anions. Atom point charges for PIL anions were determined from Spartan 08 modelling at the 3-21G* basis set and Hartree–Fock (HF) theory level. ε is in kJ.mol⁻¹, σ is in Å and q is in Coulombs

Thiocyanate			Formate				Nitrate				Hydrogen Sulphate				
Aton	3	σ	q	Aton	3	σ	q	Ato	a e	σ	q	Atom	3	σ	q
\mathbf{S}_{T}	1.046	3.55	-0.560	C _F	0.276	3.50	+0.678	No	0.711	3.25	+0.845	O ₁	0.879	2.96	-0.721
C_{T}	0.276	3.50	+0.140	O_1	0.879	2.96	-0.837	O_1	0.879	2.96	-0.615	Ho	0.126	2.50	+0.423
N_{T}	0.711	3.25	-0.580	O_2	0.879	2.96	-0.837	O_2	0.879	2.96	-0.615	S	1.046	3.55	+1.596
				$H_{\rm F}$	0.126	2.50	-0.543	O ₃	0.879	2.96	-0.615	O_2	0.879	2.96	-0.766
												O ₃	0.879	2.96	-0.766
												O_4	0.879	2.96	-0.766

The three contrasts for each IL were fit simultaneously by normalizing for isotope populations. This was achieved by sequentially defining the atomic mass number and relative isotopic substitution for each unique atom type in the hydrogeneous (H-), partially-deuterated $(d_{3}$ - or d_{4} -) and fully deuterated $(d_{8}$ -) liquids. Examples of this for EAN and EtAN are presented in Figure 2.



Figure 2 Molecular structure and atom types of (A) Ethylammonium Nitrate (EAN) & (B) Ethanolammonium Nitrate (EtAN). In each case, the blue numbers refer to the inputted bond lengths (Å) between atom types. All cation bond angles were made to be 109.47° (tetrahedral) but with rotational freedom. Anion (O–N_o–O) bond angles were set to 120° defining an x-y plane.

Once the reference potential had stabilised for a box of 250 ion pairs, the empirical potential was enabled, and slowly raised to gain a better convergence between the measured neutron diffraction structure factor, S(Q) and EPSR fit. From this simulated box of ions, many structural quantities can be calculated using internal EPSR operations to analyse the bulk structure of the liquids. The main output which will be presented here are partial pair radial distribution functions (or $g_{ij}(r)$ plots) and spatial density functions (SDF) which map the intermolecular distribution of atoms and ions.

2.4 Atomic Force Microscopy

The invention of the Atomic Force Microscope (AFM) allowed near-surface molecular ordering to be studied on a wide variety of substrates.^[24-29] Initially developed to image the topography of insulating surfaces with a sharp tip,^[30] AFM has become a standard tool in physical chemistry for high resolution surface force measurements.^[31,32] The AFM can probe a range of attractive and repulsive forces acting at solid-liquid interfaces, such as van der Waals,^[33] electrostatic,^[33] hydrophobic,^[34] hydrodynamic,^[35] and solvation forces,^[36] among others. In principle, these forces can be measured to as low as 10⁻¹¹ N, corresponding to interactions between a single atoms and a surface or even between two individual atoms.^[37] The force-resolution is sensitive to the AFM tip geometry,^[38,39] spring constant^[40] and apparent roughness.^[41]

Accurate force data derived from AFM experiments enables the structure of solid-liquid interfaces to be elucidated across vertical and lateral dimensions or under static and dynamic operating conditions. This has lead to advances in the design of everyday materials and processes (batteries, detergents, mineral extraction) through enhanced understanding of interfacial structure-property relationships. In more fundamental research, the AFM has allowed scientists to test and refine the theoretical models used to describe intermolecular and surface forces.^[37] The following section describes our *in situ* AFM protocol for investigating IL double layer structure at the Au(111) interface.

2.4.1 Principles of Atomic Force Microscopy

The operation of an AFM is well-described in literature and the interested reader is referred to technical reviews by Butt,^[31] Gan^[32] or Bhushan.^[42] Briefly, the AFM operates by scanning over the sample surface with a sharp tip situated at the apex of a flexible V-shaped Si₃N₄ cantilever. A piezoelectric scanner is employed to move the sample in three dimensions

relative to the tip with sub-nanometer accuracy when a voltage is applied (c.f Figure 3). Changes in surface topography or in probe-sample forces cause the tip to deflect either towards or away from the surface, depending on whether the interaction is attractive or repulsive. This deformation of the cantilever is detected by changes in the interference pattern of the reflected beams on a quartered diode. The AFM tip is generally in intimate repulsive contact with the surface (contact mode) via a feedback loop applied to the to the *z* portion of the *xyz* piezoelectric scanner.



Figure 3 A schematic representation of an Atomic Force Microscope (AFM).

Force curves were acquired continuously using a Digital Instruments NanoScope IIIa Multimode AFM in contact mode in an incubator at 21°C. The scan rate and scan size were between 0.1 - 0.5 Hz and 10 - 50 nm respectively. Cantilevers were sharpened Si₃N₄ tips (Digital Instruments, CA) with the batch average spring constant of 0.07 N/m \pm 0.005. One standard cantilever was used for each set of experiments. Between experiments, the tip was carefully rinsed in Milli-Q H₂O and irradiated with ultraviolet light for 40 min prior to use. To avoid contamination, tips were carefully rinsed in Milli-Q water between experiments, dried under filtered N₂ stream and irradiated with ultraviolet light for 40 minutes immediately prior to use. The ILs were held in a fluid cell sealed using a silicone O-ring. This cell was



modified for in situ electrochemical measurements as shown in



Figure 4. The changes made were inspired by a design proposed by Wanless *et al.*^[43]



Figure 4- AFM fluid cell (A) and complete setup (B) for *in situ* electrochemical measurements.

A thin cylindrical strip of Cu metal and 0.25 mm Pt wire were used as the counter electrode (CE) and quasi-reference electrode (RE), respectively. The CE and RE were cleaned firstly in dilute ~0,1 M HCl acid solution and then washed with distilled ethanol and Milli-Q H₂O and dried using filtered N2. The CE was mounted with the O-ring in the groove of the fluid cell. This was to ensure that the effective area of the CE is relatively large and axially symmetric with respect to the WE and to establish an equipotential WE surface. The RE was located

directly above the centre of the WE surface by securing the Pt wire through the outlet valve of the fluid cell. The electrodes were connected to an EG & G Princeton Applied Research Model 362 Scanning Potentiostat to provide potentiostatic control of the Au(111) surface.

The features of the AFM force curves at a given surface potential did not alter over a 48 h period. Typical start distances for force scans were 30–50 nm from the Au(111) surface. The maximum applied force in contact was between 30 and 500 nN. However, no evidence for structure was detected at forces greater than 30 nN in any system. Repeat experiments revealed that the number and period of the steps was constant. Every surface potential was studied over three or more separate experiments.

Table 11- Name, Structure, molecular weight (MW), density (ρ), molecular volume (M_v), ion pair diameter (D_m), melting point (T_m) and H_2O content of the IL examined via AFM experiments. M_v is determined from ρ and MW. D_m is found by taking the cube root of M_v . C is shaded grey, N is blue, F is yellow, S is orange, P is pink, O is red. H are not shown. (Thesis Chapters notation: C=Chapter, A=Appendix)

IL	Abbreviation	Structure	MW (g.mol ⁻¹)	ρ (g.cm ³)	M _v (nm ³)	D _m (nm)	MP (°C)	H ₂ O content	Thesis Chapters
1-ethyl-3- methylimidazolium bis(trifluoromethane sulfonyl) imide	[EMIm]TFSA		391	1.51	0.43	0.75	-15	2ppm	A2, A4
1-butyl-1- methylpyrrolidinium bis(trifluoromethane sulfonyl) imide	[Py _{1,4}]TFSA)		422	1.41	0.50	0.79	-6	2ppm	A2, A4
1-butyl-3-methyl- imidazolium hexaflurophosphate	[BMIm]PF ₆		284	1.37	0.34	0.70	12	< 0.1 v/v%	A2, A4
1-ethyl-3- methylimidazolium tris(pentafluoroethyl)- trifluorophosphate	[EMIm]FAP		556	1.71	0.54	0.83		< 3 ppm	C8, A5, A6, A9
1-butyl-1- methylpyrrolidinium tris(pentafluoroethyl)- trifluorophosphate	[Py _{1,4}] FAP	e e e e e e e e e e e e e e e e e e e	587	1.45	0.67	0.89		< 3 ppm	C8, A5, A6, A8, A9
1-hexyl-3- methylimidazolium tris(pentafluoroethyl)- trifluorophosphate Hmim FAP	[HMIm]FAP		612	1.66	0.59	0.84		< 3 ppm	C9, A6, A7, A8, A9

2.5 Chapter 2 References

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CHAPTER 3

C3: Amphiphilicity Determines Nanostructure in Protic Ionic Liquids

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3.1 Abstract

The bulk structure of the two oldest ionic liquids (ILs), ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN), is elucidated using neutron diffraction. The spectra were modelled using empirical potential structure refinement. The results demonstrate that EAN exhibits a long-range structure of solvophobic origin, similar to a bicontinuous microemulsion or disordered L_3 -sponge phase, but with a domain size of only 1 nm. The alcohol (-OH) moiety in EtAN interferes with solvophobic association between cation alkyl chains resulting in small clusters of ions, rather than an extended network.

3.2 Introduction

Solvents perform an essential role in chemistry by mediating interactions between dissolved atoms and molecules. Solvents can influence the kinetics, thermodynamics, and even the yields and favoured products of a particular reaction.^[11] These effects have long been recognized,^[2] and generated significant interest in the way solvent molecules arrange in the bulk. Equally, the intermolecular forces responsible for liquid structuring have received much scientific attention, as they provide a route to understanding colligative solvent properties from first principles.^[1,3] To date, the majority of research has considered the organization of uncharged liquid molecules, notably water.^[4-6] Recently, ionic liquids (ILs) have emerged as potential replacements for conventional solvents, mostly due to the desire for "greener" alternatives^[7] and their tuneable physicochemical properties.^[8,9] ILs are composed entirely of ions, and as such are subject to strong electrostatic interactions in addition to other cohesive interactions common to all liquids.

In this paper, the complete bulk liquid structure of the two oldest known ILs is elucidated. Ethylammonium nitrate (EAN) (m.p. 12°C) was discovered by the German chemist Walden in 1914.^[10] Walden also provided a basic definition of an IL that is still accepted today: "*water-free salts … which melt at relatively low temperatures, about up to 100* °C."^[3] Even earlier than this, in 1888, Gabriel reported the synthesis of a salt with m.p. of 52-55°C, ethanolammonium nitrate (EtAN).^[11] However, it has been widely observed that EtAN can exist as a metastable liquid at ambient temperatures with a thermal transition at -25.2 °C.^[12] EAN and EtAN belong to the protic class,^[13] meaning that they are formed by proton transfer from a Brønsted acid to a Brønsted base. This proton transfer is a chemical equilibrium, leading to classifications of "poor", "superionic", and "good" protic ILs^[14] from comparisons with ideal aqueous behavior using Walden plots of molar conductivity *versus* fluidity. EAN

and EtAN have both been shown to be good ILs,^[14] and thus may be considered pure mixtures of anions and cations.

A key feature of the acid-base synthesis protocol is that hydrogen bond donor and acceptor sites are created on the ions. This enables protic ILs to form 3-D hydrogen-bond networks reminiscent of water.^[15,16] This property has prompted numerous studies of surfactant self-assembly in protic ILs, and in many cases, correlations to aqueous systems could be drawn.^[17] Evans *et al.* investigated the size^[18] and thermodynamics^[19] of micelle formation for ionic surfactants in EAN, and soon afterwards the formation and properties of lipid bilayer^[20] and liquid crystal phases.^[21,22] Later, the behaviour of non-ionic surfactants was examined, with micelles,^[23,24] liquid crystalline phases,^[24-26] adsorbed structure at the graphite interface,^[27] and microemulsions characterized.^[24,28] The driving force for all these forms of self-assembly is "solvophobicity",^[29] which is analogous to the hydrophobicity in water, but for a non-aqueous solvent. Beyond this field, protic ILs such as EAN and EtAN are being investigated in a growing number of fundamental^[30-34] and applied^[35-39] chemical settings.

Until recently, protic ILs were thought to be structurally homogeneous. However, in 2008 Atkin and Warr^[40] and Umbeyashi *et. al.*^[41] probed the structure of EAN using small angle neutron scattering (SANS) and large angle X-ray scattering (LAXS) respectively. Both studies concluded that EAN is structurally hetereogeneous, with polar and apolar domains propagated through the bulk due to solvophobic, electrostatic and hydrogen bonding interactions.

In this paper, neutron diffraction measurements have been performed to provide atomic detail on the ionic arrangement of EAN and EtAN. The approach used in this study is similar to investigations of liquid water by Soper^[4] and aprotic ILs by Hardacre *et. al.*^[42]

3.3 Experimental Section

Three chemically identical, but isotopically different samples of EAN and EtAN were synthesized: fully hydrogeneous, partially deuterated, and fully deuterated. Selective deuteration enables *contrast variation*; because hydrogen and deuterium have different scattering lengths (${}^{1}\text{H} = -0.3741 \text{ x}10^{-12} \text{ cm}$, ${}^{2}\text{H} = +0.6671 \text{ x}10^{-12} \text{ cm}$ respectively) molecular regions of interest can be highlighted in a neutron diffraction experiment.

Hydrogeneous protic ionic liquids ethylammonium nitrate (H-EAN) and ethanolammonium nitrate (H-EtAN) were prepared via slow addition of concentrated nitric acid HNO₃ (BASF, 69 w/w%) to a chilled solution (<10°C) of either hydrogeneous ethylamine (Merck–Schuchardt 70% wt%) or hydrogeneous ethanolamine (Sigma-Aldrich 99 wt%) and distilled water. During the acid addition, the mixture was rapidly stirred to ensure dispersal of any heat generated. The excess aqueous solvent was removed in each case by a number of steps. Firstly, the samples were rotor evaporated for several hours at 40°C. The resultant solution was heated overnight in an oil bath at 105°C under a nitrogen atmosphere. This leads to water contents undetectable by Karl Fisher titration (<0.01 v/v%). The liquids were thoroughly purged with filtered nitrogen gas between rotor evaporation and oil bath steps, to prevent the formation of coloured nitrous oxide impurities.

Partially deuterated liquids d_3 -EAN and d_4 -EtAN were prepared by performing the same equimolar acid-base reaction in fresh deuterium oxide D₂O (99% Sigma Aldrich) rather than water. ¹H-NMR experiments reveal that, on average, 2.5 out of 3 amino hydrogens are replaced with deuterium.^[40] Similar ¹H-NMR testing on a *Bruker* Advance 300 MHz instrument revealed 17.6% ¹H isotope and 82.3% ²H isotope present on the ethanolammonium cation's hydroxy proton.

Deuterated amines $1,1,1,2,2-d_5$ -ethylamine (CD₃CD₂NH₂) and $1,1,2,2-d_4$ -ethanolamine, (HOCD₂CD₂NH₂) (CDN Isotopes) were used to synthesized fully deuterated analogues d_8 -

EAN and d_8 -EtAN respectively. ¹H-NMR and ²H-NMR analysis by the manufacturer showed >98% isotopic exchange. d_8 -EAN was prepared on a vacuum line, trapping the 1,1,1,2,2-d₅- ethylamine gas with liquid nitrogen and subsequently introducing both fresh deuterium oxide D₂O and nitric acid. 1,1,2,2-d₄-ethanolamine, (a liquid at room temperature) was prepared as per the synthesis for partially deuterated ionic liquids.

Neutron diffraction data for each contrast was collected over the Q range 0.05 to 50 Å⁻¹ on the SANDALS time of flight (TOF) diffractometer located at ISIS research facility, Rutherford Appleton Laboratories, UK. This corresponds to an incident neutron wavelength, λ varying between 0.05-4.5 Å. Banks of zinc sulphide scintillator detectors located between 0.75 and 4.0 m from the sample provided continuous angular monitoring of diffracted neutrons over the 20 range 3.8- 39°.^[43]

The ionic liquids were loaded into 1mm thick flat plate cans. The cans are made of a titanium-zirconium alloy (67.5% Ti and 32.5% Zr) of known atom density of 0.0541 atoms/Å³ and wall thickness of 1 mm. It provides a chemically inert, null scattering environment in which to analyze the liquids. Prior to loading, diffraction measurements were made on the empty cans, empty instrument and a vanadium standard sample for the purposes of data correction and normalization. The ionic liquids were sealed in the cans using PTFE Orings.

The experiments were conducted at 298K or 338K under vacuum. The sample chamber was left to equilibrate for 10 minutes prior to measurements. The temperature was maintained to $\pm 0.1^{\circ}$ by a Julabo FP50 temperature controller. The weight of the (can + IL) for each sample was measured before and after measurement to ensure no IL evaporation in the vacuum chamber. The net run time for each system was at least 8 hours.

Data analysis was carried out using a collection of FORTRAN programs described in the ATLAS manual.^[44] Standard corrections were applied for neutron scattering data:

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normalisation to the incident flux, absorption and multiple scattering corrections, Ti-Zr can subtraction followed by normalisation to absolute units by dividing the measured differential cross section by the scattering of a vanadium standard of known thickness. Finally, calibration for single atom scattering, and hydrogen inelasticity corrections, are applied.

Once the data was normalized, the data fitting was performed using Empirical Potential Structure Refinement (EPSR).^[45,46] Firstly, a reasonable molecular skeleton for the anions and cations was developed from *ab initio* molecular orbital calculations in Spartan 08^[47] software (c.f. Table 1). The three-dimensional geometry was optimized (bond lengths, bond angles and atom point Coulombic charges etc.) at the 3-21G* basis set and Hartree-Fock (HF) theory level.



Figure 1- Molecular structure and atom types of (**A**) Ethylammonium (EA⁺) cation (B) Nitrate anion (C) Ethanolammonium (EtA⁺) cation. Carbon and nitrogen atoms are distinguished using subscripts as per the position in the anion/cation molecular skeleton. Hydrogen is similarly defined as being bonded to the x carbon or the y nitrogen.

 Table 1- Lennard-Jones and Coulombic charge parameters used to define the ethylammonium nitrate

 (EAN) and ethanolammonium nitrate (EtAN) EPSR reference potential.

Ethylammonium Cation				Nitrate Anion				Ethanolammonium Cation				
Atom	$\epsilon (kJ.mol^{-1})$	$\sigma\left(\mathring{A}\right)$	q (e)	Atom	ε (kJ.mol ⁻¹) σ (Å)	q (e)	Atom	$\epsilon (kJ.mol^{-1})$	$\sigma\left(\mathring{A}\right)$	q (e)	
C ₁	0.276	3.50	+0.263	No	0.711	3.25	+0.845	C ₁	0.276	3.50	+0.091	
C _M	0.276	3.50	-0.411	0	0.879	2.96	-0.615	C_2	0.276	3.50	+0.315	
Ν	0.711	3.25	-0.529					Ν	0.711	3.25	-0.589	
H_M	0.126	2.50	+0.143					O_1	0.879	2.96	-0.753	
H_1	0.126	2.50	+0.069					H_1	0.126	2.50	+0.124	
H_N	0.126	2.50	+0.366					H_2	0.126	2.50	+0.020	
								H_N	0.126	2.50	+0.382	
								Ho	0.126	2.50	+0.502	

An EPSR^[46] model was developed consisting of 500 anions and 500 cations in a simulation box, consistent with the measured diffraction data, and specified physical constraints including molecular structure, atomic overlaps, and liquid density. Atomic and molecular translations and rotations were governed by the standard rules for a Monte Carlo simulation with respect to a reference potential of Lennard-Jones plus Coulombic interactions (c.f. Table 1). The potential has been corrected following an iterative algorithm^[46] until agreement between the simulated and experimental structure factors was reached. The three contrasts for each IL were modelled simultaneously with the same box by normalizing for isotope populations. From the simulated box of ions generated, many structural quantities can be calculated to analyse the bulk structure of the liquids.

3.4 Results & Discussion

The diffraction patterns of the three isotopic substitutions of ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN) at 298K are shown in Figures 2A and 2B, respectively. In each case the diamonds represent the experimental data and the solid lines represent the fits. The EPSR modeling protocol determines an ensemble of 500 cations and 500 anions that is consistent with this measured neutron diffraction spectra and the specified physical constraints including molecular structure, atomic overlaps, and liquid density.

The EPSR model produces good fits to the SANDALS data over the entire Q range examined. Some discrepancies between the fits and data appear in the Q range $< 1.5 \text{ Å}^{-1}$ where the data shows an upturn in intensity. This is principally due to residual inelastic scattering by light hydrogen atoms that is not completely removed by correction methods. As such, it is more pronounced for hydrogen-rich samples.^[48]



Figure 2- Experimental (dots) and EPSR fitted (solid line) intensity as a function of Q (Å⁻¹) for (**A**) ethylammonium nitrate (EAN) and (**B**) ethanolammonium nitrate (EtAN) analogues at 298K; fully deuterated (d_8 -EAN, d_8 -EtAN) (blue), partially deuterated (d_3 -EAN, d_4 -EtAN) (green) and fully hydrogeneous (H-EAN, H-EtAN) (red). The intensities are offset to +1.20, +0.60 & +0.20 respectively. The orange arrows in both Figures point to the peaks in the data corresponding to bulk correlation lengths. The atom colours for the inset ion pairs are: H (white), D (green), C (grey), N (blue), O (red).

A key feature in Figure 2A is the sharp peak at 0.625 Å⁻¹ in d_3 -EAN. This provides strong evidence for a bulk correlation length, and indicates long range liquid order. The peak position agrees with that determined in EAN in previous scattering experiments by Atkin and Warr^[40] (0.66 Å⁻¹) as well as by Umebayshi *et. al.*^[41] (0.62 Å⁻¹). From the Bragg equation a repeat spacing of 10.1 Å is obtained for the peak at 0.625 Å⁻¹, indicating regular structure within the liquid on this length scale. This is significantly larger than the ethylammonium cation, nitrate anion or EAN ion pair dimension, so cannot be attributed to scattering from single ionic species present in EAN. Rather, the distance is consistent with twice the calculated ion pair dimension (2 × 5.3 Å), which suggests that correlations between adjacent ion pairs are propagated through the liquid.

The corresponding peak in d_4 -EtAN, at 0.76 Å⁻¹, is *much* less intense (Figure 2B). This peak position corresponds to a repeat distance of 8.21 Å. (Small angle neutron scattering data confirm this change in structure peak, c.f. Supplementary Information). This is significantly less than twice the EtAN ion pair dimension (2 × 5.4 Å) but too large to be ascribed to a single ion pair or constituent ions. Thus, the repeat distance arises from a structure different to that of EAN.

Interionic partial radial g(r) distribution correlations were extracted from the EPSR models and are shown in Figures 3A and 4A for EAN, and Figures 3B and 4B for EtAN, along with labelled molecular skeletons. Note that no intraionic correlations are included. The peak positions and atom coordination numbers for EAN and EtAN are summarised in Tables 2 and 3. Many other partial radial distribution functions have also been obtained and are presented in the Supplementary Information. These site-site correlations inform on separations between atoms and the angles between triplets of atoms, but since they are spherically averaged, do not directly probe the orientation of the ions. However, as the peak intensity is a consequence of the relative number of nearest neighbour atoms, integration over a defined distance gives the atom coordination number over that range. The cut-off distances used to calculate atom coordination numbers (c.f. Tables 2 and 3) were determined primarily from the peak positions and widths. In most cases, the distance at which the first coordination shell ended and the second began was between 4.5 Å and 5.0 Å for EtAN and EAN (respectively), in accordance with the ion pair dimensions and bulk liquid repeat spacings.

In Figure 3A, the N₀-N₀ g(r) provides a good indication of the anion-anion separation in EAN, as the nitrogen atom is the centre of mass for the nitrate species. One clear peak in the curve is present at ~3.3 Å and a second broad feature is also observed at ~5.9 Å that likely to be associated with the anion-anion separations across the second shell. Integration of the first peak region yields anion-anion coordination number of 0.92 for 0 < r < 4.0 Å, and 6.07 for

4.0 < r < 6.5 Å. This suggests an individual anion is directly associated with only one anion in the first coordination shell. The analysis below indicates this is a result of anion-anion stacking. Over the first + second coordination sphere, the anion is associated with seven anions in total, c.f. Table 2.

The ethylammonium (EA⁺) ion has no obvious center of mass, but analysis of the $C_M - C_M$, $C_M - C_1$, $C_M - N$, $C_1 - C_1$ and N - N radial distribution functions elucidate the cation-cation arrangement (c.f. Figure 3A). In the $C_M - C_M$ function a prominent correlation length is observed at ~3.5 Å. The $C_M - C_1$ data is bimodal, with two moderately intense peaks at ~3.9 Å and ~4.7 Å. The $C_M - N$ profile shows a maximum at ~5.4 Å. The order of cation-cation atom separations is therefore $C_M - C_M < C_M - C_1 < C_M - N$. This indicates that adjacent methyl carbons are on average closer and more strongly associated than methyl to methylene carbons or methyl carbon to ammonium nitrogen. This is consistent with the form of the corresponding hydrogen g(r) plots ($H_M - H_M$, $H_M - H_1$, $H_M - H_N$) in Figure 4A; the peak in the $H_M - H_M$ data at a shorter distance than $H_M - H_1$ or $H_M - H_N$. In $C_1 - C_1$ and N - N (Figure 3A) broad correlations are observed, with approximate peak positions of ~5.0 Å and ~ 5.4 Å respectively. These results are consistent with the ethyl chains being segregated from the ammonium headgroup on adjacent cations. As the cation-cation coordination number from the $C_1 - C_1$ g(r) for 0 < r < 5.0 Å is 2.02, ethyl chain segregation is likely to be represented between nearest-neighbour cations.

The nature of the cation–anion interaction can be elucidated from Figure 3A, from separations between the N₀ nitrogen and the main atoms on the cation backbone. The strongest correlation is the Coulombic attraction between N₀ and the ammonium nitrogen. The peak distance of this N₀ – N correlation is ~3.6 Å, and integrating between 0 < r < 4.0 Å produces a coordination number of 2.98. This suggests three anions are associated with the ammonium headgroup of the cation. Notably, the N – N₀ peak distance is also close enough

to facilitate hydrogen bonds between the amine hydrogens and nitrate oxygens. This is confirmed by the $H_N - O$ peak at ~2.4 Å, consistent with the measured H-bond length in a similar system.^[49] The coordination number for this g(r) for 0 < r < 3.0 Å is 2.83, indicating that on average, almost all of the available amine hydrogens participate in hydrogen bonding. The distance from N₀ to the methylene and methyl carbons, C₁ and C_M increases from to ~4.1 Å and ~4.3 Å, respectively. This shows the nitrate ion is closer to and thus prefers to solvate ionic segments of the cation over non-ionic segments. Moreover, the differences between peak positions on the N₀ – N and N₀ – C₁ or N₀ – C₁ and N₀ – C_M functions are much smaller than the corresponding C₁ – N or C₁ – C_M bond distances. This suggests that a single anion does not reside directly above the ammonium group, as this would produce N₀ – X correlations that run approximately through the C₃ rotation axis defined by the N nitrogen and C₁ carbon. Thus, a more complex anion-cation interaction must be present that facilitates hydrogen bonding and ionic interactions.

The partial radial distribution functions of EtAN (Figure 3B and 4B) in general reveal a similar, but lower level of ordering than EAN, consistent with the weaker low-angle correlation peak at ~0.76 Å⁻¹.

Whilst the shape of the two ILs' anion-anion correlations are somewhat alike, compared to EAN, the features of the $N_0 - N_0$ distribution in EtAN are less pronounced. Poorly-defined peaks in this data appear at ~3.5 Å, ~5.6 Å, and possibly even at ~7.9 Å. The coordination numbers over 0 < r < 4.3 Å and 4.3 < r < 6.5 Å are 1.09 and 4.96 respectively, c.f. Table 3. This suggests that, like for EAN, each anion is associated with one other nearest neighbor anion in the first co-ordination sphere, whereas across the first + second coordination sphere, there are only six anions. The $N_0 - N$, $N_0 - C_1$, and $N_0 - C_2$ distribution functions exhibit similar structure to EAN, with peaks at ~3.5Å, ~4.1 Å and ~4.3 Å respectively. However, EtAN also exhibits a distinct $N_0 - O_1$ peak at 3.6 Å, which suggests that the nitrate anion is

associated with both the ammonium and terminal hydroxyl groups, both of which can donate hydrogen bonds. This is supported by the $H_0 - O$ and $H_N - O$ profiles (c.f. Figure 4B) which have intense maxima at 2.5 Å and 2.3 Å. The coordination numbers for these g(r)'s between 0 < r < 3.0 Å are 1.83 and 2.62 respectively. This demonstrates that anions are associated with both ends of the cation; one with the hydroxyl group (hydrogen bonding with two out of three nitrate oxygens) and three with the ammonium group (hydrogen bonding with any of the nitrate oxygens).

EtAN cation-cation radial distribution functions ($C_2 - C_2$, $C_2 - C_1$ and $C_2 - N$, c.f. Figure 3B) are all bimodal, and the relative amplitudes and peak positions appear basically the same at ~3.8 Å and ~5.0 Å. The $C_1 - C_1$ plot shows a broad feature with maxima at ~3.9 Å and ~5.0 Å. The corresponding cation-cation coordination number in the $C_1 - C_1$ g(r) is 1.97, indicating two cations are distributed between 0 < r < 4.5 Å. The $C_2 - O_1$ distribution has a weak peak at ~3.5 Å, indicating the cations may be solvophobically associated. This is also indicated by the $O_1 - O_1$ profile, with a peak present at ~3.2 Å, close enough to facilitate hydrogen bonding between hydroxyls on adjacent cations. It is clear that the hydroxyl group can also hydrogen bond with the amino hydrogens, as hydrogen correlations $H_0 - O_1$ and $H_N - O_1$ have peaks at ~2.4 Å and ~2.5 Å respectively (c.f. Figure 4B). However, the corresponding coordination numbers for $H_0 - O_1$ and $H_N - O_1$ between 0 < r < 3.0 Å are 0.28 and 0.38 respectively, indicating that this oxygen acceptor site cannot always participate in hydrogen bonding due to steric hindrance. These findings collectively suggest solvophobic alkyl chain clustering is much weaker in EtAN due to the addition of the hydroxyl group to the cation alkyl chain.



Figure 3- EPSR derived partial radial g(r) distribution functions for (**A**) EAN and (**B**) EtAN interionic atom–atom (carbon, nitrogen and oxygen) correlations between 2.0 - 10.0 Å. The intensities are offset to 0.0, +1.0, +2.0, +3.0 etc. Corresponding g(r) plots between EAN and EtAN are coloured the same. The inset shows a labelled EAN and EtAN molecular skeleton.



Figure 4- EPSR derived partial radial g(r) distribution functions for important (**A**) EAN and (**B**) EtAN interionic hydrogen correlations between 2.0 – 10.0 Å. The intensities are offset to 0.0, +1.0, +2.0, +3.0 etc. Corresponding g(r) plots between EAN and EtAN are coloured the same. The inset shows a labeled EAN and EtAN molecular skeleton.

Table 2- Summary of important Ethylammonium Nitrate (EAN) interionic partial radial g(r) distribution data extracted from the EPSR model sorted by the ion-ion interaction. From left to right the columns report g(r) function, Peak Position and Coordination Number between limits α and β in the 1st ion shell, Peak Position (if present) and Coordination Number between limits α and β in the 2nd ion shell.

Correlat	tion		1 st Shell	2 nd Shell			
Ion Ion	Atom-atom	Peak 1	Coord. #	Peak 2	Coord. #		
1011-1011	g(r)	(Å)	(α - β)	(Å)	(α - β)		
Anion Anion	$N_O - N_O$	3.3	0.92 (0.0-4.0)	5.9	6.07 (4.0-6.5)		
AIII0II -AIII0II	$N_O - O$	3.0	2.97 (0.0-4.0)	4.6	17.6 (4.0-6.5)		
	$C_M - C_M$	3.5	3.16 (0.0-5.0)	-	7.54 (5.0-7.0)		
	$C_M - C_1$	3.9	2.00 (0.0-4.2)	4.7	2.81 (4.2-5.8)		
Cation Cation	$C_M - N$	5.4	1.81 (0.0-5.0)	-	6.77 (5.0-7.0)		
Cation - Cation	$C_1 - C_1$	5.0	2.02 (0.0-5.0)	-	7.10 (5.0-7.0)		
	N - N	5.4	1.83 (0.0-5.0)	-	7.12 (5.0-7.0)		
	$H_M - H_M$	2.6	5.86 (0.0-3.0)	3.6	2.88 (3.0-4.5)		
	$C_1 - N_0$	4.1	3.06 (0.0-4.5)	-	3.71 (4.5-6.0)		
	N – O	3.0	6.01 (0.0-3.7)	4.7	3.11 (4.0-5.5)		
Cation -Anion	$N_{O} - N$	3.6	2.98 (0.0-4.0)	-	6.08 (4.0-7.0)		
	$N_0 - C_M$	4.3	3.12 (0.0-5.0)	-	4.85 (5.0-6.5)		
	$H_N - O$	2.4	2.83 (0.0-3.0)	3.9	6.11 (3.0-4.5)		

Table 3- Summary of important Ethanolammonium Nitrate (EtAN) interionic partial radial g(r) distribution data extracted from the EPSR model sorted by the ion-ion interaction. From left to right the columns report g(r) function, Peak Position and Coordination Number between limits α and β in the 1st ion shell, Peak Position (if present) and Coordination Number between limits α and β in the 2nd ion shell.

Correlati		1 st Shell	2 nd Shell			
Ion Ion	Atom-atom	Peak 1	Coord. #	Peak 2	Coord. #	
1011-1011	g(r)	(Å)	(α-β)	(Å)	(α-β)	
Anion Anion	N _O -N _O	3.5	1.09 (0.0-4.3)	5.6	4.96 (4.3-6.5)	
Allon – Allon	$N_{O} - O$	3.0	2.48 (0.0-4.0)	4.6	15.7 (4.0-6.5)	
	$C_2 - C_2$	3.8	1.94 (0.0-4.5)	5.0	2.99 (4.5-6.0)	
	$C_2 - C_1$	3.8	2.22 (0.0-4.5)	5.0	3.12 (4.5-6.0)	
	$C_2 - N$	3.8	1.83 (0.0-4.5)	-	3.03 (4.5-6.0)	
	$C_2 - O_1$	3.5	1.99 (0.0-4.0)	4.5	2.69 (4.0-5.5)	
Cation Cation	$C_1 - C_1$	3.9	1.97 (0.0-4.5)	5.0	4.35 (4.5-6.0)	
Cation – Cation	$H_2 - H_2$	2.4	0.83 (0.0-3.0)	-	2.48 (3.0-4.5)	
	N - N	5.7	0.71 (0.0-4.5)	-	7.81 (4.5-7.0)	
	$O_1 - O_1$	3.2	0.98 (0.0-4.0)	4.5	2.24 (4.0-5.3)	
	$H_0 - O_1$	2.4	0.28 (0.0-3.0)	-	-	
	$H_N - O_1$	2.5	0.38 (0.0-3.0)	-	-	
	$N_O - N$	3.5	3.87 (0.0-4.5)	-	2.37 (4.5-6.0)	
	$N_0 - C_1$	4.1	3.86 (0.0-4.5)	-	2.28 (4.5-6.0)	
Anion – Cation	$N_0 - C_2$	4.3	2.06 (0.0-4.5)	-	5.01 (4.5-6.3)	
	$N_O - O_1$	3.6	2.06 (0.0-4.5)		3.43 4.5-6.0)	
	$H_N - O$	2.3	2.62 (0.0-3.0)	3.8	6.21 (3.0-4.5)	
	$H_0 - O$	2.5	1.83 (0.0-3.0)	-	4.32 (3.0-4.5)	

A comprehensive description of the structural arrangements in our samples can be obtained from spatial density functions (SDF), which represent a 3D reconstruction from the partial radial distribution functions. In Figures 5A-D and 6A-D, the probability distribution of ions are shown for the first coordination shell around the cations and anions for EAN and EtAN. The cut-off distances for these probability surfaces are approximately half the repeat spacing determined from the position of the bulk correlation peaks (Figures 2A & 2B, and Figure 1 in Supplementary Information), and thus capture the nearest-neighbour arrangements that lead to liquid structure. However, due to EtAN's peak broadness, its SDF plots (Figure 5B, 5D, 6B & 6D) encompass a slightly larger volume to ensure all interionic associations were represented. For both SDF sets, anion density is coloured green and calculated as the most probable region (above a certain cut-off probability, specified in the top left hand corner of the figure) the No nitrogen occupies in space. Likewise, cation density is coloured yellow and calculated as most probable region the C1 carbon occupies in space. The C1 and N0 atoms were chosen as they are the central atoms for the cations and anions respectively, and in the former case, has the advantage of investigating possible amphiphilic contact between cations. Figures 6A & 6B show the distribution of nitrate anions relative to a central ethylammonium (EA^{+}) or ethanolammonium (EtA^{+}) cation respectively. For EAN, three distinct lobes of anion density are found in the first coordination shell, symmetrically distributed in the x-y plane around the amino hydrogens and suggest three anions solvate each cation headgroup. The H_N – O partial radial distribution function in Figure 4A indicated the nitrate oxygen is pointing towards the amino hydrogen partner. These orientations demonstrate the importance of hydrogen bonds for determining the local arrangement of ions in protic ionic liquids, and thereby longer range order and bulk properties, and is consistent with previous work.^[15,16,40,41]

Similar ordering of anions is seen in Figure 6B for EtAN, but with an additional lobe on the underside of the ethanolammonium (EtA⁺) cation. This is consistent with H-bonding between a nitrate oxygen and the –OH proton. When the surface probability threshold is raised above 30%, (not shown) the anion lobe in the foreground (negative x-axis) becomes smeared down the EtA⁺ backbone towards the hydroxyl group. This suggests that nitrate anions in EtAN may disrupt solvophobic association by forming H-bonding head-tail (–NH₃ … O-N₀-O … HO–) bridges along a single EtA⁺ cation or between adjacent cations.

The local arrangement of neighbouring cations, shown in Figures 6C & 6D are strikingly different. Between 0.0-5.0 Å in EAN (Figure 6C), the most probable distribution appears as two symmetric lobes around the alkyl cation segments, totally segregated from the charged ammonium. This is as vivid a representation of an amphiphilic interaction between ethylammonium cations as one could imagine, and confirms the structure suggested by the partial radial distribution function data in Figure 4. The observed 10.1 Å repeat spacing indicates that this key cation-cation arrangement is repeated throughout the bulk liquid. Whilst curvature cannot be determined from SDF plots, the volume ratios of alkyl to ionic components for EA⁺ were are near unity.^[40] In a previous article^[40] we argued that this means the structure cannot possess a high degree of curvature due to simple packing arguments and concluded a *locally* lamellar morphology is most probable. The cation-cation interaction shown here is consistent with this suggestion.

In EtAN, the arrangement between neighbouring cations is remarkably different. Rather than associating with the cation alkyl group, the C_1 carbon is located above (z-axis) and in front of (x-axis) the central cation amine group. Thus the inclusion of the alcohol group has the effect of disrupting solvophobic attractions between alkyl groups. This results in a much less ordered liquid arrangement.



Figure 6- EPSR spatial density distributions of ions as a function of angular position and distance relative to a central (**A**) & (**C**) Ethylammonium (EA⁺) or (**B**) & (**D**) Ethanolammonium (EtA⁺) cation Nitrate NO_3^- anion distribution is coloured green and defined as the most probable regions the N_C nitrogen occupies in 3-D space. Cation distribution is coloured yellow and defined as the most probable regions the C₁ carbon occupies in 3-D space. The scale of the viewpoint windows is ±5.5 Å Atom colours for the central cations are: H (white), C (grey), N (blue), O (red).

While significant differences between EAN and EtAN were observed for ion distribution around the cations, the distribution of ions around the nitrate anions is essentially the same for both ILs. Nearest neighbor nitrates are stacked in the plane of the ion in both EAN and EtAN (see Figure 7A & 7B). This is rationalized on the basis of maximizing the distance between like charges. Interestingly, the same ordering is also observed in the unit cell crystal structure of methylammonium nitrate,^[49] which can be described as an intercalated bilayer of H-bonded ammonium and nitrate ions and non-H-bonded methyl groups. The [CH₃NH₃⁺][NO₃⁻] unit cell dimension of 10.4 Å along this axis is also broadly consistent with the correlation length of d_3 -EAN. Likewise, the distributions of cations around the central anion are similar for EAN and EtAN. Three cation lobes represented by the C₁ methylene are evident in Figures 7C & 7D, distributed symmetrically about the nitrate C_3 rotation axis, and bisecting the angle defined by O-N_O-O covalent bonds. This is consistent with the formation of H-bonds and strong electrostatic interactions around the ammonium headgroup.



Figure 7- EPSR spatial density distributions of ions as a function of angular position and distance relative to: (A) & (C) EAN's Nitrate anion or (B) & (D) EtAN's Nitrate anion. Anion density is coloured green and defined as the most probable regions the N₀ nitrogen occupies in 3-D space. Cation density is coloured yellow and defined as the most probable regions the C₁ carbon occupies in 3-D space. The scale of the viewpoint windows is ± 5.5 Å. Atom colourings for the central anions are: N (blue), O (red).

The propagation of these local arrangements at longer length scales can be seen in snapshots of the fitted EPSR simulation boxes. Views through one face of representative configurations of EAN and EtAN simulations boxes equilibrated at 298K are shown in Figures 8 and 9, respectively. Figures 8A-C (EAN) and Figures 9A-C (EtAN) each show the same configurations: only the positions of the carbons are shown in 8B and 9B, representing the non-polar regions of the liquid, whereas 8C and 9C show only the anion positions (cations hidden). The partial radial distribution correlations and SDF plots discussed previously are

derived from the average local ion environments present in these boxes, plus averaging over about 3000 configurations similar to the ones shown in Figures 8 and 9.



Figure 8- Snapshot of fitted ethylammonium nitrate (EAN) bulk structure at thermal equilibrium (298K). From left to right, the front face of the 3D simulation box of (**A**) 500 EA⁺ & 500 NO₃⁻ (**B**) Apolar -C-C- domains only (-NH₃ and NO₃⁻ omitted) and (**C**) Anionic 500 NO₃⁻ only (500 EA⁺ omitted) is presented. Atoms colouring are: C (grey), H (white), N (blue), O (red)



Figure 9- Snapshot of fitted ethanolammonium nitrate (EtAN) bulk structure at thermal equilibrium (298K). From left to right, the front face of the 3D box of: (**A**) 500 EtA⁺ & 500 NO₃⁻ (**B**) Apolar -C-C-domains only (-NH₃ –OH, and NO₃⁻ omitted) and (**C**) 500 NO₃⁻ only (500 EtA⁺ omitted) is presented. Note that in (**A**) the cationic –OH oxygen is coloured yellow. This provides a visual confirmation of different bulk structuring compared to EAN (c.f. Figure 8A). Other atom colourings are: C (grey), H (white), N (blue), O (red)

In EAN local domains of white (hydrogen) and grey (carbon) as well as areas dominated by red (oxygen) and blue (nitrogen), reveal nanoscale heterogeneity in the IL; apolar domains of carbon and hydrogen atoms, and ionic domains of nitrogen and oxygen. The structure shown in Figure 8A-C is bicontinuous, consisting of two interpenetrating networks of polar ions and

nonpolar hydrocarbon. It is structurally analogous to various disordered, self-assembled in three (or more) component mixtures, such as bicontinuous phases seen microemulsions^[28,50] and sponge phases,^[51-54] but on a length scale at *least* an order of magnitude smaller. EAN is structurally most closely related to the disordered L_3 sponge phase, as first suggested by Atkin and Warr,^[40] and supported by Umbeyashi et. al.'s modelling.^[41] This is evident from the channels present in the cation carbons only system (Figure 8B) which demarcate the positions available to the charged groups. As the image is of the front face of a 3-D prism, areas where the black background colour is seen are indicative of channels traversing the assembly. The structure presented is reminiscent of a disordered bilayer, as expected for a sponge. Similar cation passages are evident in the anions-only system of Figure 8C. While L_3 sponge phases are frequently observed for concentrated aqueous surfactants, EAN must form the smallest L_3 -sponge phase imaginable; the domain size is only 10.1 Å or (2 + 2 =) 4 carbons long. This equates to an enormous internal surface area as polar-apolar interfaces are in abundance; future catalytic,^[39] particle stability^[55] and self-assembly^[17] experiments may exploit this finding. Methylammonium nitrate has similar patterns of ordering^[49] but is a crystalline solid at room temperature (m.p 383K).

The corresponding snapshot of the EtAN simulation box differs from EAN in a number of ways. While the extent of the nitrate structures looks similar (Figures 8C and 9C), the intervening voids, corresponding to white (hydrogen) and grey (carbon) apolar regions (Figure 9B) are both smaller and less obviously networked in EtAN. There is no extensive cation carbon segregation in Figure 9B; the alkyl chains instead appear sporadically distributed through the fluid as small but polydisperse clusters. These results collectively suggest small clusters of ions are present in EtAN, compared to layered domains in EAN. This difference is consistent with the cation – cation coordination numbers being lower for

EAN (2.02) than for EtAN (2.97) and with anion –anion coordination numbers being virtually the same EAN (0.92) and EtAN (1.09).

Most striking, however, is the much greater degree of correlation between successive polar (or apolar) domains in EAN. The well-defined, alternating arrangement of polar and apolar regions is more regular and propagates over longer distances in the liquid, and this is naturally the origin of the pronounced correlation peak at the lowest scattering angles.^[40] This closely parallels structure in bicontinuous (L₃)-sponge phases, which can be characterized by an order parameter correlation function, $\gamma(r)^{[56]}$

$$\gamma(r) = \frac{d}{2\pi r} e^{-r/\xi} \sin\left(\frac{2\pi r}{d}\right)$$
[1]

Here *d* is a quasiperiodic repeat distance between adjacent polar (or non-polar) domains, and ξ is a correlation length, describing the decay of that periodicity. Bicontinuous structures can be distinguished from weakly-structured mixtures by the presence of such a scattering peak^[57], which arises when $\xi > d$,^[28,56] and equates to the presence of an amphiphilic self-assembly structure. Ternary microemulsions mixtures as are divided into weakly- and strongly-structured on this basis, and strongly-structured microemulsions are said to form only when the surfactant is *sufficiently amphiphilic*. The present results argue strongly for the existence of a similar distinction between weakly- and strongly-amphiphilic ionic liquids, here exemplified by EtAN and EAN, respectively.

These results mean it is possible to make broader conclusions regarding EAN and EtAN solvation behavior. The hydroxyl moiety is in a sense a solvophobic switch; when covalently tethered to the ethylammonium cation it disrupts amphiphilic contact between alkyl groups. This serves to decrease the bulk IL correlation length and a clustered liquid structure forms.

In this light, we are now in a position to reinterpret the results of classical EAN studies performed over a quarter century ago. The first notable paper, by Mirejovsky and Arnett,^[58]

concluded that water, but not EAN, undergoes fluctuations in its hydrogen bond network when alcohols are introduced. The present results suggest instead that alcohol dissolution into EAN would be analogous to solubilization or cosurfactancy, in which solute molecules are incorporated into one of the many polar-apolar interfaces in the fluid; the hydrophilic moiety in an ionic region and the hydrophobic component residing in the bilayer-like alkyl domain. Thus, the amphiphilic character of individual alcohol molecules will be locally well-solvated by similar molecular groups and the larger EAN bulk structure (and H-bond network) will remain relatively undisturbed. Unlike water, the pre-existing structure of EAN ensures that there is no need for H-bond fluctuations or reorganization to accommodate a small amphiphile, at least at low concentrations.

A comparable oversight of the consequences of a nanostructured solvent morphology was recently made by Reichardt^[59] who suggested that EAN is nearly as polar as water on the basis of normalized values for solvatochromic probe dyes (0.954 for EAN, 1.000 for H₂O). The solvatochromism of probe dye used, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate ($E_T(30)$), is primarily affected by electron-pair donor-acceptor interactions, i.e. H-bonding. Although $E_T(30)$ is large compared to the structural length scale in EAN, it will principally probe the H-bonding capacity of EAN, and hence the value obtained is probably a good indication of the relative polarity in these regions. At best it will report a weighted average of the environments it samples, as it does in complex fluids.^[60,61] This is not the same as the average polarity of EAN, which has domains that are significantly more polar and also significantly less polar than water in the bulk.

We would also postulate that the high degree of molecular segregation in EAN plays a strong role in critical phenomena observed for binary mixtures of EAN and n-octanol.^[62-64] Many studies have been devoted to this system recently, as a transition from mean-field to Ising-like behaviour is noted when the EAN mole fraction is between of 0.766^[64] and 0.77^[62] or

temperatures from 44.06^[64] to 42.2^[62] °C. However, it has been consistently overlooked that the specific, short-range solvophobic interactions between cations are present alongside H-bonding and Coulombic forces, which will contribute to unusual "solvophobic demixing".

A recurrent theme in studies of surfactant self-assembly in EAN^[17-21,23,25,27,65] is the need for higher surfactant concentrations and longer alkyl chains (by about four -CH₂- units) to produce effects correspond to those observed in water. Nonionic surfactants in EAN are less effective amphiphiles than in water: The hydrophobic tails are more soluble but the polar, polyoxyethylene groups are less well solvated. While the polar headgroups of surfactants should be fairly effectively solvated by the H-bond donors and acceptors in the ionic domains of EAN, the opposing "hydrophobic hydration" of the alkyl tails^[66] is largely absent. The EAN apolar domains are expected to be a much more hospitable environment for hydrophobic moieties like alkyl surfactant tails than water, whence their much greater solubility.^[18] Incidentally, these apolar domains are expected to be able to accommodate a methane molecule without significant disruption, as per Evans *et. al.*'s suggestion nearly three decades ago.^[67]

Nevertheless, the existence of amphiphilic aggregates in EAN requires a solvophobic driving force. As a surfactant molecule is invariably much larger than 10.1 Å, the combined size of ionic and apolar liquid nanodomains, it cannot simply reside at the interface between charged and alkyl regions without disturbing the overall L_3 -sponge network. Introducing a surfactant most likely induces a different liquid structure from that of the bulk in order to accommodate head group solvation as well as the alkyl chain. At sufficiently high concentrations, solvophobic interactions within the IL itself will expel dissolved monomers, forcing them to associate by a process analogous to the expression of the hydrophobic effect in water.^[65]

surfactants in EtAN can similarly be explained by its nanostructure. As extensive apolar
domains are not formed in EtAN, the surfactant alkyl chain cannot be so easily accommodated. This suggests surfactant solubility is chiefly controlled by hydrogen bonding to the ions, as in EAN. Thus the lower solvation of the polar groups is not compensated by an "alkyl-friendly" nanostructure in EtAN, which leads to surfactant aggregation or precipitation at low concentrations due to the disruption of EtAN's hydrogen bond network, and consequently to cmc values similar to that obtained in water.^[68]

These results also provide a new framework to interpret interfacial IL nanostructure.^[69] EAN forms seven or more layers at macroscopic solid^[30,70] or air^[71] interfaces, each approximately 5 Å thick. EtAN forms at most two.^[72] That EtAN is so similar to solvation layer formation in simple molecular solvents^[73-75] only emphasises the peculiar behaviour of EAN, which we explain as a surface-induced orientation and stacking of the randomly oriented bilayer that already exists in the bulk EAN sponge, as we have suggested previously.^[40] Once again this transition has parallels in concentrated aqueous surfactant systems;^[76] a convoluted sponge morphology cannot be accommodated near a single boundary or confined between two macroscopic surfaces,^[77] instead a stacked bilayer architecture is favored.

3.5 Conclusions

Neutron diffraction has been used to elucidate the bulk structure of the two oldest ILs, EAN and EtAN. Diffraction data was acquired between 0.05 to 50 Å⁻¹ on three chemically identical, but isotopically different samples of EAN and EtAN, and the spectra fit using empirical potential structure refinement (EPSR), allowing the atomic arrangements of the liquids to be determined.

Unlike conventional solvents, both ILs were found to be structurally heterogeneous, with correlation lengths of 10.1 Å (EAN) and 8.21 Å (EtAN) indicating a consistent spacing between like ions in the liquid. EAN is the more structure of the two liquids, with neat, well-

defined local organization of charged and uncharged molecular groups; the anions in EAN are associated exclusively with the ammonium group due to hydrogen bonding and electrostatic attractions, whilst adjacent cation alkyl chains are aggregated together via solvophobic interactions, and a bicontinous 'sponge' structure forms in the bulk. Because of EAN's C_2 alkyl group, and the fact that no other solvent is present, it is difficult to conceive of a sponge structure with smaller dimensions. The local ion arrangements in EtAN are similar to EAN, especially with respect to distribution of ions around the anions. However, the addition of the alcohol (-OH) moiety in EtAN disrupts solvophobic contact between cation alkyl chains resulting in small clusters of ions in the bulk, rather than a sponge. Further investigation of the effect of ion molecular structure on protic ionic liquid nanostructure is ongoing.

3.6 Supporting Information

Section 1- Small Angle Neutron Scattering (SANS)



Figure S1- Small angle neutron scattering spectra on the LoQ instrument at ISIS for partially deuterated analogues of ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN) at 298K and 333K. d_3 -EAN at 298K (blue diamonds), d_3 -EAN at 333K (green triangles), d_4 -EtAN at 298K (red squares) and d_4 -EtAN 333K (purple crosses).





Figure 3- EPSR derived partial radial distribution functions for important EAN inter-atomic correlations (**A**) $C_1 - X$ between 2.0 – 8.0 Å (**B**) $N_0 - X$ (**C**) N - X. The intensities are offset to +1.0, +2.0, +3.0, etc.



Section 2- Additional g(r) functions for EAN



Section 3- Additional g(r) functions for EtAN

Section 4- Single Atom Scattering Calibration

Calibration for single atom scattering, particularly inelastic scattering of hydrogen, was performed by subtracting a stretched exponential in real-space and through the top-hat convolution correction.

Table 1- Calibration for single atom scattering function parameters for the IL systems as performed in GUDRUN software.

IL System	Stretche	Top Hat width		
	Amplitude	Decay const.	Scaling Const.	_
H-EAN	8.0	3.0	0.75	0.3
d_3 -EAN	8.0	3.0	0.9	0.3
d_8 -EAN	0.0	0.0	1.0	0.3
H-EtAN	8.0	3.0	1.1	0.3
d_3 -EtAN	4.5	3.0	0.9	0.3
d_8 -EtAN	0.0	0.0	1.0	0.3

3.7 References

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CHAPTER 4

C4: Pronounced sponge-like nanostructure in propylammonium nitrate

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4.1 Abstract

The structure of the ionic liquid propylammonium nitrate (PAN) has been determined using neutron diffraction. Empirical potential structure refinement (EPSR) fits to the data show that PAN self-assembles into a quasi-periodic bicontinuous nanostructure reminiscent of an amphiphile L_3 sponge phase. Atomic detail on the ion arrangements around the propylammonium cation and nitrate anion yields evidence of hydrogen bonding between ammonium and nitrate groups and of strong alkyl chain aggregation and interdigitation The resultant amphiphilic PAN nanostructure is more pronounced than that previously determined for ethylammonium nitrate (EAN) or ethanolammonium nitrate (EtAN).

4.2 Introduction

Ionic liquids (ILs) are an important class of solvents often referred to as 'designer solvents' because liquid properties can be tuned by variations in chemical structure.^[1] ILs are unusual among solvents in that they consist entirely of ions, with no neutral molecules present.^[2] In the last decade or so, research in ILs has flourished in concert with "green chemistry",^[3,4] but also because these solvents have many performance advantages over conventional solvents in a variety of contexts. For example, ILs have been used to great effect in organic synthesis,^[5] catalysis,^[6] electrochemistry,^[7] surfactant self-assembly,^[8] particle stability^[9] and in energy applications.^[10,11] However, the molecular factors that mediate this improved solvent performance have yet to been ascertained, on account of an incomplete knowledge of the bulk nanostructure.

Whilst it is common to think of the internal organization of liquids as structurally homogeneous, in recent years many publications have shown ILs to possess long range liquid order or nanostructure.^[12-21] This is remarkable, because virtually every other class of solvent lacks structure beyond a preferred organization between adjacent molecules;^[22-26] in ILs, the local ion arrangements are propagated over much greater distances due to strong clustering of like molecular groups. In neutron^[15-18] and X-ray^[19-21] scattering studies, this is indicated by the appearance of a so called prepeak or first sharp diffraction peak^[27-30] at low (<1 Å⁻¹) scattering angles. Although there is still some disagreement as to how the first sharp diffraction peak in ILs should be interpreted,^[16,31] one explanation points to a bicontinuous bulk structure of polar and apolar domains driven by Coulombic, hydrogen bonding and solvophobic^[32] interactions between ions. The degree of IL bulk liquid structure can be correlated with how surfactant-like the IL is, with more pronounced structure reported for increasing cation alkyl chain length^[15,16,19,21] or cation amphiphilicity^[18] and conversely, ILs lacking long range bulk order have been identified for short chain (<C₄) imidazolium salts.^[19,33] This behaviour invites comparisons to self-assembly in aqueous surfactant dispersions, microemulsions or liquid crystals,^[34] (albeit on length scales at least an order of magnitude lower^[1]), and is likely to be key for many bulk IL properties.

In this article, we report the bulk structure of propylammonium nitrate (PAN) using neutron diffraction together with empirical potential structure refinement (EPSR)^[35] modelling. PAN is a protic IL^[36] formed by proton transfer from a Brønsted acid (nitric acid) to a Brønsted base (propylamine). PAN has shown to be a useful solvent for self-assembly,^[37,38] electrochemistry,^[39] liquid-liquid extractions^[40] and chromatography.^[40,41]

To date, the bulk structure of PAN is a topic of some contention in the IL community. Apart from the most basic structural characteristics such as its "good" ionic composition^[42] and capacity to hydrogen bond,^[43] atomic detail on PAN's bulk structure has yet to be reported. Small angle neutron scattering (SANS)^[15] and small- and wide-angle X-ray scattering (SAXS and WAXS)^[21] data have suggested a locally smectic or sponge-like bulk structure of polar and non-polar domains. This was concluded from the observation of a peak at low Q in both spectra at 0.54 Å⁻¹, which corresponds to a repeat distance (11.9 Å) from the Bragg equation of approximately twice the ion pair dimension (5.6 Å). However, in a recent review article, Castner and co workers^[31,44] questioned whether the appearance of a scattering a peak at low Q for PAN indicates a bulk structure of polar/nonpolar domains, given the size of the ions and alkyl chain involved. Alternatively, Kennedy and Drummond concluded PAN is composed of a polydisperse mixture of aggregated ions from electrospray ionisation mass spectrometry (ESI-MS) measurements, with the C₈A₇⁺ species (C = cation, A = Anion) in the greatest abundance.^[45] Recent theoretical calculations by Ludwig support these ESI-MS findings and showed that this C₈A₇⁺ aggregate to be a thermodynamically favoured ion arrangement for PAN in the gas phase due to the strength of the hydrogen bond network.^[46] The goal of this work is to clarify the nature of the bulk liquid structure in PAN.

4.3 Experimental Section

Two chemically identical, but isotopically different IL samples were prepared: fully hydrogeneous propylammonium nitrate (H-PAN)and partially deuterated propylammonium nitrate ($C_3H_7ND_3NO_3$, d_3 -PAN). Selective deuteration enables molecular regions of interest to be highlighted in the neutron diffraction experiment via *contrast variation*.

H-PAN was prepared via slow addition of concentrated nitric acid HNO₃ (BASF, 69 w/w%) to a chilled solution (<10°C) of propylamine (Sigma-Aldrich 99 wt%) and distilled water. Excess water was removed firstly by rotor evaporation for several hours at 40°C and then by heating overnight in an oil bath at 105°C under a nitrogen atmosphere. This leads to water contents undetectable by Karl Fisher titration (<0.01 v/v%). The liquids were thoroughly purged with filtered nitrogen gas between rotary evaporation and oil bath steps, to prevent the formation of coloured nitrous oxide impurities.

The partially-deuterated liquid d_3 -PAN was synthesised by performing the equimolar acidbase reaction in fresh deuterium oxide D₂O (99% Sigma Aldrich) rather than water. ¹H-NMR experiments reveal that, on average, 2.5 out of 3 amino hydrogen atoms are replaced with deuterium.^[18]

Neutron diffraction measurements were performed on the SANDALS instrument at the ISIS research facility, Rutherford Appleton Laboratories, UK. The neutron wavelength range is 0.05-4.95 Å, and data were collected over the Q range 0.1 to 50 Å⁻¹.

The ionic liquids were contained in chemically inert, null scattering $Ti_{0.68}Zr_{0.32}$ flat plate cans during the neutron diffraction experiment. The can dimensions are 35x35 mm² with a 1 mm path length and 1mm wall thicknesses of known atom density, 0.0541 atoms/Å³. Prior to loading, diffraction measurements were made on the empty cans, empty instrument and a vanadium standard sample for data correction and normalization. The ionic liquids were sealed into the cans using PTFE O-rings.

Diffraction patterns were collected at 298K under vacuum. The sample chamber was left to equilibrate for 10 minutes prior to measurements with the temperature maintained to $\pm 0.1^{\circ}$ by a Julabo FP50 temperature controller. The weight of the filled can for each sample was measured before and after measurement to ensure no IL evaporation had occurred. The net run time for each system was at least 8 hours.

Data analysis was carried out using GUDRUN, described in the ATLAS manual.^[47] This performed various standard corrections for neutron scattering data including normalisation to the incident flux, absorption and multiple scattering corrections, Ti-Zr can subtraction as well as normalisation to absolute units by dividing the measured differential cross section by the scattering of a vanadium standard of known thickness. Single atom scattering and hydrogen inelasticity corrections were also applied.

Empirical Potential Structure Refinement (EPSR)^[35] was used to fit the diffraction data. EPSR performs a Monte Carlo simulation governed by Lennard-Jones potentials, atomcentered point charges as well as chemical and physical constraints such as molecular structure and liquid density. The simulation box was composed of 500 nitrate anions and 500 propylammonium cations, the molecular geometries of which (bond lengths, bond angles and atomic point charges, etc.) were optimized prior to fitting using Spartan 08^[48] software at the 3-21G* basis set and Hartree-Fock (HF) theory level (c.f Figure 1 and Table 1).



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Figure 1- Molecular structure and atom types of propylammonium (PA^+) cation and nitrate anion. Carbon and nitrogen atoms are distinguished using subscripts as per the position in the anion/cation molecular skeleton. Hydrogen is similarly defined as being bonded to the x carbon or the y nitrogen. Atomic and molecular translations and rotations used to refine the EPSR model were guided by comparing the residuals from the simulations with experimental data in *Q*-space over many iterations. The two IL contrasts were fitted simultaneously with the same box by normalizing for isotope populations. From the simulated box of ions, many structural quantities can be calculated using internal EPSR commands to interrogate PAN structure.

Propylammonium Cation			Nitrate Anion				
Atom	ϵ (kJ.mol ⁻¹)	$\sigma\left(\mathring{A}\right)$	q (e)	Atom	ε (kJ.mol ⁻¹)	σ (Å)	q (e)
C ₃	0.276	3.50	-0.653	No	0.711	3.25	+0.845
C_2	0.276	3.50	-0.037	0	0.879	2.96	-0.615
C_1	0.276	3.50	+0.108				
Ν	0.711	3.25	-0.734				
H_3	0.126	2.50	+0.209				
H_2	0.126	2.50	+0.095				
H_1	0.126	2.50	+0.118				
H_N	0.126	2.50	+0.421				

 Table 1-EPSR
 Lennard-Jones and Coulombic charge parameters to model propylammonium nitrate.

4.4 Results and Discussion

Figure 2 shows the diffraction spectra for the two isotopic substitutions of propylammonium nitrate (PAN) at 298K. Excellent agreement between the measured SANDALS data (diamonds) and EPSR fit (solid lines) is obtained across the entire Q-range. Residual inelastic scattering by hydrogen atoms is responsible for the slight discrepancy between data and fit below 0.35 Å⁻¹, which is, as expected, more pronounced for the hydrogen-rich H-PAN sample.

Evidence of long-range structural correlations in PAN is apparent in both diffraction patterns from the sharp peaks at 0.530 Å⁻¹, indicated by the arrows. The peak position is consistent with that reported previously by Atkin and Warr^[15] and Greaves *et. al.*^[21] from SANS and

SWAXS data respectively. The repeat spacing for this peak extracted from the Bragg equation is 11.9 Å, which is significantly larger than the any single ionic species in PAN. However, it is consistent with twice the PAN ion pair dimension. This indicates that correlations are propagated through the liquid as long-range order, as suggested previously.^[15] The intensity of the low-angle peak is much greater in d_3 -PAN than H-PAN due to the scattering contribution of amino hydrogen atoms in their physical locations in liquid PAN, which is described below.



Figure 2- Experimental (dots) and EPSR fitted (solid line) intensity as a function of Q (Å⁻¹) for propylammonium nitrate (PAN) analogues at 298K; partially deuterated (d_3 -PAN) (green) and fully hydrogeneous (H-PAN) (red). The intensities are offset to +0.75 & +0.25 respectively. The orange arrows point to the peaks in the data corresponding to bulk correlation lengths. The atom colouring for the inset PAN ion pairs are: H (white), D (green), C (grey), N (blue), O (red).

Partial pair correlation functions, $g_{ij}(r)$, for PAN interionic atom-atom correlations in the EPSR model are presented in Figure 3. Figure 3A shows cation-anion and anion-anion distributions whereas Figure 3B presents cation-cation g(r). (Additional partial radial distribution data for PAN is provided in the Supplementary Information, including intraionic correlation functions.) Integration over a particular radius yields atom coordination numbers. The peak positions and corresponding atom coordination numbers for all atom-atom

correlations are summarised in Table 2. In general, the g(r) data closely resembles that reported for EAN,^[18] and suggests similar liquid structure.

As the N₀ nitrogen is the centre of mass on the nitrate, distances from the N₀ atom can be used to show anion-anion and anion-cation arrangements. In Figure 3A, the N₀-N₀, O-O and N₀-O distributions are all quite similar; N₀-N₀ and O-O both show a clear peak at 3.3 Å followed by a broader one at approximately 5.5 Å, whereas N₀-O peaks are less clearly defined,. Integration between 0.0 < r < 4.0 Å yields coordination numbers of 2.83 and 2.84 for O-O and N₀-O respectively, and 0.96 for N₀-O, consistent with each anion being associated with one other nitrate in its first coordination shell. The analysis below shows that this corresponds to anion-anion stacking, similar to other nitrate ILs.^[18,49]



Figure 3- EPSR derived partial radial g(r) distribution functions for important PAN (A) cation-anion or anion-anion and (B) cation-cation interionic correlations between 2.0 –12.0 Å. The intensities are vertically offset by 0.0, +1.0, +2.0, +3.0 etc.

The most prominent anion-cation correlation in Figure 3A is the intense peak at 3.5 Å in the N_0 -N g(r). This arises from electrostatic and hydrogen bonding attractions between the nitrate anion and ammonium cation. The coordination number for the first shell is 3.18, which

indicates the number of anions solvating each cation. The first correlation peaks between N₀ and the C₁–C₃ cation propyl carbons both broaden and lie at increasingly larger separations as one moves away from the ammonium group along the alkyl chain. This is what one would expect from a flexible chain oriented away from an ammonium head group H-bonded to the nitrate. The sharp peak observed at 2.3 Å for the O-H_N g(r) also supports experimental findings^[43] of hydrogen bonding in PAN. The corresponding first coordination shell of 2.91 suggests that on average all amino protons participate in hydrogen bonding. Together, these results suggest three anions are strongly associated with the cationic ammonium group rather than the uncharged alkyl chain of the cation. Further, the N₀-N and O-H_N coordination numbers near 3 suggest that the ions may form an extended network of H-bond donors and acceptors as proposed in 1981 by Evans et al.^[50] (see further below).

Table 2- First and second peak positions and corresponding coordination numbers for propylammonium nitrate (PAN), derived from interionic partial radial g(r) distribution data extracted from the EPSR model. (α - β) denotes range over which integration was carried out to determine the quoted coordination number.

			1 st Shell	2 nd Shell	
	Atom-atom	Peak 1	Coord. #	Peak 2	Coord. #
	g(r)	(Å)	(α - β)	(Å)	(α - β)
Anion -Anion	$N_{O} - N_{O}$	3.3	0.96 (0.0-4.0)	5.5	6.96 (4.0-7.0)
	0-0	3.4	2.83 (0.0-4.0)	5.6	14.9(4.0-6.5)
	$N_O - O$	3.3	2.84 (0.0-4.0)	6.2	20.5 (4.0-7.0)
Anion – Cation	$N_O - C_3$	4.5	1.42 (0.0-4.5)	5.6	4.91 (3.0-6.0)
	$N_O - C_2$	4.4	1.75 (0.0-4.5)	5.4	5.97 (3.0-6.0)
	$N_O - C_1$	4.1	2.85 (0.0-4.5)	5.0	6.02 (3.0-6.0)
	$N_O - N$	3.5	3.18 (0.0-4.4)	-	5.67 (2.7-6.0)
	O - N	3.1	2.19 (0.0-3.9)	4.7	2.91 (3.9-5.5)
	$O - H_N$	2.3	2.91 (0.0-3.0)	3.8	6.94 (3-4.6.0)
Cation – Cation	$C_3 - C_3$	3.7	2.82 (0.0-4.5)	-	5.17 (3.0-6.0)
	$C_3 - C_2$	3.9	1.42 (0.0-4.5)	4.8	4.98 (3.0-6.0)
	$C_3 - C_1$	4.0	0.92 (0.0-4.5)	5.1	4.34 (3.0-6.0)
	$C_3 - N$	5.2	0.40 (0.0-4.5)	7.7	3.36 (3.0-6.0)
	$C_2 - N$	5.5	0.41 (0.0-4.5)	-	3.71 (3.0-6.0)
	$C_1 - N$	5.6	0.40 (0.0-4.5)	-	4.11 (3.0-6.0)
	N - N	5.4	0.64 (0.0-4.4)	7.5	4.89 (3.0-6.0)
	$C_2 - C_2$	4.0	2.09 (0.0-5.0)	5.0	4.70 (3.0-6.0)
	$C_1 - C_1$	4.2	1.61 (0.0-4.6)	5.2	3.96 (3.0-6.0)

Although the propylammonium (PA⁺) cation has no central reference atom, cation-cation arrangements can be determined by comparing correlation peaks in the C₃-X and N-X g(r) data. The C₃-C₃ g(r) exhibits the most intense cation-cation peak at 3.7 Å showing strong nearest-neighbour correlations between terminal methyl carbons, whereas the C₃-C₂ g(r) profile has a less pronounced primary peak and a similarly intense second peak at 4.7 Å. C₃-C₁ has two even broader peaks, culminating in the relatively featureless C₃-N profile. The first shell coordination numbers for the C₃-X decrease from 2.82 (C₃) to 1.42 (C₂), 0.92 (C₁) and 0.40 (N) towards the charged end of the cation.

In contrast the N–X profiles all have very broad correlation peaks at distances > 5.0 Å, and coordination numbers less than 1 (*c.f.* Table 2). This shows that the ammonium group is not strongly associated with neighbouring cations in the first coordination shell.

Pair-correlation functions are angular averages, and so do not reveal anisotropy in the local atomic arrangements. Spatial distribution functions (sdf) for PAN ion distributions in the first coordination shell are shown in Figures 4A-F. These are a reconstruction of the g(r) data in 3-space as probability surfaces, and provide a fine detail on ion arrangements in bulk PAN. A low cut off probability of 10% was used in order to highlight the most favoured arrangements nearest neighbour ions. Probabilities are calculated for atoms within a radial cut-off distance of 6.0 Å from a different reference atom origin as shown in each Figure.

The distributions of atoms in neighbouring anions and cations relative to a central nitrate are shown in Figure 4A and Figure 4B respectively. Neighbouring nitrates, represented by their N₀ centre of mass, appear as two green lobes stacked along the z-axis. This anion-anion arrangement is likely favourable in PAN because it maximises the distance between like charges. However, a first shell coordination number of 0.96 indicates that only one of these anion lobes is occupied on average.

Three yellow cation lobes in Figure 4B show the symmetrical distribution of the cation C_1 carbon about the nitrate C_3 rotation axis, and bisecting the angle defined by O–N_O–O covalent bonds. This is consistent with hydrogen-bonding and electrostatic attractions between the anion and cation. The same features arise in Figure 4C, which depicts the corresponding arrangement of nitrate centres of mass around C_1 .



Figure 4- EPSR spatial density distributions of ions as a function of angular position and distance relative to a central (A) & (B) nitrate anion or (C), (D), (E) & (F) propylammonium (PA⁺) cation. The inset (G) shows the atoms definitions used in the plots: nitrate NO₃⁻ anion distribution is coloured green and defined as the most probable regions the N₀ nitrogen occupies in 3-D space whereas cation distribution is coloured yellow, orange or red and defined as the most probable regions the probable regions the C₁, C₂ or C₃ carbon occupies respectively. The scale of all viewpoint windows is 5.5 Å. Atom colours for the central ion are: H (white), C (grey), N (blue), O (red).



The nitrates show a clear preference for positions around the ammonium headgroup, with no density observed around the propyl chain. The fact that three lobes are observed in the plot suggest that three anions solvate each cation, and is consistent with the cation-anion first shell coordination numbers given in Table 2. The ion orientation in these lobes can even be deduced because the first peak on the H_N -O is at a smaller separation than the on the N-O g(r) (c.f. Figure 3A). This suggests that in each nitrate anion, all three oxygens are oriented towards their corresponding amino protons to facilitate H-bonding. A network of such strong, directional attractions invites comparison with the dense H-bond network of water and its capacity to manifest a hydrophobic effect, which excludes alkyl and other non-polar moieties. The cation-cation spatial distribution functions (Figures 4D, 4E and 4F) are a striking demonstration of the segregation of the propyl carbons from the ammonium and nitrate charged groups, and provides strong evidence for a solvophobic interaction between cation alkyl chains. The two yellow lobes in Figure 4D show the interionic C_1-C_1 distribution. These are parallel to and approximately in the same plane as the C_1 - C_2 covalent bond. Integration of the first C_1 - C_1 peak in Table 2 suggests that both of these lobes are fully occupied in the first coordination shell.

The C₂–C₂ distribution (Figure 4E) is also strongly localised in a symmetric orange band around the propyl chain and segregated from the ammonium group. At lower probabilities (<5%), this band partitions into three lobes; a central lobe collinear to the C₁-C₂ bond as well as two smaller lobes on either side. The C₂-C₂ coordination number in the first shell indicate that between these three sites, two C₂ carbons can be found.

From Figure 4F, the most favoured site for C_3 - C_3 distribution in the first coordination shell is directly below the C_2 - C_3 covalent bond. These distributions yield a vivid representation of cation alkyl chain aggregation into non-polar domains through a solvophobic effect, and demonstrates that nearest-neighbour cation propyl tails are clustered together in the bulk. Previous studies have been unable to elucidate the nature of alkyl chain packing in ILs. Is it like a bilayer in a lamellar phase or lipid membrane, consisting of two well-segregated "backto-back" monolayers, or less ordered and with significant chain interdigitation? Figure 5 presents evidence of moderate alkyl chain interdigitation in PAN, which is seen in C_3 - C_3 sdf distributions at probabilities above 20%. The single lobe observed in Figure 4F swells, and three new sites emerge, 120° apart, to form a claw-like structure wrapped around the methyl group and extending "up" the propyl chain. This reveals the most likely position of neighbouring C_3 carbons that leads to the C_3 - C_3 coordination number of 2.82.



Figure 5- EPSR spatial density distributions of propylammonium (PA⁺) cation's C₃ carbon ions as a function of angular position and distance relative to a central PA⁺ cation. The scale of the viewpoint window is 5.5 Å. Atom colourings for the central ion are: H (white), C (grey), N (blue), O (red).

Such chain interdigitation is strongly reminiscent of various surfactant self-assembly structures in which alkyl chains are disordered and highly interdigitated to optimise packing while remaining sequestered from the polar headgroups and aqueous solution. This suggests that packing arguments similar to those developed for surfactant assemblies^[51] may be an important consideration in IL nanostructure. Understanding packing constraints may provide new fundamental insights into the nature of these nanostructures by predicting the curvature in the polar/apolar interface. This may prove useful in practical applications such as IL solubility rules, because the packing constaints and extent of apolar/polar segregation is

expected to influence IL's ability to dissolve other solutes. These aspects will be further addressed in a subsequent manuscript.^[52]

Figure 6 shows a representative snapshot of the PAN liquid equilibrium structure simulation box, derived from the EPSR model fit to the neutron diffraction data; all the local ion-ion correlations discussed above are accumulated from averages of the environment represented by many such equilibrated configurations. Figure 6A shows all atoms in the PAN simulation box; (B) shows only the cation carbon atoms in the propyl chains, and (C) shows only the nitrate anions and ammonium cations. These box representations present a visual model of the g(r) and sdf results over much longer length scales

Each snapshot shows the structure of PAN to be bicontinuous, consisting of two interpenetrating networks of (i) polar, nitrate and ammonium groups and (ii) non-polar propyl chains. These figures also reveal a characteristic periodicity or structural length scale, represented by the length of a chord drawn e.g. through a non-polar region between midpoints of adjacent polar regions (or vice versa). The nanostructure that emerges is reminiscent of well-known, disordered, self-assembled aqueous systems such as bicontinuous microemulsions^[53] and L_3 or sponge phases.^[54,55] Two interpenetrating domains can clearly be identified in the box: an apolar region dominated by white (hydrogen) plus grey (carbon) atoms aggregated together as well as a polar region comprised of red (oxygen) plus blue (nitrogen) atoms. The type of ordering shown in these boxes is consistent with an L_3 -sponge bulk structure but on exceptionally small (11.9 Å) scale.^[15] This clearly shows the existence of nanoscale hetereogeneiety in PAN on a length scale slightly larger than that observed in EAN.^[18] Notably, the PAN correlation length is still much smaller than that in traditional sponge structures familiar to colloid scientists; ternary mixtures typically tens to hundreds of nanometers in size. In comparision, the non-polar domain in PAN are at most six carbons long.

Figure 6B and Figure 6C provide detail on the arrangement in the apolar and polar areas respectively. These pictures are particularly striking given that the intervening black voids correspond to the space avaliable for the oppoisite domain; in both cases the black areas are networked and channel-like in appearance. The degree of contrast and persistence of the voids is all the more remarkable when we recall that each snapshot is a view through a one face of a cube. The voids are larger and more apparent in Figure 6B because the volume of the polar domain is slightly larger than the apolar domain.



Figure 6- Snapshot of fitted propylammonium nitrate (PAN) bulk structure at thermal equilibrium (298 K). From left to right, the front face of the 3D simulation box of (A) 500 PA⁺ & 500 NO₃⁻ (B) Apolar -C-C- domains only ($-NH_3$ and NO_3^- omitted) and (C) Ionic domain (500 NO₃⁻ + 500 NH₃⁺ omitted) is presented. Atoms colouring are: C (grey), H (white), N (blue), O (red).

In most respects, the bulk structure of PAN is analogous to the model we previously reported for EAN.^[18] Whilst some minor differences can be found, for example cation-cation coordination numbers are slightly higher in PAN than EAN, the conclusions remain identical; these two ILs exhibit long range structure of solvophobic origin, similar to a L_3 -sponge phase. The increase in alkyl chain length serves only to strengthen the segregation of charged and uncharged molecular groups because a stronger solvophobic driving force for cation alkyl chain aggregation exists. Consequently, corresponding cation-cation coordination numbers should be higher in PAN because there is a greater inclination to form an apolar domain. This is also physically manifested in the diffraction data where PAN has a more pronounced bulk correlation peak at low Q. The reason that PAN and EAN's bulk structures differ from EtAN is that the cations in the former case are neatly amphiphilic; the addition of the hydroxyl moiety on EtAN interferes with solvophobic association between cation chains, which leads to small clusters of ions in the bulk instead of an extended network.^[18]

No evidence of discrete aggregated ion species such as the $C_8A_7^+$ unit (C = cation, A = Anion)^[45,46] was observed in either liquid. This could be because the EPSR fitting is determines the thermodynamically stable bulk structure for the ILs and neutron diffraction is insensitive to any potential transient aggregated arrangements that may be constantly deforming and reforming. Alternatively, the $C_8A_7^+$ unit may be an artefact of the method of fragmentation into the gas phase, and not reflective of any underlying liquid structure. Nonetheless, $C_8A_7^+$ could be the most stable aggregate in the IL gas phase or at the IL-gas interface, given this interfaces' unusually high surface roughness.^[56]

4.5 Conclusions

Neutron diffraction and empirical potential structure refinement (EPSR) has revealed that PAN is structurally heterogeneous, with a structural correlation length of 11.9 Å corresponding to twice the dimension of the ion pair. EPSR fitting suggests that PAN selfassembles into a disordered L_3 -sponge phase, similar to EAN, but with a larger non-polar domain size because of the extra methylene unit. Spatial density plots show that this nanostructure is generated by strong electrostatic and hydrogen bonding attractions between ions which drive a solvophobic segregation of the non-polar alkyl chains. However, sdf plots demonstrate the propyl chains are interdigitated to some extent, which suggests that packing arguments need to be considered in future studies of ionic liquid bulk structure.

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CHAPTER 5

C5: How Water Dissolves in Protic Ionic Liquids

[Reproduced from Robert Hayes, Silvia Imberti, Gregory Warr, Rob Atkin in *Angew. Chem. Int. Ed.*, Volume 52, pages 4623-4627 (2013)]



5.1 Abstract

When equally massed water and protic ionic liquid ethylammonium nitrate (EAN) are mixed a bicontinuous nanostructure results. This nanostructure resembles aqueous surfactant sponge phases but has length scales at least an order of magnitude smaller. The local structure of both the water and the ionic liquid are strikingly similar to that found in the pure liquids.

5.2 Introduction

In recent years, ionic liquids (ILs) have emerged as useful chemical solvents for an enormous number of processes and technologies.^[1, 2] Their constituent ions have more complex chemical structures than inorganic salts; by incorporating large, sterically-mismatched anions and cations, ILs melt at low temperatures because, compared to typical inorganic salts, Coulombic attractions are weakened and lattice-packing arrangements frustrated.^[3] ILs are regarded as 'designer solvents', as molecular control over liquid properties is possible depending on how the ions are functionalized. Hydrogen-bonding can play a key role in IL chemistry.^[4-6] Whereas most inorganic salts cannot H-bond and are dominated by electrostatic interactions between ions, many ILs have extensive H-bonding capacity. For example, H-bond donor and acceptor sites are created during synthesis of protic ionic liquids (PILs).^[2] This enables some PILs to develop dense H-bond networks and thus mirror a number of water's remarkable structural^[5] and solvent^[2] properties. Finally, ILs have the capacity to self-assemble, forming well-defined nanostructures in the bulk phase^[7-13] as well as at interfaces.^[3, 14-16] IL nanostructure arises because at least one of the ions (frequently the cation) is amphiphilic, with distinct charged and uncharged moieties.^[9] This drives segregation of ionic and non-ionic groups in ILs, reminiscent of self-assembly in aqueous surfactant mesophases.^[3, 12]

Here we elucidate the bulk solvent structure of mixtures of a PIL, ethylammonium nitrate (EAN), and water, c.f. Figure 1. EAN is one of the oldest known,^[17] and most extensively studied PILs. As EAN is completely miscible with water, this raises questions such as, how do EAN and water mix? Are the forces that lead to self-assembly in pure EAN^[9] sufficient to maintain a solvophobic nanostructure? What is the nature of ion solvation in such mixtures? If nanostructure persists in aqueous mixtures and key solvent properties retained, this will

increase PIL utility by offering an additional mechanism for tuning liquid behaviour and lowering the overall cost of the solvent medium.

While primitive (continuum solvent) models of dilute aqueous electrolyte solutions are generally successful, understanding ion-water interactions and concentrated solutions has proved challenging, and is complicated in part by the absence of a satisfactory model for liquid water.^[18, 19] Structure in aqueous electrolyte solutions is understood in terms of Hofmeister^[20] and hydrophobic^[21] effects, which can only be probed using sophisticated experimental^[22-24] and computational^[25-27] techniques. Solvated ions induce a different local structure of water molecules in the first, and even the second or third solvation shells, to accommodate the dissolved species. This leads to ions being classified as either "structure making" or "structure breaking" through the creation of "solute cavities".^[28]

Recent, growing interest in IL + water mixtures has been motivated, at least in part, by the desire to understand the dramatic changes in IL solvent properties that have been observed upon water contamination.^[29] Water is probably the most common impurity in ILs; even nominally hydrophobic ILs absorb significant quantities of water when exposed to the atmosphere.^[30] Many computational studies have examined changes in IL solvent structure by dissolved water, often over the full concentration range.^[31-35] At low water concentration, these predict that IL nanostructure is relatively unperturbed, but at high water content the system resembles aqueous solutions of ionic surfactants. However, these studies have overwhelmingly investigated aprotic ILs; largely absent are corresponding studies of PILs and experimental verification of the findings. Only one paper^[11] has directly investigated the structure of PIL – water mixtures. Small- and wide-angle X-ray scattering (SWAXS) was used to investigate the effect of water on a range of PILs. For neat PILs like EAN, the SWAXS spectra showed peaks in the data consistent with nanoscale structure, which were essentially invariant with increasing water content. A micelle-like model was proposed for

the solution structure, with water located in the bulk polar domains and associated with the charge groups on the ions.



Figure 1- Molecular structure and atom types of the ethylammonium (EA^+) cation, nitrate (NO_3^-) anion and water molecule. Different C, N, O and H atoms in solution are distinguished using subscripts.

5.3 Results & Discussion

Figure 2 presents the neutron diffraction data and EPSR^[36] fits to the three 1:6 mol:mol EAN + water mixtures at different neuron contrasts (d_3 -EAN + D₂O, d_8 -EAN + H₂O, and d_8 -EAN + D₂O). Excellent agreement is obtained across the entire angular (Q-)range. The data closely resemble those previously obtained on the same instrument for different isotopomers of pure EAN.^[9] Notably, a sharp peak is detected at low (<1 Å⁻¹) angles, as previously reported in neutron^[8, 9] and x-ray^[11, 37] scattering for pure EAN and EAN+H₂O^[11], but is absent in pure water or other similar molecular solvents. This indicates a repeat distance of 10.1 Å is present in the bulk solution.



Figure 2- Experimental (dots) and EPSR fitted (solid line) scattered intensity as a function of Q (Å⁻¹) for 1:6 mol:mol EAN+water contrasts at 298K; d_3 -EAN + D₂O (bottom), d_8 -EAN + H₂O (middle), d_8 -EAN + D₂O (top). Data for different isotopic substitutions are offset for clarity.

Figures 3A-G show atom-atom partial radial distributions, g(r), and their corresponding 3D reconstructed spatial density functions (sdf) for key selected atomic species in these mixtures. The g(r) show changes in an atom's local density (atoms/Å³) as a function of separation (Å), normalized to its bulk value. This means that g(r) intensity is not directly comparable between different systems because the density of any atom is different in EAN+H₂O and pure EAN etc., despite the similar total bulk atom densities for all atoms in the systems; EAN+H₂O (0.1023), pure EAN (0.1011) and H₂O (0.1002). Integration over a particular radius yields atom coordination numbers. A more complete set of g(r)'s, sdf plots as well as their coordination numbers from the EAN + water mixture are provided in the Supplementary Information in Table 2.



Figure 3- EPSR derived data for key atom-atom pair correlations in (**A**) EAN-EAN (**B**) H_2O - H_2O . g(*r*) data for pure H_2O and pure EAN is shown as black dots sourced from Ref [9] and [22]). The

intensities are offset for clairty. The inset shows a close up of the O_w - O_w g(r) between 3.0 – 8.0 Å. (C-G) EPSR spatial density function (sdf) plots which show 3D reconstructions of g(r) data. Sdf legends indicate 20% probability surfaces of atom₁ ordering around atom₂ between the given radial limits.

The main ion-ion pair correlation functions are presented in Figure 3A, and compared with our previous results for pure EAN. The peak position for the anion-cation (N_0 -N) correlation is very similar to pure EAN but slightly narrower and shifted to slightly smaller separation. Conversely, nearest-neighbour correlations between anions (N_0 - N_0), the charged part of the cation (N-N), and the uncharged part of the cation (C_M - C_M) are weaker in the EAN + water mixture than in pure EAN. The strong cation – anion (N_0 -N) correlation peak and the persistence of the low-angle scattering peak are both inconsistent with simple dilution of ions by water. Thus, water must *change* the liquid nanostructure but not destroy it; EAN + water is not an unstructured homogenous solution.

Integration of the N-N_O peak yields a coordination number of 1.82, significantly lower than pure EAN (2.98). This means that while each cation is solvated by 3 anions in pure EAN, only ~2 anions are present in the first solvation shell in the EAN + water mixture. For correlations between like species [anions- anions (N_O-N_O), the charged part of the cation (N-N), and the uncharged part of the cation], the corresponding coordination numbers are much reduced compared to pure EAN (in brackets) at 0.34 (0.92) for N_O-N_O; 0.74 (1.83) for N-N; and 0.96 (3.16) for C_M-C_M.

The EPSR-derived spatial density plots (Figure 3C-F) show the most probable 3D arrangement of ions around the ethylammonium (3C, D) and nitrate (3E, F) ions in EAN + water. The arrangement of cations around anions (and vice versa) shown in 3D and 3E is virtually identical to that determined previously for pure EAN, as would be expected from the similarity in the N-N₀ g(*r*). Figure 3C shows the position of the cation methyl carbons. While the C_M-C_M g(*r*) data reveals that fewer C_M atoms are present in the first C_M solvation shell,

their *arrangement* is similar to that found in pure EAN. This shows that the key interactions driving bulk PIL nanostructure are maintained on dilution; solvophobic aggregation of cation alkyl chains and H-bonding between ammonium moiety and nitrate ions are still clearly evident, leading to a local apolar and polar domain structure in the EAN + H₂O mixture.

Strikingly, the water-water structure differs little from that determined from scattering studies of pure water. In Figure 3B, correlation peaks can be identified in the mixture at 2.3 Å and 3.7 Å for H_w-H_w (2.4 Å and 3.7 Å in pure water) and 1.8 Å and 3.2 Å for O_w-H_w (1.8 Å and 3.3 Å).^[18] Of greater significance is the $O_W - O_W g(r)$, which has been the traditional yardstick for comparing models of water. The mixture shows a sharp peak at 2.8 Å, in perfect agreement with scattering from pure water at ambient temperatures,^[18] and consistent with previous findings that the nearest-neighbour O_W-O_W distance is not affected by dissolved ions.^[22, 23] At larger separations, the $O_W - O_W g(r)$ shows two broader, weaker correlations at approximately 4.4 Å and 7.1 Å (c.f 3B inset). That the peak at 4.4 Å is so close its pure water counterpart at 4.5 Å^[18] is remarkable, as this is characteristic of the tetrahedral H-bonding network in water. For inorganic salt solutions, this peak moves inwards to shorter distances with increasing ion concentrations,^[22, 23, 26] becoming a shoulder on the first peak at similar ion concentrations to the present study, indicating a distorted H-bond network. Instead, Figure 3B shows a decrease in peak amplitude, but with a miniscule inward shift. These results imply that the second water shell has not collapsed into the first and that the essential features of water's bulk H-bond network are retained in the EAN + water mixture. The distinctly tetrahedral appearance of the sdf plot (Figure 3G) supports this conclusion and is also perfectly analogous to pure bulk water.^[18, 19]

Evidence for strong H-bonding between the two liquid components is seen in peaks at 1.8 Å for anion-water (O-H_W) and 1.6 Å for cation-water (H_N-O_W) g(r)'s and the prominent lobes adjacent to H-bonding donor and acceptor sites in Figure 4B-E. The two components are

effectively interchangeable as H-bond donors and acceptors e.g. the arrangement of N_0 and O_W around the amino N are virtually identical (Figure 3D and 4B), and N and N_0 together (Figures 4D and 4E) match the distribution of O_W around O_W (Figure 3G). Thus the cation and anion densities are positioned to maximise H-bonding with nearest-neighbour water molecules. The methyl carbon displays no such local structure, and remains well away from the water molecules. This is consistent with the maintenance of an amphiphilic nanostructure in the mixture with a well-defined interface between the non-polar ethyl groups on one side, and amino cation, nitrate anion and water on the other.

Integration of the g(r) peaks gives coordination numbers of 1.10 (O-H_W) and 0.47 (H_N-O_W). These values suggest that the anion participates in more H-bonding interactions with water molecules than the cation and so is the principle ion involved in stabilizing the water-ion interface. This is not altogether surprising given that the cation alkyl chains are locally sequestered in a hydrophobic core (Figure 3C) and that the ammonium group is already well-solvated by at least two anions (Figure 3D). Thus, the anion is more available for anion-water H-bonding.



Figure 4- EPSR derived partial radial g(r) distribution functions for key (**A**) NO₃⁻-H₂O and EA⁺-H₂O correlations. The intensities are offset for clarity. (**C-G**) spatial density function (sdf) plots which show 3D reconstructions of g(r) data. Cation density is coloured yellow, anions green, water blue. Sdf legends indicate 20% probability surfaces of atom₁ ordering around atom₂ between the given radial limits. Atom colourings in the central species are: C (grey), H (white), N (blue), O (red).

How can this mixture support two local microenvironments so similar to the pure liquid components? Figure 5A-D shows four representations of a single fitted, equilibrated simulation box. The structure is bicontinuous, with cation ethyl groups (4D) clearly clustered together and separated from each other by polar regions as in pure EAN. However the water (4B) and EAN (4C) snapshots, separate EAN and H₂O domains are also evident. This is a significant departure from traditional ion-water interactions at high concentration as the ions are segregated from the water phase but are still completely miscible because ion self-assembly occurs in a fashion similar to surfactant solutions but on a length scale an order of magnitude smaller.^[3] This means that a well-defined *interface* must exist in the liquid mixture, consisting of the non-polar ethyl groups on one side, and amino cation, nitrate anion and water on the other.



Figure 5- Snapshots of the fitted EAN + H₂O bulk structure at 298 K (A) 500 EA⁺, 500 NO₃⁻ & 3000 H₂O (B) 3000 H₂O (ions omitted) (C) 500 EA⁺ & 500 NO₃⁻ (water omitted) (D) Apolar -C-C-

domains only $(-NH_3^+, NO_3^-)$ and H_2O omitted). C is grey, H is white, N is blue is and O is red. The g(r) data and SDF plots derived from the averaging the local ion environments present in over 5000 such equilibrated simulation boxes.

In the polar domains, local structures closely resembling pure water and pure EAN correlations arise, confirming that these interactions are unaffected by mixing. However, correlations between like groups (anions, cation charged group, cation uncharged group) are reduced because of cation-H₂O and anion-H₂O correlations. Because water is principally associated with the charged groups on the ions, its net effect is to increase the effective headgroup size of the cation, which raises the interfacial curvature around the non-polar regions. This changes the EAN nanostructure from a near-zero mean curvature, or locally flat L_3 -sponge-like in pure EAN,^[9] to a branched (locally cylindrical) network or mesh^[38] in EAN + water. A mesh-like nanostructure also provides a fairly good qualitative explanation of why the C_M-C_M coordination numbers should decrease upon water addition; fewer nearest neighbours atoms can pack in a locally-cylindrical 3-D mesh than a locally-planar L_3 -sponge and so these parameters must likewise decrease.

Because the local structure of water in the polar domain closely resembles that of pure water; aside from molecules associated with the charged groups on the ions, water is insensitive to the presence of the IL. An total inventory of each water molecule's four potential H-bonds at this concentration consists, on average, of 2.5 with other waters, one with the anion, and 0.5 with the cation ammonium group at the polar/apolar interface.

5.4 Conclusions

A higher curvature network structure accounts for the similarity in the EAN ion pair arrangements, the reduction in correlations between like species, and the preservation of solvophobic interactions that produce liquid nanostructure. Water neither simply dilutes the molecularly dispersed ions of an IL, nor does it just swell the polar region of the existing IL nanostructure. Instead, interactions between water and the charged groups of the IL change the curvature of the interface, transforming it into a related, but different, nanostructure. This reveals yet another unanticipated example of EAN's amphiphilicity, and of the rich structural polymorphism in ILs and their mixtures.

5.5 Experimental Section

In these experiments we have selectively replaced hydrogen with deuterium on water molecules (H₂O or D₂O), ethylammonium cations (d_3 -EA⁺, d_8 -EA⁺), or both, to obtain structural information on three chemically identical, but isotopically different samples of the EAN + H₂O system (d_3 -EAN + D₂O, d_8 -EAN + H₂O, d_8 -EAN + D₂O). Chemically identical, but isotopically different samples of EAN were prepared as described previously.^[9] Solutions of 1:6 mol:mol EAN:H₂O were then made by mixing the pure EAN isotopomers with either RO water or fresh D₂O (99% Sigma Aldrich). Neutron diffraction data were collected on the SANDALS diffractometer (Q-range 0.05-50 Å⁻¹) located at ISIS research facility, Rutherford Appleton Laboratories, UK. All other experimental details, including protocols of Gudrun data normalization, can be found in Ref.^[9]

Data fitting was performed using Empirical Potential Structure Refinement (EPSR).^[36] In this study, the simulation box consisted of 3000 H₂O molecules and 500 EAN ion pairs, with the reference pair interaction potential defined using the values in Table 1 (Supplementary Information). This generates a 3D model of the liquid system via a standard, iterative Monte Carlo framework that is refined against the measured diffraction data as well as liquid parameters including density and molecular structure. EPSR fits the three SANDALS contrasts simultaneously using the same model, by normalizing for isotope populations. Table 1 shows Lennard-Jones and Coulombic charge parameters for EPSR modelling.
5.6 Supplementary Information

Part 1- SANDALS measurements & EPSR data fitting

Table 1- Lennard-Jones and Coulombic charge parameters for EPSR modelling of EAN & wa	ater.
Note, many different atomic potentials for water were tested in EPSR modelling, however the best	fits
were produced with SPC/E values.	

Eth	ylammon	ium C	ation		Nitrate A	Anion		Water				
Atom	ε (kJ.mol ⁻¹	σ) (Å)	q (e)	Atom	ε (kJ.mol ⁻¹	σ) (Å)	q (e)	Atom	ε (kJ.mol ⁻¹)	Σ (Å)	q (e)	
C ₁	0.276	3.50	+0.263	No	0.711	3.25	+0.845	O_W	0.650	3.166	-0.8476	
C _M	0.276	3.50	-0.411	Ο	0.879	2.96	-0.615	H_{W}	0.00	0.00	+0.4238	
Ν	0.711	3.25	-0.529									
H_{M}	0.126	2.50	+0.143									
H_1	0.126	2.50	+0.069									
H_N	0.126	2.50	+0.366									
C_1	0.276	3.50	+0.263									

Part 2- partial radial g(r) distribution data

Table 2- Summary of important Ethylammonium Nitrate (EAN) + Water interionic partial radial g(r) distribution data extracted from the EPSR model. From left to right the columns report g(r) function, Peak Position and Coordination Number between limits α and β in the 1st ion shell, Peak Position (if present) and Coordination Number between limits α and β in the 2nd ion shell.

Correla	tion		1 st Shell		2 nd Shell
Ion Ion	Atom-atom	Peak	Coord. #	Peak	Coord. #
1011-1011	g(<i>r</i>)	1 (Å)	(α - β)	2 (Å)	(α - β)
Anion Anion	$N_{O} - N_{O}$	3.7	0.34 (0.0-4.0)	5.4	6.07 (4.0-6.5)
Amon –Amon	$N_O - O$	4.7	4.68 (0.0-5.5)	6.8	23.6 (0.0-8.5)
	$C_M - C_M$	3.6	0.96 (0.0-5.0)	6.4	3.2 (5.0-7.0)
Cation	$C_M - C_1$	3.9	0.25 (0.0-4.2)	5.1	1.42 (4.2-5.8)
Cation	$C_M - N$	4.3	0.75 (0.0-5.0)	6.3	3.22 (5.0-7.0)
Cation	$C_1 - C_1$	4.5	0.58 (0.0-5.0)	5.8	3.55 (5.0-7.0)
	N - N	5.5	0.74 (0.0-5.0)	6.9	3.42 (5.0-7.0)
	$C_1 - N_O$	4.1	3.19 (0.0-5.5)	6.8	5.81 (0.0-7.5)
	N - O	2.7	2.93 (0.0-3.7)	4.5	5.49 (4.0-5.5)
Cation -Anion	$N_{O} - N$	3.4	1.82 (0.0-4.0)	4.6	3.17 (4.0-7.0)
	$N_O - C_M$	3.8	2.30 (0.0-5.0)	5.1	1.96 (5.0-6.5)
	$H_N - O$	1.6	1.25 (0.0-3.0)	3.2	3.92 (3.0-4.5)
	$O_W - O_W$	2.8	4.03 (0.0-3.3)	4.4	18.69 (0.0-6.0)
Water-Water	$O_W - H_W$	1.8	1.48 (0.0-2.4)	3.2	12.34 (0.0-4.0)
	$H_W - H_W$	2.3	4.13 (0.0-3.0)	3.7	12.73 (3.0-4.5)
	$O_W - N_O$	3.4	6.43 (0.0-4.5)	5.8	21.30 (4.5-7.0)
Water – Anion	$O_W - O$	2.8	1.8 (0.0-3.3)	4.5	8.49 (3.3-5.2)
	$H_W - O$	1.8	1.10 (0.0-2.3)	7.1	5.47 (2.3-4.0)
	$O_W - N$	2.7	1.60 (0.0-4.2)	4.4	0.58 (4.2-4.8)
Water Cation	$O_W - C_1$	3.3	0.71 (0.0-4.1)	4.5	1.02 (4.1-5.2)
water – Cation	O _W -C _M	3.4	0.70 (0.0-4.0)	4.6	1.00 (4.0-5.2)
	$O_W - H_N$	1.6	0.47 (0.0-2.3)	3.2	3.22 (2.3-4.0)



Figure 1- EPSR derived partial radial g(r) distribution functions for important anion-anion & anion-water interionic atom–atom correlations between 2.0– 12.0 Å.



Figure 2- EPSR derived partial radial g(r) distribution functions for important cation-cation and cation-water interionic atom-atom correlations between 2.0 – 12.0 Å. The intensities are offset to 0.0, +1.0, +2.0, +3.0 etc.



Figure 3- EPSR derived partial radial g(r) distribution functions for important cation-water and anion water H-bonding correlations between 0.0 - 8.0 Å. The intensities are offset to 0.0, +1.0, +2.0, etc.

Part 3- Additional box pictures-



Figure 4- Snapshots of the fitted ethylammonium nitrate (EAN) + water bulk structure at 298 K.

Unless otherwise stated, C is grey, H is white, N is blue is and O is red:

- (A) $500 \text{ EA}^+ \& 500 \text{ NO}_3^- (3000 \text{ H}_2\text{O omitted})$ (B) 500 EA^+ , $500 \text{ NO}_3^- \& 3000 \text{ H}_2\text{O}$
- (C) $3000 \text{ H}_2\text{O} (500 \text{ EA}^+ \& 500 \text{ NO}_3^- \text{ omitted})$ (D) $500 \text{ EA}^+ (500 \text{ NO}_3^- \& 3000 \text{ H}_2\text{O} \text{ omitted})$

(**E**) As per B, but NO_3^-O atoms yellow

(**F**) 500 NO₃⁻ (500 EA⁺ & 3000 H₂O omitted)

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CHAPTER 6

C6: The nature of hydrogen bonding in protic ionic liquids

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6.1 Abstract

The size, direction, strength, and distribution of hydrogen bonds in several protic ionic liquids (PILs) has been elucidated using neutron diffraction and computer simulation. There is significant variation in PIL hydrogen bond interactions ranging from short and linear to long and bi-/trifurcated. The nature of the PIL's hydrogen bonds reflects its macroscopic properties.

6.2 Introduction

Since the days of Latimer and Rodebush,^[1] much interest has been directed to understanding how liquids hydrogen (H-) bond.^[2-7] Whilst H-bonds are not unique to,^[8, 9] or present in all liquids,^[4] they are important in chemistry because H-bonds can induce solvent structure; the H-bond is a strong, directional interaction compared to other forces between liquid molecules (eg. van der Waals, π - π , hydrophobic or solvophobic interactions). In most liquids, Hbonding results in a preferred orientation between nearest neighbour species, e.g. dimers of formic acid.^[10] However, multiple H-bonds can act co-operatively over longer distances exemplified by water's tetrahedral network structure.^[1, 7, 11] Thus, H-bonds are key to many aspects of liquid chemistry including dynamics, solute solvation and macroscopic physical properties.^[4]

This manuscript systematically examines how protic ionic liquids (PILs) H-bond. PILs are an emerging class of solvents composed entirely of ions,^[12, 13] formed by to proton transfer from a Brønsted acid to a Brønsted base.^[14] Despite their pure ionic composition, H-bonds are a hallmark of PILs.^[15-18]

Whilst it is widely accepted that PILs H-bond,^[12] its contribution to solvent (nano-)structure^[19-29] and macroscopic physical properties^[12, 14, 30] is difficult to deconvolute from other ion-ion interactions. Here we use model fits^[31] to neutron diffraction data to examine the local arrangement of H-bonding atoms in PILs (c.f. Table 1). Unlike other techniques, neutron diffraction is sensitive to the positions of hydrogen atoms, allowing the location of hydrogens participating in H-bonds to be unambiguously determined. Strikingly, we show that H-bond direction and strength can be related to macroscopic physical properties.

The past thirty years has witnessed considerable progress towards structure-property relationships in liquids, aided in part by greater knowledge of intermolecular forces.^[4] A consistent theme is that the liquid phase is not 'unstructured' as it can possess time-averaged

bulk structure. In scattering experiments, this is manifested as peaks in the measured structure factor S(q), which corresponds to repeating inter- or intramolecular correlations in the bulk. This is shown for various primary alkylammonium salt PILs in Figure S₁-S₄ in the Supplementary Information, which presents S(q) neutron diffraction data and the empirical potential structure refinement (EPSR)^[31] model fits for EASCN, BASCN, EAHS and EAF with multiple isotopic substitutions. We reported the diffraction spectra for EAN and PAN previously.^[23, 24] Structures are detailed in Table 1. Notably, every PIL has nanoscale structure that can only be fitted with bicontinuous sponge-like models (c.f. Supplementary Information).

6.3 Results & Discussion

The nature of the H-bonds formed in the PILs is probed in three different ways in Figure 1. Data is presented as a distribution of: H_N ...X distances (H-bond lengths, *hbl*) via partial radial pair correlation functions (Figure 1A); N-H_N...X angle (H-bond angles, θ) via angle probability distributions (Figure 1B); combined 3D structure (distance + angle) via spatial density function (sdf) plots (Figure 1C-H). Because each PIL has multiple (often chemically identical) acceptor sites, in this manuscript we focus on the dominant H-bonds for each system; data for less important H-bond interactions are examined in the Supplementary Information.

In Figure 1A, the first peak in the g(r) functions shows the average PIL H-bond lengths (*hbl*). EASCN (1.71 Å) and EAHS (1.62 Å) possess much shorter *hbl*s than other PILs. The H-bond angle probability distributions (P_{θ}) (Figure 1B), which have been corrected for a conical^[32] distribution, show that short H-bonding PILs have maxima at 180°, indicating a *linear* N-H_N...X arrangement is favoured. Conversely, the long H-bonding PILs have maxima at ~110°, indicating *bent* H-bonds are preferred.

Table 1. PIL name, structure, melting point (T_m), glass transition temperature (T_g), ionic conductivity (κ), viscosity (η), hydrogen bond length (*hbl*), most probable hydrogen bond angle (θ_{max}), percentage of linear H-bonds (\mathscr{G}_{linear}) and Δr . Subscripts are used to distinguish atoms on the ions. *hbl* and θ_{max} determined from peaks in Figure 1A & 1B respectively. $\mathscr{G}_{linear} = \int_{165}^{180} P_{\theta} d\theta$ from data in Figure 1B (Note $\int_{0}^{180} P_{\theta} d\theta = 100$). $\Delta r = \sum r_{vdW} - hbl$, which is the difference between the sum of van der Waals radii of H-bonded atoms and the measured *hbl*.

Protic Ionic Liquid	Ion Structure	T _m (°C)	T _g (°C)	κ (mS.cm ⁻¹)	η (cP)	hbl (Å)	θ_{max} (°)	% _{linear}	Δr (Å)
Ethylammonium Thiocyanate (EASCN)	$\begin{array}{c} C_2 \\ H_2 \\ H_1 \\ C_1 \\ H_N \end{array} \overset{N_T}{\underset{H_N}{}} C_T \\ F_T \\ F_T \\ SCN-: 2 \text{ acceptor} \end{array}$	41	-	-	-	1.71 ^[a]	180 ^[b]	53.1 ^[b]	0.99 ^[c]
Ethylammonium Hydrogen Sulphate (EAHS)	$\begin{array}{c} H_{1} \\ C_{2} C_{1} \\ H_{2} \\ 0_{4} \\ S \\ 0_{3} \\ 0_{3} \\ 0_{3} \\ 0_{3} \\ 0_{3} \\ 0_{3} \\ 0_{3} \\ 0_{4} \\ 0_{3} \\ 0_{4} \\ 0_{1} \\ 0_{4} \\ 0_{3} \\ 0_{4} \\ 0_{1} \\ 0_{3} \\ 0_{4} \\ 0_{3} \\ 0_{4} \\ 0_{1} \\ 0_{3} \\ 0_{4} \\ 0_{3} \\ 0_{4} \\ 0_{1} \\ 0_{4} \\ 0_{3} \\ 0_{4}$	40	-84	4.4 ^[d]	128	1.62 ^[a]	180 ^[b]	59.8 ^[b]	0.97 ^[c]
Ethylammonium Formate (EAF)	$EA^{+}: 3 \text{ donor}$	-15	-106	12.16 ^[d]	23	2.43 ^[a]	109 ^[b]	7.5 ^[b]	0.22 ^[c]
Ethylammonium Nitrate (EAN)	$EA^{+}: 3 \text{ donor}$ $RO_{3}^{0}: 3 \text{ acceptor}$	12	-91.5	26.9 ^[d]	32	2.37 ^[a]	109 ^[b]	12.1 ^[b]	0.28 ^[c]
Propylammonium Nitrate (PAN)	H_3 H_2 H_1 C_3 C_2 C_1 H_N O_1 O_2 N_0 O_3 $PA^+: 3 \text{ donor}$ $NO_3^-: 3 \text{ acceptor}$	3	-	12.97 ^[e]	67	2.34 ^[a]	112 ^[b]	13.7 ^[b]	0.31 ^[c]
Butylammonium Thiocyanate (BASCN)	$\begin{array}{c} H_3 H_1 \\ H_4 C_2 C_2 N \\ H_4 H_2 \\ N_T C_T S_T \\ BA^+ : 3 \text{ donor} \\ SCN^- : 2 \text{ acceptor} \end{array}$	20.5	-	-	97	2.61 ^[a]	106 ^[b]	5.7 ^[b]	0.09 ^[c]
^[a] Derived from d ^[b] Derived from d	ata in Figure 1A ata in Figure 1B		^[d] S ^[e] S	ourced from ourced from	Ref 12 Ref 27	2			

^(b) Derived from data in Figure 1B ^[c] Calculated from *hbl* values and data in Ref 35.



Figure 1- EASCN (red crosses), EAHS (green triangles), EAF (blue pluses), EAN (black circles) PAN (pink rectangles) & BASCN (purple diamonds). H-bond distances: (**A**) partial radial H_N ^{...}X g(r) data. H-bond angles: (**B**) normalized angle distributions plot of N-H_N^{...}X triplet for all H-bond lengths up to the first local minimum in the g(r) data in (**A**). H-bond distance + angle: (**C**–**H**) sdf plots of H-bond acceptor location as a function of distance & angular position from the H-bond donor (ammonium nitrogen). The sdf data is a combined 3D representation of (**A**) & (**B**) with 20% probability surfaces shown. Note, the number of data points in the black and white version of (**B**) has been reduced for clarity.

To elucidate this point it is useful to compare the fraction of linear H-bonds ($\%_{linear}$) (Table 1) in each PIL, calculated by integrating the angular probability distributions in Figure 1B between 165°-180° (note, by definition $\int_0^{180} P_{\theta} d\theta = 100\%$). As expected, EASCN and EAHS have the highest percentage of linear H-bonds at 53.1% and 59.8% respectively. However in long *hbl* liquids, less than 15% of all H-bonds are linear, and this varies considerably with anion structures. For example, $\%_{linear}$ is much lower in EAF (7.5%) than EAN (12.1%) even though both formate and nitrate are trigonal planar species with multiple oxygen H-bond acceptors. Likewise, there is no simple relationship between the fraction of linear H-bonds and cation alkyl chain length, but it does depend on ion packing factors detailed below.

The number of H-bond acceptor atoms per ammonium hydrogen $(R_{X:H_N})$, determined from converged coordination numbers, is presented in Table 2. These coordination numbers are reflect the number of potential acceptor atoms lying within a specified radius from each H_N hydrogen, defined to include the nearest-neighbour maximum (Figure 1A). In EASCN and EAHS, there is one acceptor atom for each ammonium hydrogen $(R_{X:H_N} = 1)$, and short, strong H-bonds form with 180° as the most probable bond angle.

All other PILs examined have longer *hbls*, and acceptor atoms are not close enough to each H_N atom for strong, linear H-bonds to form. Here the distribution of bond angles broadens markedly and the most probable bond angle changes from linear to ~110°. In these liquids, averages of $R_{X:H_N}$ ~2 (EAN and PAN) or ~3 (EAF and BASCN) acceptor atoms fall within the (larger) first coordination shell range of each hydrogen. (This need not equate to 6 or 9 acceptor atoms solvating each ammonium group, as acceptor atoms will be doubly-counted if they fall within the coordination radius of two different H_N hydrogens.)

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In crystalline solids, $R_{X:H_N}$ of 2 are associated with bifurcated H-bonds^[3, 6, 8, 33] and 3 with trifurcated H-bonds,^[3, 6, 8] and similar relationships between $R_{X:H_N}$ and H-bond geometry have been reported, notably for dithiocyanate,^[34] thiocyanate^[35, 36] and sulphate^[37] anions in

the Cambridge Structural database. The bifurcated and trifurcated definitions must be applied with caution for PILs because the ions are in motion rather than fixed in a lattice, so the $R_{X:H_N}$ and angle distributions represent the average liquid state. Nonetheless, the similarity of correlations between the *hbl*, θ , and $R_{X:H_N}$ data for these PILs and the crystalline solids is striking, making it likely that bifurcated and trifurcated H-bonds are present in these solvents, although they may not be long lived.

These H-bonding structures are represented in Figure 1C-H using sdf plots, which depict the most probable 3D distribution of H-bond acceptor atoms around the donor group. The radial cut-offs in the sdf plots capture all possible *hbl* represented up to the first local minima in the g(r) data (Figure 1A). A low 20% probability surface was used as it highlights the most favoured H-bonding arrangement.

Table 2 PIL H-bond classification via ion packing factors. Atom coordination numbers show # of acceptor atoms X around a H_N proton between limits α and β . $R_{X:H_N}$ is the ratio of Total number of Acceptor sites for each H_N Donor site ($R_{X:H_N}$). The error in each coordination number is about ±0.05.

Protic Ionic Liquid	Atom- atom g(r)	Coord. Number $(\alpha - \beta)$	$R_{X:H_N}$	H-bond Classification	
FASCN	$H_{\rm N}-N_{\rm T}$	0.55 (0-2.50)	1.01	Simple	
EASCIN	$H_{\rm N}-S_{\rm T}$	0.46 (0-2.50)	1.01	Shipe	
	$H_N - O_1$	0.05 (0-2.25)			
EAUS	$H_N - O_2$	0.34 (0-2.25)	1.02	Simple	
EARS	$H_{\rm N}-O_3$	0.32 (0-2.25)	1.02	Simple	
	$H_{\rm N}-O_4$	0.31 (0-2.25)			
	$H_{\rm N}-O_1$	0.56 (0-3.00)			
EAN	$H_N - O_2$	0.55 (0-3.00)	1.63	Bifurcated	
	$H_N - O_3$	0.52 (0-3.00)			
	$H_N - O_1$	0.68 (0-3.00)			
PAN	$H_{\rm N}-O_2$	0.72 (0-3.00)	2.10	Bifurcated	
	$H_N - O_3$	0.70 (0-3.00)			
EAE	$H_N - O_1$	1.35 (0-3.25)	2.77		
EAF	$H_N - O_2$	1.32 (0-3.25)	2.67	B1 / Trifurcated	
DASCN	$H_N - N_T$	1.57 (0-3.50)	2 10	Tuiferna ata d	
DASCN	$H_N - S_T$	1.53 (0-3.50)	5.10	Trifurcated	

EASCN (Figure 1C) and EAHS (Figure 1D) have three small symmetric acceptor lobes, slightly above the plane of the $-NH_3^+$ group, each collinear to the N-H_N covalent bonds. This is the origin of the strong H-bonding in these systems; the acceptor atoms are arranged around $-NH_3^+$ in a 1:1 ratio that maximises linear H-bonding interactions.

Other PILs have markedly different sdf plots, reflecting differences in *hbl*, θ , and $R_{H_N:X}$. In EAN and PAN (Figure 1F & 1G), three acceptor lobes are still present, but they are larger, more asymmetric, and the majority of density is off the N–H_N bond axis. This is consistent with EAN and PAN having a large proportion of bent H-bonds.

EAF and BASCN (Figure 1E & 1H) also have asymmetric acceptor lobes, as well as additional density directly above the $-NH_3^+$ group. For both of these PILs, the lobes roughly bisect the H_N -N- H_N angles, and bent H-bonds are favoured. Because the lobes above the NH_3^+ group form acute angles to the N- H_N donors, it is likely that this corresponds to anions electrostatically attracted to the cation, rather than conventionally H-bonded.

As the cation and anion in each system form more than one H-bond, all PILs build up dense, cooperative H-bond networks in the bicontinuous nanostructure. The relative H-bond strengths in these networks can be determined from Δr values (c.f. Table 1), which is the difference between sum of the van der Waals radii^[38] of the H-bond donor-acceptor triplet $(\sum r_{vdW})$ and the measured *hbl*. Whilst the van der Waals definition of H-bonds is outdated,^[8] Δr is known to be proportional to H-bond strength,^[39] and is about 3× larger for EASCN and EAHS than other PILs.

Differences in H-bonding are reflected in macroscopic physical properties (c.f Table 1), particularly for PILs with a common ion. The strong, linear H-bonding PILs have more 'solid-like' character, whereas weaker, bent H-bonding systems display more 'liquid-like' properties. For example, T_m and T_g are known to increase with cohesive interactions; in ethylammonium PILs, the trend in T_m and T_g is the same as that for H-bond strength EASCN> EAHS> EAN> EAF. Table 1 also shows a strong correlation with properties linked to ion mobility; η increases and κ decreases as H-bonding is enhanced (and *vice versa*), except for EAF. However, EAF is difficult to dry and is known to thermally degrade,^[12, 14] either of which could contribute to lower than expected conductivity.

Interestingly, we see no correlation between ΔpK_a and PIL H-bonding (c.f Table 4). This is at first surprising, as H-bonding is analogous to incipient proton transfer and PILs are formed by proton transfer. In aqueous systems, small ΔpK_a values produce strong H-bonds because the proton is shared evenly between the acid and base. On this basis, EAF would have the strongest H-bonds while interactions in the remaining PILs would be reduced but of similar magnitude. However many groups have noted that pK_a 's for aqueous systems, are not directly applicable to pure salt media (PILs \approx 10M salt solutions). The results presented here confirm this suggestion and offer a chemical explanation: bent H-bonds.

5.4 Conclusions

The ion arrangements in PILs are a consequence of the balance between intermolecular forces and the physical dimensions of the ions. Whilst similar bicontinuous sponge-like nanostructures form in all systems, there is significant variation in the nature of H-bonds in present. This means that that PIL nanostructure controls the H-bond strength and structure by dictating the relative orientations of the cations and anions to each other; the distribution of H-bond geometries is related to the ability of each PIL to accommodate H-bonds in the bicontinuous arrangement rather than inducing a different bulk structure. When the nanostructure is such that a relatively high proportion of H-bonds are linear ($R_{X:H_N} \sim 1$), attractions between ions increase and physical properties become more solid-like. At higher $R_{X:H_N}$ ratios, bifurcated or trifurcated H-bonding results, producing weaker, bent H-bonds, decreasing cation-anion attractions and more fluid-like material.

5.5 Experimental Section

EAN, EAF, EAHS and PAN were synthesized via acid-base neutralization from appropriate concentrated reagents.^[23] EASCN and BASCN were prepared according to the method described by Poole et al.^[40] Chemically identical, but isotopically different contrasts for each PIL were made by selectively replacing hydrogen with deuterium on the exchangeable (d_3 - or d_4 - contrasts) or exchangeable and non-exchangeable (d_8 - or d_9 - contrasts) groups.^[23]

Neutron diffraction data were collected on the SANDALS diffractometer (Rutherford Appleton Laboratories, UK) and S(q) extracted as detailed in Ref.^[23] Empirical Potential Structure Refinement (EPSR)^[31] was used to model the PILs. This models the bulk structure of 500 ion pairs via a standard, iterative Monte Carlo framework that is refined against the measured SANDALS data as well as other liquid parameters (c.f. Supplementary Information).

5.6 Supplementary Information

Part 1: Additional notes on EPSR fits

Table 2- Lennard-Jones and Coulombic charge parameters for EPSR modelling of PIL cations. Atom point charges were determined from Spartan 08 modelling at the 3-21G* basis set and Hartree–Fock (HF) theory level. ε is in kJ.mol⁻¹, σ is in Å and q is in Coulombs.

Ethy	Ethylammonium Cation				ylammo	onium C	Cation	Butylammonium Cation				
Atom	3	σ	q	Atom	3	σ	q	Atom	3	σ	q	
C ₁	0.276	3.50	+0.263	C ₃	0.276	3.50	-0.653	C ₁	0.276	3.50	-0.055	
C_2	0.276	3.50	-0.411	C_2	0.276	3.50	-0.037	C ₂	0.276	3.50	+0.037	
Ν	0.711	3.25	-0.529	C ₁	0.276	3.50	+0.108	C ₃	0.276	3.50	-0.049	
H_2	0.126	2.50	+0.143	Ν	0.711	3.25	-0.734	C_4	0.276	3.50	-0.130	
H_1	0.126	2.50	+0.069	H ₃	0.126	2.50	+0.209	Ν	0.711	3.25	+0.586	
H_N	0.126	2.50	+0.366	H_2	0.126	2.50	+0.095	H_1	0.126	2.50	+0.026	
				H_1	0.126	2.50	+0.118	H_2	0.126	2.50	+0.029	
				H _N	0.126	2.50	+0.421	H ₃	0.126	2.50	+0.030	
								H_4	0.126	2.50	+0.039	
								H _N	0.126	2.50	+0.108	

Table 3- Lennard-Jones and Coulombic charge parameters for EPSR modelling of PIL anions. Atom point charges were determined from Spartan 08 modelling at the 3-21G* basis set and Hartree–Fock (HF) theory level. ε is in kJ.mol⁻¹, σ is in Å and q is in Coulombs.

Thiocyanate				Nitrate				Formate				Hydrogen Sulphate			
Atom	3	σ	q	Atom	3	σ	q	Atom	3	σ	q	Atom	3	σ	q
ST	1.046	3.55	-0.560	No	0.711	3.25	+0.845	C _F	0.276	3.50	+0.678	O ₁	0.879	2.96	-0.721
CT	0.276	3.50	+0.140	O_1	0.879	2.96	-0.615	O_1	0.879	2.96	-0.837	Ho	0.126	2.50	+0.423
N _T	0.711	3.25	-0.580	O_2	0.879	2.96	-0.615	O_2	0.879	2.96	-0.837	S	1.046	3.55	+1.596
				O ₃	0.879	2.96	-0.615	$H_{\rm F}$	0.126	2.50	-0.543	O_2	0.879	2.96	-0.766
												O_3	0.879	2.96	-0.766
												O_4	0.879	2.96	-0.766



Figure S₁-S₄: Experimental (dots) and EPSR fitted (solid line) structure factor S(q) as a function of q (Å⁻¹) for different analogues of (S₁) ethylammonium thiocyanate (EASCN); (S₂) butylammonium thiocyanate (BASCN) (S₃) ethylammonium hydrogen sulphate (EAHS) and (S₄) ethylammonium formate (EAF). The neutron diffraction data was collected at temperatures above the melting points of each system: 298 K for BASCN, EAF & EAHS (metastable liquid), or 325K for EASCN. Fully hydrogeneous (H-) is red, partially deuterated (d_3 -) is green and fully deuterated (d_8 -) is blue.

Part 3: The Bulk Nanostructure of PILs EASCN, EAHS, EAF, BASCN

Snapshots of the EPSR models show that each system forms a bicontinuous sponge-like nanostructure in the bulk, with clear segregation of polar and apolar domains,



Figure S₅-**S**₂₀: Snapshots of the fitted bulk structure structures for the protic ILs at 298 K: EASCN (**S**₅-**S**₈, top row), EAHS (**S**₉-**S**₁₂, second row), EAF (**S**₁₃-**S**₁₆, third row), BASCN (**S**₁₇-**S**₂₀, bottom row). The columns show a different representation of each protic IL's bulk structure of 500 anions + 500 cations: all atoms (Column 1), anions only (Column 2), Cations only (Column 3) and cation alkyl carbons (Column 4). C is grey, H white, N blue, O red & S yellow. The g(r) data, P₀ distributions and sdf plots are derived from averaging the local ion environments in ~5000 of such equilibrated simulation boxes.

Part 4- Additional Notes on H-bonding in EASCN

 $\begin{array}{ll} EA^{+} & \mbox{Three chemically identical donor atoms } H_{N} \\ SCN^{-} & \mbox{Two non-equivalent acceptor atoms } (N_{T}, S_{T}) \end{array}$



In EASCN, there is evidence of two types of H-bonds: $N\text{-}H_N^{\cdots}N_T$ and $N\text{-}H_N^{\cdots}S_T$



Figure S₂₁-**S**₂₂: The nature of H-bonding in EASCN. N-H_N···N_T correlations are red and N-H_N···S_T are green. (**S**₂₁) partial radial g(r) distribution functions. (**S**₂₂) normalized angle distributions plot of donor-acceptor triplet N-H_N···X for all H-bond lengths up to the first local minimum in the g(r) data in **S**₂₂.



Figure S₂₃-**S**₂₄: The nature of H-bonding in BASCN. N-H_N···N_T correlations are purple and N-H_N···S_T are green. (**S**₂₃) partial radial g(r) distribution functions. (**S**₂₄) normalized angle distributions plot of donor-acceptor triplet N-H_N···X for all H-bond lengths up to the first local minimum in the g(r) data in **S**₂₃.

Part 6- Additional Notes on H-bonding in EAHS

 $\begin{array}{ll} EA^{+} & \mbox{Three chemically identical donor atoms } (H_{N}) \\ HSO_{4}^{-} & \mbox{Four acceptor atoms } (O_{1}, O_{2}, O_{3}, O_{4}) \end{array}$

One donor atom (H₀)



(dominant) (rarer)



Figure S₂₅-**S**₂₈: The nature of H-bonding in EAHS. Cation-Anion H-bonds (**S**₂₅ & **S**₂₆) and Anion-Anion H-bonds (**S**₂₇ & **S**₂₈) are examined on the top and bottom rows respectively. (**S**₂₅, **S**₂₇) partial radial g(r) distribution functions. (**S**₂₆, **S**₂₈) normalized angle distributions plot of donor-acceptor triplet N-H_N...X for all H-bond lengths up to the first local minimum in the g(r) data in **S**₂₅ or **S**₂₇.

Part 7- Additional Notes on H-bonding in EAN

EA⁺ Three chemically identical donor atoms H_N NO₃⁻ Three equivalent acceptor atoms (O₁, O₂, O₃)

In EAN, all the possible H-bonds are equivalent: $N-H_N\cdots O_1$, $N-H_N\cdots O_2$ and $N-H_N\cdots O_3$





Figure S_{33} : The nature of H-bonding in EAN. The partial radial g(r) distribution functions show that

the O₁, O₂ and O₃ oxygens are equivalent.



In EAF, there are two equivalent H-bonds: $N-H_N \cdots O_1$, $N-H_N \cdots O_2$





Figure S₃₄-**S**₃₅: The nature of H-bonding in EAF. (**S**₃₀) partial radial g(r) distribution functions. (**S**₃₁) normalized angle distributions plot of donor-acceptor triplet N-H_N···O_X for all H-bond lengths up to the first local minimum in the g(r) data in **S**₃₀.

Part 9- The relationship between Δp Ka and H-bonding in PILs

Table 4. PIL name, structure, and ΔpK_a where $\Delta pK_a = pK_a$ (Brønsted Acid, BA) – pK_a (Brønsted Base, BB) in PIL synthesis. All pK_a and pK_b values were sourced from Reference 14.



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CHAPTER 7

C7: Effect of cation alkyl chain length & anion type on protic ionic liquid nanostructure

[Submitted to Journal of Physical Chemistry C (2014) by Robert Hayes, Silvia Imberti, Gregory Warr, Rob Atkin]

7.1 Abstract

The local and long-range bulk liquid structures of four primary alkylammonium protic ionic liquids (PILs), ethylammonium hydrogen sulfate, ethylammonium formate, ethylammonium thiocyanate and butylammonium thiocyanate, are determined using neutron diffraction and computer simulations and compared to those determined previously for ethylammonium nitrate and propylammonium nitrate. All these PILs arrange into a sponge-like bicontinuous nanostructure consisting of polar and apolar domains. Lengthening the cation alkyl chain leads to nanostructures where the polar and apolar domains are better segregated, with the ions in more precisely defined positions relative to one another. Changing the anion (for the same cation) has comparatively little effect on structure. The reason all these PIL adopt low curvature sponge-like morphologies, despite the marked changes in the cation and anion structures, is because the preferred areas of the non-polar and polar fragments within the nanostructure are similar.

7.2 Introduction

Protic liquids are an important class of solvents that have the capacity to act as a proton donor.^[1,2] They are used extensively in academia and industry because of their useful physiochemical properties and low cost. Common examples of *molecular* protic solvents include water, alcohols, ammonia, carboxylic acids and amides.

Protic ionic liquids (PILs) are a subset of ionic liquids (ILs)^[3,4] that have recently gained widespread scientific attention. Unlike traditional protic solvents, PILs are composed entirely of anions and cations, with no neutral species present. Low melting points in ILs are achieved by using large, sterically-mismatched anions and cations or by making one of the ions (usually the cation) surfactant-like with long hydrophobic groups.^[5] This weakens Coulombic interactions and frustrates lattice packing compared to inorganic salts. Ions are formed in PILs via proton-transfer from equimolar combination of a Brønsted acid and a Brønsted base. Walden plots of molar conductivity *versus* fluidity have shown that most PILs are "good" ionic systems, and thus are essentially pure mixtures of anions and cations.^[3] PILs are currently used for organic synthesis,^[4,6] catalysis,^[4,6] electrochemistry,^[7] colloid science,^[8,9] tribology,^[10] and industrial processes,^[4,11] and they have stimulated several new areas of research.^[12-16]

The first ILs isolated were the PILs ethanolammonium nitrate (EtAN)^[17] (mp 55°C) and ethylammonuim nitrate (EAN)^[18] (mp 12.5°C). PILs attracted little scientific interest^[19] until a series of papers in the 1980s.^[20-24] More recently, X-ray and neutron scattering data have shown that many PILs have sponge-like bulk nanostructure due to the formation of polar and apolar domains.^[25-31] Nanostructure in PILs results from electrostatic and hydrogen bonding attractions between charged groups leading to the formation of polar domains. Cation alkyl groups are repelled from these regions, and forced to cluster together into apolar regions. The level of segregation in the PIL bulk depends on ion amphiphilicity, with longer cation alkyl

chains^[28,32-34] producing better defined nanostructure.^[27] "Non-amphiphilic" ions have a clustered nanostructure rather than a bicontinuous morphology.^[27,31] PIL nanostructure is relatively insensitive to the dissolution of water,^[35,36] alcohols,^[37] and alkanes^[37] even at relatively high concentrations.

Thus, while much is now known about PIL nanostructure, the precise arrangement of ions within these liquids has been determined only for EAN, EtAN and PAN.^[27,28] The results presented here will provide a deeper understanding of how the length of the cation alkyl chain and the anion type affect PIL nanostructure through examination of ethylammonium hydrogen sulfate (EAHS), ethylammonium formate (EAF), ethylammonium thiocyanate (EASCN) and butylammonium thiocyanate (BASCN) (c.f. Figure 1), and comparison with those previously-reported nitrate PILs.



Figure 1. Molecular structure showing atom labelling convention of (**A**) ethylammonium (EA^+) (**B**) propylammonium (PA^+) (**C**) butylammonium (BA^+) (**D**) hydrogen sulfate (HS^-) (**E**) formate (F^-) (**F**) thiocyanate (SCN^-) and (**G**) nitrate (N^-) . Atoms are identified via subscripts as per their position in the molecular skeleton.

Experimental Section

Hydrogenous (*H*-), partially deuterated (d_3 -) and fully deuterated (d_8 -) PILs were prepared to provide different contrasts for neutron scattering experiments. *H*-EAHS and *H*-EAF were synthesized via acid-base neutralization from concentrated hydrogenous reagents as described previously.^[27] *H*-EASCN and *H*-BASCN were prepared according to the method of Poole *et al.*^[38] with hydrogenous chemicals.

The partially deuterated samples were prepared by selectively replacing hydrogen with deuterium on the exchangeable ammonium and hydrogen sulfate protons. This was achieved by washing volumes of the corresponding hydrogenous compound at least three times in excess fresh D_2O (99% Sigma Aldrich) (where mol:mol of D_2O :PIL >3:1), and removing excess aqueous solvent after each wash by rotary evaporation. Previous ¹H-NMR experiments reveal that, on average, 2.5 out of 3 amino hydrogens are replaced with deuterium *per wash* in D_2O .^[26]

1,1,1,2,2- d_5 -ethylamine (CD₃CD₂NH₂, gas at STP) was used to synthesized fully deuterated analogues d_9 -EAHS and d_8 -EAF. NMR and GC analysis by the manufacturer (CDN Isotopes) showed >99% isotopic exchange and >99.5% chemical purity (respectively) of the sample. The gas was used as received by trapping it in D₂O on a Schlenk line with liquid nitrogen. Perdeuterated PILs were subsequently prepared by reacting the mixture with either concentrated formic or sulfuric acid as per *H*- contrasts.

Water was removed from EAHS via rotary evaporation for several hours at 40°C, and then heating overnight in a 110°C oil bath in a N₂ atmosphere. This led to pure PIL samples with water contents less than 10 ppm. As EAF is known to thermally degrade,^[4] it was purified solely by rotary evaporation mostly at room temperature, with occasional warming to 40°C. Water contents in EAF samples were thus slightly higher than other PILs, at ~0.1 wt%.

Neutron diffraction patterns were collected on the SANDALS diffractometer (Rutherford Appleton Laboratories, UK). Empirical Potential Structure Refinement (EPSR)^[39] was used to model the diffraction data in a simulation box of 500 ion pairs. Initial charge and Lennard-Jones parameters used in the EPSR simulation are listed in Table 1. Further details regarding the instrument, data normalization and fitting procedure have been described elsewhere.^[27,28]

Table 1. Lennard-Jones (ϵ kJ mol⁻¹ and σ Å) and charge (q, elemental charge) parameters for EPSR modelling of PIL cations and anions. Atom point charges were determined from Spartan 08 modelling at the 3-21G* basis set and Hartree–Fock theory level. Atoms are labelled as shown in Figure 1.

]	Ethylammonium				Propyla	mmon	ium	Butylammonium				
atom	3	σ	Q	atom	3	σ	q	atom	3	σ	q	
C_1	0.276	3.50	+0.263	C ₁	0.276	3.50	+0.108	C ₁	0.276	3.50	-0.055	
C_2	0.276	3.50	-0.411	C_2	0.276	3.50	-0.037	C_2	0.276	3.50	+0.037	
Ν	0.711	3.25	-0.529	C ₃	0.276	3.50	-0.653	C_3	0.276	3.50	-0.049	
H_1	0.126	2.50	+0.069	Ν	0.711	3.25	-0.734	C_4	0.276	3.50	-0.130	
H_2	0.126	2.50	+0.147	H_1	0.126	2.50	+0.118	Ν	0.711	3.25	+0.586	
H_N	0.126	2.50	+0.366	H_2	0.126	2.50	+0.095	H_1	0.126	2.50	+0.026	
				H ₃	0.126	2.50	+0.209	H_2	0.126	2.50	+0.029	
				H _N	0.126	2.50	+0.421	H_3	0.126	2.50	+0.030	
								H_4	0.126	2.50	+0.039	
				-				H_N	0.126	2.50	+0.108	

Thiocyanate					For		Nitrate				Hydrogen Sulfate				
atom	3	σ	q	atom	Е	σ	q	atom	3	σ	q	atom	3	σ	q
ST	1.046	3.55	-0.560	C _F	0.276	3.50	+0.678	No	0.711	3.25	+0.845	O ₁	0.879	2.96	-0.721
CT	0.276	3.50	+0.140	O_1	0.879	2.96	-0.837	O ₁	0.879	2.96	-0.615	Ho	0.126	2.50	+0.423
N_{T}	0.711	3.25	-0.580	O_2	0.879	2.96	-0.837	O_2	0.879	2.96	-0.615	S	1.046	3.55	+1.596
				$H_{\rm F}$	0.126	2.50	-0.543	O ₃	0.879	2.96	-0.615	O_2	0.879	2.96	-0.766
												O ₃	0.879	2.96	-0.766
												O_4	0.879	2.96	-0.766

7.4 Results

Figure 2 shows the neutron diffraction data as structure factors, S(q) for EASCN, BASCN, EAHS, and EAF in the range 0.0 < q < 20 Å⁻¹. The general form of the spectra (peak shape, positions etc) resembles previous x-ray^[31] and neutron diffraction^[27-29,35] data for similar primary alkylammonium PILs. Multiple spectra are acquired for each PIL by varying H/D isotopic composition. This enables the positions of protons that participate in H-bonding (on the cation ammonium group) or those which may be associated with ion self-assembly (on the cation alkyl group) to be highlighted.



Figure 2: Experimental (dots) and EPSR fitted (solid line) structure factors S(q) *vs.* q (Å⁻¹) for different isotopomers of (**A**) ethylammonium thiocyanate (EASCN); (**B**) butylammonium thiocyanate (BASCN) (**C**) ethylammonium hydrogen sulfate (EAHS) and (**D**) ethylammonium formate (EAF). The neutron diffraction data was collected at temperatures above the melting points of each system: 298 K for BASCN, EAF & EAHS, or 325K for EASCN. Fully hydrogenous (H-) contrasts are red, partially deuterated (D_3 -) contrasts are green and fully deuterated (D-) contrasts are blue.

Good agreement between data and EPSR fit (solid lines) for each data set is obtained across the entire q-range. All the contrasts for a given PIL are fit with the same model simultaneously, which provides confidence these structures are correct.

The key feature of these PILs in Figure 2 is the peak at low-q in all the partially deuterated samples (Peak 1). Peak 1 is also visible but lower intensity in H-PILs, but absent in perdeuterated samples due to the lower contrast. Spectra at all contrasts have high q peaks (>1.5 Å⁻¹), corresponding to inter- or intra-ionic correlations.

The position of Peak 1 is independent of the anion type, but becomes sharper and more intense as it shifts to lower q with longer cation alkyl chain, moving from 0.63 $Å^{-1}$

(ethylammonium, EA⁺) to 0.53 Å⁻¹ (propylammonium, PA⁺) to 0.48 Å⁻¹ (butylammonium, BA⁺). This peak position indicates long-range periodic order in these PILs, and corresponds to increasing repeat spacings ($l_1 = 2\pi/q$) of 10, 12, and 13Å, respectively (see Table 2). The changing peak shape suggests stronger segregation between and ordering of polar and apolar domains, and is similar to results reported for aprotic ILs.^[33, 34]

Table 2. Summary of low angle neutron diffraction peaks for partially deuterated EASCN, BASCN, EAHS, EAF, EAN^[27] and PAN^[28]. The repeat spacings of the two lowest-angle peaks l_1 and l_2 are calculated via the Bragg equation. Also shown are calculated "bilayer-like" repeat spacings distances, l_{bilayer} (based on the Tanford^[40] equation) and $2D_m$ (based on PIL molar volumes).

		Calcul	ated			
PIL	Peak 1 (Å ⁻¹)	l ₁ (Å)	Peak 2 (Å ⁻¹)	l ₂ (Å)	$l_{\text{bilayer}}(\text{\AA})$	2D _m (Å)
EASCN	0.62	10.1	1.76	3.69	11.0	11.0
EAHS	0.63	10.0	1.60	3.93	11.0	11.0
EAN	0.62	10.1	1.69	3.73	11.0	10.6
EAF	0.63	10.0	1.65	3.82	11.0	10.6
PAN	0.53	11.9	1.62	3.89	13.6	11.2
BASCN	0.48	13.2	1.60	3.93	16.2	13.0

The l_1 repeat spacings correspond closely to *twice* the PIL ion pair dimension, D_m , estimated from their density and molecular weight c.f Table 2.^[24] They are also consistent with the upper bound of the repeat spacing expected from the molecular dimensions of a bilayer-like arrangement consisting of alkyl chains in methyl-methyl contact, separating polar ammonium groups and anions on either side using the Tanford equation,^[40] $l_{bilayer}$. Peak 1 thus corresponds to structural periodicity arising from scattering contrast between segregated (deuterated) polar domains and (hydrogenous) cation alkyl chain regions.^[26-28]

The second lowest-angle peak (Peak 2) is a prominent feature in all H/D contrasts. This peak, and its corresponding repeat spacing, l_2 (Table 2), exhibits less clearly-defined trends with alkyl chain length, and more variability with anion. It has been suggested on the basis of Xray scattering measurements of primary alcohols that Peak 2 is related to the distance between adjacent alkyl chains.^[31] However there are many possible ion-pair distances that could give rise to such a correlation. Castner *et al*.^[41,42] have demonstrated that each peak or valley in an IL structure factor may be a combination of many different cation-cation (head-head, head-tail, tail-tail), anion-anion and cation-anion correlations, making both positive and negative scattering contributions. This means that Peak 2 is likely the sum of multiple ion-ion correlations, and should be interpreted cautiously.

After convergence to the multiple-contrast neutron-diffraction data sets, EPSR simulations for all these systems yield remarkably similar pictures of a liquid structure that consists of segregated polar and apolar domains. Representative snapshots showing instantaneous ion arrangements in the fitted EPSR boxes are shown in Figure 3.

As we have reported previously for EAN and PAN,^[27,28] every PIL examined here clearly exhibits an amphiphilic nanostructure comprised of distinct, interpenetrating networks of polar and apolar domains. These are also shown in Figure 3, where each snapshot has been deconstructed to show the arrangement of anions (column 2), and complementary network formed by the cations (column 3) that occupy each other's void spaces. Of course the anion and cationic ammonium groups remain in close proximity due to electrostatics and H-bonding (*vide infra*), giving rise to the solvophobic segregation of the alkyl moieities into non-polar domains (shown in column 4.)



Figure 3: Snapshots of the fitted simulation box of 500 PIL ion pairs at 298 K: The columns show different representations of the bulk structure: all atoms (Column 1), anions only (Column 2), Cations only (Column 3) and cation alkyl carbons (Column 4). C is grey, H is white, N is blue, O is red and S is yellow. Carbon atoms on anions are orange in column 1 only.

Both polar and nonpolar domains form connected networks that span each simulation box, yielding an isotropic bicontinuous nanostructure with a three-dimensional polar/nonpolar periodicity. As the alkyl chain length increases, the apolar regions become larger and so does the repeat spacing of the nanostructure and, consequently, the position of diffraction Peak 1. Figure 3 also shows that the extent of segregation of non-polar chains from polar domains increases with alkyl chain length: Although it is relatively easy to find isolated ethyl- groups 'dissolved' within the polar domains (voids in column 4 of Figure 3), no such propyl- or butyl- chains can be seen in the polar regions of PAN and BASCN.

Nanostructure variation is less pronounced with changes in anion at fixed cation size. The repeat spacings from Peak 1 are almost the same for all four ethylammonium PILs, as seen in Table 2 and as expected from a nanostructure whose nonpolar domain sizes are constrained to be no more than twice the ethyl chain length. The small differences observed may arise from different charge distributions and H-bond capacity, or from different molar volumes and packing of various anions. This can be seen to some degree in column 2 of Figure 3. Among the EA⁺ salts, EAN stands somewhat apart, with the most distinct bicontinuous structure and the more structured apolar domains. Among the remaining PILs, EAF's apolar domains are the next most-ordered, and in EAHS and EASCN the carbon is more evenly interspersed.

While the nonpolar domain sizes are determined by the physical size of the alkyl moiety, the polar domain size must also be tightly constrained in order to give rise to a nanostructure correlation peak and a repeat spacing. In ILs this must be due to a combination of electrostatics, requiring electroneutrality in the polar network formed by cationic groups and

anions, and the local packing constraints determined by H-bond donor and acceptor availability. In a previous article,^[29] the detailed H-bonding arrangements in PIL polar domains was determined. While the type of hydrogen bonding did affect physical properties, it was *not* a key determinant of nanostructure. In the following, the means by which ion-ion interactions and packing geometry control PIL nanostructure are elucidated.

Figure 4 shows partial pair correlation functions, $g_{N-X}(r)$, between the cation ammonium nitrogens (N) and the central atom of each anion (X), and also those between cation nitrogens, , $g_{N-N}(r)$. (Corresponding anion-anion correlations are presented in the Supporting Information.) All PILs examined have similar $g_{N-X}(r)$, characterised by a sharp, intense nearest-neighbour peak at r = 3.3 - 3.6 Å, followed by a trough and then a second, broader peak centred around 8 Å. The high degree of spatial ordering of ionic groups within all these PILs can also be seen in the longer-range cation-cation correlations between ammonium nitrogen centres, $g_{N-N}(r)$, which exhibit a peak near 5Å, corresponding to the minimum or correlation hole in the cation-anion $g_{N-X}(r)$'s. Integration of the cation-anion peaks (Table 3) reveals that each NH₃ charged centre has at least three nearest neighbours.

The nearest-neighbour arrangements of anions around each cation and vice versa are also shown in Figure 4, in the form of spatial distribution function (sdf) probability distibutions. The radial limit for the sdf plots is determined by the position of the first minimum in the g(r) data which varies slightly depending on the system. A 20% probability surface is used so that the most favored nearest-neighbour ion arrangements are captured. The presence of multiple lobes in the sdf plots shows that more than one ion solvates the charged group of each counterion, consistent with the coordination numbers in Table 3. Because the associated $g_{N\cdots X}(r)$ has only one peak in the radial limits, all these lobes are equidistant from the charged site, and driven by the same ion-ion interactions. In the sdf plots, smaller lobes indicate a more ordered arrangement of the ions and thus better-defined structure in the polar domain.





Figure 4. (Top) Partial radial pair-correlation functions between cation nitrogen to anion central atom, $g_{N-X}(r)$ and between cation nitrogens, $g_{N-N}(r)$, for EAHS (\Box), EASCN (\Box), EAF (+), EAN (\Box), PAN (\Box) & BASCN (\Box); (Bottom) sdf plots of anion central atom distribution as a function of distance & angle from the cation nitrogen, cation nitrogen distribution around the anion, and cation nitrogen-cation nitrogen distribution. 20% probability surfaces are shown between the radial limits listed.
The anion@cation sdf plots for all systems show that all anions are highly localised around the ammonium groups in three preferred orientations, strongly correlated to the ammonium N-H bond directions, and hence to H-bond formation, but also oriented away from the alkyl groups. The lobes are large in EASCN and EAHS suggesting less well-defined structure in the polar domain. As the coordination number for the N···S and N···C_T g(r)'s are both 3.6 (Table 3), all three lobes are occupied by HSO₄⁻ or SCN⁻ anions. The lobes for EASCN are closer to the ammonium group than in EAHS, consistent with the g(r) peak positions, and shows that the linear SCN⁻ anion can pack closer to the cation charge than the larger tetrahedral HSO₄⁻ anion. EAN and PAN plots are similar to this, but are noticeably triangular in shape. This suggests reasonably well-defined anion arrangements around the cation polar domain. One small additional lobe occurs in both EAF and BASCN, directly above the ammonium group. We have discussed this feature elsewhere, and attribute it to a purely electrostatic attraction between cation and these anions.^[29]

Table 3. Coordination numbers of anions around cation ammonium nitrogens. These are determined from partial pair correlation functions with anion central atoms, $g_{N-X}(r)$, by integration from 0 through the first peak at r_{max} until $g_{N-X}(r)$ returns to 1 (denoted β), see Figure 4A.

PIL	g _{N-X} (r)	<i>r_{max}</i>	Coord. #	β
		(Å)		(Å)
EASCN	$N-C_T$	3.33	3.6	4.25
EAHS	N - S	3.75	3.6	4.50
EAN	$N-N_{O}$	3.60	3.0	4.00
EAF	$N-C_F$	3.63	3.8	4.40
PAN	$N-N_{\mathrm{O}}$	3.51	3.2	4.40
BASCN	$N-C_T$	3.44	3.4	4.75

Cation@anion sdf plots differ considerably between PILs as the anion geometry changes. This reflects differences in the distribution of charge and H-bond acceptor sites on the anions. As noted previously,^[27,28] the characteristic three-lobed N@N₀ probability surfaces are very similar in EAN and PAN. The lower symmetry in formate compared to nitrate means that only one of these lobes is seen in N@C_F for EAF.

In EAHS, the three cation lobes solvate oxygen atoms O_2 , O_3 , O_4 (c.f Table 3) of the HSO₄⁻ anion, but there is no cation density detected around the OH (O₁) oxygen. This is consistent with the greater negative charge on these oxygens compared with OH.

In contrast with the marked similarities in cation-anion arrangements in PAN and EAN, $N@C_T$ distributions in EASCN and BASCN are noticeably different, implying different Hbonding structures within the polar regions.^[29] In EASCN the most probable arrangement for the cation lies in a spatially diffuse band around the C–N bond in SCN⁻. This likely because the nitrogen is smaller, more negatively charged than sulfur atoms on the thiocynate anions. Additionally, the H-bond strength is greater for N-H···N than N-H···S.^[43] In BASCN, three elongated lobes are symmetrically distributed around the carbon atom of the SCN⁻, meaning there is no preference for either end of the anion in BASCN. This suggests that H-bonding is less important for nanostructure in BASCN than EASCN, or that the cation arrangement the polar domain is restrictive.

Figure 4 shows that the highly-oriented lobe structure is also evident at greater distances in cation@cation N····N correlations. These sdf plots show nearest-neighbour ammonium nitrogens are wrapped around the ammonium charge centre and oriented away from the non-polar alkyl groups. This cation density is situated at greater distances than the anion@cation lobes, leading to shells of negative and then positive charge around each ammonium centre. In this way, electroneutrality is observed within the polar domain of the bicontinuous nanostructure.

Anion-anion correlations (Supplementary Information, Figure S1) are much more varied due to the differing symmetries of the anions examined, typically giving rise to multiple peaks in their g(r). However, this has surprisingly little overall effect on the development of the solvophobic nanostructure (Figure 3); bicontinuous nanostructures are obtained in all cases, due to cation amphiphilicity.

The strong orientational correlations between neighbouring ions in these PILs are consistent with a dense, three dimensional H-bond network, the details of which have been thoroughly examined previously.^[29] Here we shall only briefly recapitulate the key points. Most significantly, sdf plots clearly show that the H-bond network exists exclusively within the polar domains in all these systems; in every case the interaction of anions with the methyl or methylene hydrogens on the cations is negligible. H-bond length and angle distributions revealed that EAHS (H-bond length = 1.62 Å) and EASCN (1.71 Å) form a high population of short, strong and linear H-bonds, whereas all other systems favoured longer, and bent Hbonds which are predominantly bifurcated in EAN (2.37 Å) and PAN (2.34 Å) or trifurcated in EAF (2.43 Å) and BASCN (2.61 Å). Slight differences occur in H-bond lengths to the N and S centres in the thiocyanate salts but, strikingly, the angles were the same; H-bonding to both N and S were linear in EASCN and bent in BASCN. Linear H-bonds are typically only seen in thiocyanates with single H-bonds, especially to the sulphur centre.^[44,45] Bent H-bonds such as we observe in BASCN are more common in H-bond networks. This underscores the change in PIL structure upon increasing alkyl chain length from 2 to 4, but also the primary role of electrostatics in determining PIL nanostructure. Two quite different H-bond geometries are accommodated within the electrically neutral polar domains of EASCN and BASCN.

Differences between linear and bent H-bonds are also clearly evident in the different pair correlation functions between the cation nitrogen and the central (X) *versus* H-bond acceptor (A) atoms of the anions, $g_{N\cdots X}(r)$ and $g_{N\cdots A}(r)$, respectively. These are shown in supplementary information, Figure S2. Not only are the H-bond acceptor atoms on the anions closer to

nitrogen centre, consistent with strong orientation as well as with H-bonding, the anion acceptor nearest-neighbour distances from the N centre divide clearly into either short (linear) or long (bent).

Solvophobicity, like hydrophobicity^[40] but in non-aqueous media, is generated by strong electrostatic and H-bonding attractions between polar moieties that lead to the segregation of alkyl groups into apolar domains within the PILs, as seen in Figure 3. Figure 5 shows this in the form of very strong correlations between terminal methyl groups in the form of both $C_x \cdots C_x$ g(r) distributions and sdf plots for each PIL. Although differing slightly in detail, all PILs exhibit an anisotropic association structure consistent with a solvophobic effect. Key data is summarised in Table 4.

Figure 5A shows the methyl-methyl partial pair correlation functions, which characterise the non-polar domains of these PILS. Table 4 lists the optimal nearest-neighbour distances (r_{max}) for these PILs, which vary much more widely than the corresponding correlations within the polar domains. Nearest-neighbour peak heights are both lower and more variable. This shows that the packing of alkyl chains in the nonpolar domain is less ordered, implying weaker interactions between these groups. Integration of the $C_x \cdots C_x$ primary peaks yields a coordination number of ~3 (Table 4), similar to that seen in the polar domain (c.f. Table 3). In general, peak height in the $C_x \cdots C_x$ g(r) data is $C_4 > C_3 > C_2$, indicating that the alkyl chain arrangement becomes more ordered, consistent with stronger solvophobic interactions as alkyl chain length is increased. EAN is the notable exception to this trend with a prominent

 $C_2 \cdots C_2$ g(r) peak. This is likely a consequence of the strong segregation of polar/apolar domains, leading to high fraction of linearly arranged alkyl chains in EAN.

Sdf representations of the $C_x \cdots C_x$ g(r) data (Figure 5B-G) confirm cation alkyl aggregation due to solvophobic interactions. Every PIL examined exhibits a prominent probability lobe opposite the terminal methyl carbon. As the probability is reduced (not shown), this lobe is the last to disappear, indicating that the most likely arrangement is locally bilayer-like, with the terminal carbon of one cation behind the terminal carbon of another. At higher probabilities, this lobe swells around the terminal methyl into a three-branched claw-like surface that wraps "up" the uncharged portion of alkyl chain. This structure indicates alkyl chains are interdigitated in the apolar domain. Even very high probability surfaces (>80%) reveal no methyl density around the ammonium headgroup.



Figure 5. (A) Partial methyl-methyl pair correlation functions, g(r), for EAHS (\triangle), EASCN (\Box), EAF (+), EAN (O), PAN (\Box) & BASCN (\diamondsuit) and (**B**–**G**) sdf plots of methyl carbon location as a function of distance & angular position from another methyl carbon. A 20% probability surfaces is shown up to 5 Å distance.

The degree of bilayer-like order can to some extent be quantified using the fraction of $C_x \cdots C_x$ arrangements that lie within 15° of linearly opposite the CH₃-CH₂ intramolecular bond axis, $k_a = \int_{165}^{180} P_{\theta} d\theta$, (Table 4). This is greatest for EAN, consistent with it unusual g(r) (Figure 5A) and high degree of nanostructure compared to other PILs. EAHS, EASCN and PAN all have similar degree of bilayer character, whilst EAF and BASCN are noticeably lower. Smaller lobes in the sdf correlations indicate more orientational ordering of the alkyl chains in the apolar domains. The probability lobes are smallest for BASCN, which means the butyl chains are aligned most precisely relatively to one another. Together with its k_a values, this indicates some intercalation and lateral ordering within BASCN apolar domains not seen with shorter alkyl chains. Conversely, the extent of the arms of the claw-like structure is largest for EAF, consistent with a broader distribution of aggregation angles, a low fraction of bilayerlike character (k_a) and less regular structure in its apolar domains.

Table 4. Correlations between terminal methyl carbons ($C_x \cdots C_x$) on adjacent cations, where x = 2, 3, 4 for ethyl-, propyl- and butyl-ammonium PILs, showing optimal separation, r_{max} , Coordination Number (number of methyls within a distance β Å), and degree of alkyl linearity, $k_a = \int_{165}^{180} P_{\theta} \cdot d\theta$, which reports the fraction of nearest neighbour C_x carbons lying within $\pm 15^\circ$ from linearity (Note $\int_0^{180} P_{\theta} \cdot d\theta = 1.00$).

PIL	r_{max} (Å)	Coord. # (β)	k_a
EASCN	3.54	2.7 (5.00)	0.19
EAHS	3.93	3.1 (5.00)	0.19
EAN	3.51	3.2 (5.00)	0.24
EAF	4.04	2.7 (5.00)	0.14
PAN	3.72	2.8 (4.50)	0.19
BASCN	3.96	2.4 (4.75)	0.15

7.5 Discussion

All the PILs examined here exhibit a bulk nanostructure consisting of interpenetrating, bicontinuous networks of polar and apolar domains. This is seen in both long-range snapshots and in short-range nearest-neghbour arrangements derived from EPSR models, as well as in the existence of the nanostructure peak (Peak 1) in the raw neutron scattering data. The repeat spacing of the PIL nanostructure depends weakly on anion type, but increases and segregation becomes better defined with increasing cation alkyl chain length.

Such amphiphilic nanostructure invites comparison with the self-assembly of conventional amphiphiles in water and other polar solvents. We have previously described PIL nanostructure as analogous to bicontinuous microemulsions, or more closely corresponding

to L₃ (sponge) phases.^[5,27] Surfactant self-assembly phases are described by the preferred curvature of the molecules at an internal interface that separates polar from non-polar regions, which is most commonly represented by the dimensionless surfactant packing parameter. This is usually expressed as the ratio of hydrophobic chain volume to the product of the chain length and the area occupied at the interface, $v/a_0 l$.^[46,47] In this description, the shape of the nonpolar domains falls into certain ranges yielding spheres (direct micelles) if $v/a_0 l < 1/3$; locally cylindrical if $1/3 < v/a_0 l < 1/2$, planar (bilayer) if $1/2 < v/a_0 l < 1$, and so on. Bicontinuous microemulsions and sponge phases have interfaces with near-zero mean curvature, so their packing parameters typically lie in the range $v/a_0 l \sim 1$.^[48,49] While nonpolar volume and length are well-defined geometrical quantities, a_0 must often be obtained indirectly and describes the area occupied by the polar part of the surfactant.

For ionic liquids it is convenient to re-cast this parameter as the ratio of preferred areas of the non-polar and polar fragments of our PILs packed into their respective domains: a_{alkyl}/a_{polar} , where $a_{alkyl} = v/l$ assuming the nonpolar moieties pack at liquid hydrocarbon density, and a_{polar} simply replaces a_0 . Both preferred areas can be calculated from liquid densities, and from bond lengths and angles, or from molecular modeling packages.

Despite the large changes in cation and anion structure among the PILs examined here, the packing parameters vary little. These are listed in Table 5. All packing parameters are near 1, so should yield similar, bicontinuous structures with near-zero preferred curvature. All are certainly well away from conditions where discrete aggregates like direct or reverse micelles would be expected in these PILs.

This approach yields a simple "average curvature" description of observed PIL nanostructures, and suggests routes towards the design of new nanostructures by changing polar and nonpolar packing constraints. For example, secondary ammonium cations or divalent anions would both be expected to increase a_{alkyl}/a_{polar} by increasing valkyl at constant

l and a_{polar} , driving the structure first towards a network of polar tubes and then to discrete polar droplets. Adopting another approach, we have reported previously that the dissolution of 50 %w/w water into EAN changes does not simply swell the native L₃-sponge of pure EAN, but changes it into a locally cylindrical mesh of nonpolar domains.^[35] This is consistent with the expected increase in preferred polar area at constant a_{alkyl} , and consequent reduction in packing parameter.

Table 5. Packing parameters calculated for PIL bulk nanostructure: a_{alkyl} is determined using the volumes of the CH₂ (27.3 Å³) and CH₃ (54.3 Å³) with *l* calculated from the Tanford formula (see Table 2). a_{polar} is determined from remainder of the PIL molar volumes (and agrees well with the sum of the (NH₃ group + anion) volume from Spartan 04^[50] calculations at HF-6316G** basis set) and half the thickness of the polar domain.

PIL	$a_{\rm alkyl} / a_{\rm polar}$		
EASCN	1.1		
EAHS	1.0		
EAN	1.2		
EAF	1.2		
PAN	1.1		
BASCN	1.0		

7.6 Conclusion

Solvophobic nanostructure in PILs is a consequence of electrostatic attractions between the ions and packing constraints. The pronounced low q peak in the d_3 -PIL diffraction spectra is consistent with twice the PIL ion pair dimensions, indicating long range correlations in the bulk due to solvophobic segregation of the polar and apolar domains. Attractive electrostatic interactions between cations and anions produce polar domains, from which alkyl groups are excluded. This is because mixing alkyl chains into the polar domain would push cation and anion charge centres apart, which is not energetically feasible, i.e. it is the strength of electrostatic attractions that drives solvophobic assembled of the cation alkyl chains. As the cation alkyl chain length is increased the low q peak shifts to lower q (larger distances) and shell plots indicate that ions occupy better defined positions. This indicates that longer alkyl

chains lead to larger and better defined nanostructure. Conversely, changing the anion species for the same cation does not have a significant effect.

The observation that PIL nanostructure is of amphiphilic (solvophobic) origin invites comparison with aqueous surfactant structures. These are frequently rationalised using the critical packing parameter, which reveals the preferred curvature of the molecules at an internal interface separating polar and non-polar regions. In PILs, nanostructure can be analysed in a similar fashion by considering the areas of the non-polar and polar fragments packed into their respective domains. While there is substantial variation in the structures of the cations and anions employed in this work, there is little diffrence in the PIL packing parameters, which are all close to 1. This is the reason that all these PILs produce low curvature bicontinuous structures.

7.7 Supplementary Information

Anion-anion correlations (Figure S1) are much more varied due to the differing symmetries of the anions examined, typically giving rise to multiple peaks in their g(r). However, this has surprisingly little overall effect on the development of the solvophobic nanostructure (Figure 3). The similarities already noted between EAN and PAN are again evident in the NO₃⁻ stacking behaviour (Figure S1D&F), which gives them an unusually small nearest-neighbour distance (Figure S1A). The difference between nitrate and formate is especially striking in this context. Both the g(r) and sdf results show that formate forms no such stacks in EAF, but instead appears to form chains of dimer-like structures, reminiscent of arrangements in formic acid,^[51] but more swollen as they are not stabilized by anion-anion H-bonding. Like EAN and PAN, EASCN and BASCN have similar $g_{X \cdots X}(r)$, but with the largest nearest-neighbour separations of all the PILs examined.



Figure S1- Anion-anion correlation results for EAHS (\triangle), EASCN (×), EAF (+), EAN (O), PAN (\Box) & BASCN (\diamondsuit). (**A**) partial pair correlation functions $g_{X-X}(r)$ between central anion atoms (X… X). (**B**–**G**) sdf plots of anion location as a function of distance & angular position from the central anion atom. 20% probability surfaces is shown between the radial limits



Figure S2- The nature of alkyl chain aggregation in PILs. (A) partial radial g(r) distribution functions for correlations between terminal methyl carbons $C_x \cdots C_x$ (B) angle distributions of the carbon atom triplet C_{x-1} - $C_x \cdots C_x$ for for EAHS (\triangle), EASCN (×), EAF (+), EAN (\bigcirc), PAN (\square) & BASCN (\diamondsuit). The sdf plots are a 3D reconstruction of the data in (S2A) & (S2B).

Figure S4 shows the distribution of number fluctuations in slices of (**A**) 5 nm³ and (**B**) 20 nm³ volume. The number fluctuations reflect local fluctuations in the atomic density in the simulation boxes, and extend out to half the slice dimension. The Gaussian distributions are consistent with a statistical distribution of free volume (holes) in the bulk for ions migrate through, as predicted by hole theory.^[44,45] The number fluctuations is ~4 x greater in the 5 nm³ slice than 20 nm³ slice because a larger volume normalises out any density differences. A longer cation alkyl chain also leads to more pronounced number fluctuation, which is likely a consequence of greater partitioning of polar and apolar domains.



Figure S5- The distribution of number fluctuations in slices of (**A**) 5 nm³ and (**B**) 20 nm³ in EAHS (\blacktriangle), EASCN (\varkappa), EAF (+), EAN (\bullet), PAN (\blacksquare) & BASCN (\diamondsuit).

The number fluctuations indicate small but appreciable ion density flucutation in the bulk. These density fluctuations are Gaussian in shape, and become more pronounced with cation alkyl chain length. This is consistent with a distribution of unoccupied cavity space, similar to classical hole theories in molecular liquids that have been related to hydrophobic effect. Whilst the the size of the voids could not be ascertained, it is likely that they are small, and in the order of the size of individual ions, as is the case in molten salts. This is the first evidence of potential voids in a PIL, although similar void volumes have been reported in of aprotic ILs, and other disordered materials. Further work on the nature of these voids, and their role

in solvating molecular solutes in PILs is ongoing.

7.8 References

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CHAPTER 8

C8: The double layer structure of Ionic Liquids at the Au(111) Electrode Interface: an Atomic Force Microscopy investigation

[Reproduced from Robert Hayes, Natalia Borisenko, Matthew K. Tam, Patrick C. Howlett, Frank Endres, Rob Atkin *Journal of Physical Chemistry C*, Volume 115, pages 6855-6863 (2011)]



8.1 Abstract

The near surface structure of two ionic liquids (ILs), 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ($[Py_{1,4}]FAP$) and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([EMIm]FAP) at the polarised Au(111) electrode interface is probed using Atomic Force Microscopy (AFM) force measurements. The force-separation profiles suggest a multilayered morphology is present at the electrified Au(111) – IL interface, with more near surface layers detected at higher potentials. At the (slightly negative) open circuit potential multiple ion layers are present, and the innermost layer, in contact with the Au(111) surface, is enriched in the cation due to electrostatic adsorption. Upon applying negative electrode potentials (-1.0 V, -2.0 V), stronger IL near surface structure is detected: both the number of ion layers and the force required to rupture these layers increases. Positive electrode potentials (+1.0 V, +2.0 V) also enhance IL near surface structure, but not as much as negative potentials, because surface-adsorbed anions are less effective at templating structure in subsequent layers than cations. This interfacial structure is

not consistent with a double layer in the Stern – Gouy – Chapman sense as there is no diffuse layer. The structure is consistent with a capacitor-like double layer model, with a very small separation distance between the planes of charge.

8.2 Introduction

In recent years, ionic liquids (ILs) have emerged as attractive solvents in electrochemistry (eg. electrodeposition,^[1] capicitors,^[2] dye sensitized solar cells,^[3] electrowetting^[4] etc.) because they are pure liquid electrolytes and therefore intrinsic conductors of electricity. ILs exhibit many performance advantages over conventional solvents in electrochemical settings.^[5-8] For example, ILs can possess wide electrochemical and thermal windows, meaning that processes at extreme surface potentials or temperatures (respectively) can be conducted in ILs under conditions that are difficult or impossible to achieve using conventional solvents (usually aqueous electrolytes). Other important IL properties include low vapour pressure and the ability to dissolve both polar and apolar solutes. Notably, all these solvent properties are tuneable to a greater or lesser extent, insofar as the choice of anion / cation chemical structure controls the interionic forces that govern liquid behaviour.

IL based electrochemical research is complicated by the absence of a comprehensive model for the structure of the electrified solid – IL interface and resulting potential distribution. Because a potential difference between the electrode surface and the bulk IL solution exists, a capicator-like electrical double layer (ELD) must form, however the nature of the ion arrangements close to the interface is still a topic of debate. Some experiments have suggested a monolayer of adsorbed counter ions^[9,10] while others imply an adsorbed ion layer plus an electrostatically bound diffuse layer.^[11] In the absence of a clear understanding of the structure of this interface fundamental electrochemical relationships, such as that described by the Bulter-Volmer equation, cannot be applied in ILs.^[12]

Classical descriptions of an aqueous ELD use mean-field models (eg. Helmholtz,^[13] Gouy-Chapman^[14,15] and Stern^[16]). However these models are not applicable to ILs; aqueous electrolyte solutions consist mainly of neutral water molecules with some dissolved ions, whereas an IL is composed entirely of charged species. This means that the concentration of charged species at the interface will not differ greatly from the bulk. However, ion-ion and ion-surface interactions could be quite different in ILs because the ionic atmosphere is not diluted by the presence of a solvent, which leads to Debye lengths substantially less than the ion pair dimension; the Debye length is thus probably meaningless in an IL and electrostatic interactions are not appreciable over distances larger than the ion pair. Other concepts, such as the validity of IL ions as point charges may need to be re-examined because of their typically large, complicated shapes and charge delocalization. A model of the IL-electrode interface will however incorporate some aspects of mean field theory, including the finite volume of ions, which sets the upper limit for the ion concentration at the electrode interface.^[17,18]

IL interfaces are much more structured than those of molecular solvents,^[19,20] so the ion arrangement at an electrode interface is expected to be rather different to that of aqueous electrolyte systems.^[18,21,22] ILs are subject to a range of cohesive interactions (Coulombic, van der Waals, hydrogen bonding, solvophobic^[23]), leading to well-defined structural organization at interfaces due to clustering of like molecular groups. Thus, three structurally distinct regions can be identified at IL interfaces:^[24] the *interfacial* (innermost) *layer* that is composed of ions in direct contact with the second phase; the *bulk phase*, which refers to the bulk liquid region where structure depends on the degree of ion amphiphilicity;^[25] and the *transition zone*, the region over which the pronounced interfacial layer structure decays to the bulk morphology. These definitions hold for all types of IL interfaces including IL-air,^[26] IL-liquid^[27] or (importantly for this work) the solid-IL^[20] interface.

Because solid surfaces imposes a rigid constraint on ions close to the interface, changes in IL interfacial structure are most pronounced close to solid surfaces.^[20,24] AFM experiments have examined IL structure in the interfacial layer and transition zones adjacent to a variety of solid substrates.^[20,28-31] The interfacial layer has the greatest degree of organization and is enriched in cations that interact either electrostatically with anionic substrates or solvophobically with hydrophobic substrates. This innermost layer templates ion arrangements in the transition zone, which can extend up to five ion pair diameters from the interface. Oscillatory ion density profiles are detected in the transition zone. Similar findings have been reported by X-ray reflectivity studies at a charged sapphire surface.^[32,33] To date, the structure adjacent to a cationic surface has not been investigated.

The structure of the IL – electrode interface has traditionally been inferred from capitance measurements using electrochemical impedence spectroscopy. Many publications have employed this approach,^[11,34-41] with values for the point of zero charge, double layer thickness and trends in ion adsorption behaviour have been reported. However, capacitance curves only provide averaged, macroscopic structural information about this interface since it is derived from the intergral of ion profiles,^[7] and there is considerable variation in published capacitance data. The appearance of capacitance curves for similar IL – electrode combinations range from pseudo-parabolic, to "bell-" and "camel-" shaped, each of which suggest different IL – electrode interface structure. As most authors do not seriously state the quality of their liquids^[42] it remains an open question to what extent these contradicting reports are due to impurities. At the very least, this complicates analysis and makes elucidating the ion arrangements from capacitance measurements challenging; Differences could suggest issues associated with IL^[43] and electrode purity,^[11] the frequency range of EIS measurements.

Theoretical descriptions of the IL – electrode interface have not kept pace with interest in ILs for electrochemistry, most likely due to the complexity of the IL – electrode interface and the many competing influences on ion arrangements. The mean field models of Kornyshev,^[18] Oldham^[21] and Lauw *et al.*^[22] represent the most advanced descriptions of the IL – electrode interface. In many respects, these models are analogous to Bikerman-Freise description of aqueous electrolytes^[44,45] for the limiting case where solvent concentration is zero. Kornyshev's model shows good agreement with experimental capicatance data and predicts both "camel-" and "bell-" shaped capacitance curves depending on the degree of ion compressibility at the interface (i.e. the density of ion packing). Lattice saturation effects were also proposed, and refer to the increase in double layer thickness with higher surface potentials that result in decreased capacitance. Lauw *et al.* extend this to consider ion polarization close to the interface, such that as ions organise the relative permittivity of the IL changes significantly as a function of distance from the interface.^[22]

Molecular dynamics and Monte Carlo simulations can also be used to gain insight into the structure of the IL – electrode interface.^[46-49] Within a few nanometers from the surface, distinct oscillations in charge density are predicted, corresponding to layered ion arrangements. For a generic IL cation with charged heads and neutral tails, a camel shaped capacitance curve is predicted due to ion adsorption and desorption at the interface.^[47] However, current simulations generally underestimate specific IL – surface interactions as well as the potential for alkyl chain clustering that is observed in the bulk.^[50-53] Thus, at uncharged surfaces these simulations predict no ordered IL layering, which is contrary to experimental findings.^[20,28]

In this paper, we employ Atomic Force Microscopy force curve measurements to elucidate the structure of the charged Au(111) electrode – IL interface. Until now, AFM experiments in ILs have only been conducted with surfaces at open circuit potential (ocp), but recent modifications to our AFM cell have enabled force curves to be obtained as a function of potential. This enables the double layer structure of ILs to be probed. Data for two electrochemically useful (extremely pure) ILs, 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ($[Py_{1,4}]FAP$) and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([EMIm]FAP) are presented at five surface potentials: open circuit potential (ocp), -1.0 V, +1.0 V, -2.0 V, +2.0 V. These new results allow us to characterize the electrical double layer (EDL) structure of ILs and provide a new experimental framework for theoretical models.

8.3 Experimental

Samples of 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate $([Py_{1,4}]FAP)$ and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([EMIm]FAP) were purchased from MERCK as a custom synthesis in the highest available purity. Quality control measurements revealed all detectable impurities were below 10 ppm, with no hints of HF or oxides. Cyclic voltammetry, XPS and *in situ* STM testing were also performed upon delivery at Clausthal to ensure the purity of the samples. Prior to use, the liquids were dried under vacuum at 100 °C to water contents well below 1 ppm (undetectable by Karl Fischer titration) and stored in a closed bottle in a desiccator (at Newcastle).

AFM force measurements were acquired continuously using a Digital Instruments NanoScope IIIa Multimode AFM with an E scanner in contact mode. The experiments were conducted in an incubator at 21°C, as variation in temperature can influence IL interfacial structure.^[29] The scan rate was 0.1 Hz whilst the vertical scan size was kept between 10-50 nm. One standard sharpened Si₃N₄ tip cantilever (Digital Instruments, CA) was used for all experiments presented. The spring constant was measured to be (0.09 \pm 0.005) N/m (thermal noise method).^[54] The tip was cleaned immediately prior to use by careful rinsing in Milli-Q

 H_2O and irradiation with ultraviolet light for 40 min. The ILs were held in an AFM fluid cell, sealed using a silicone O-ring. These components were cleaned by sonicated in Milli-Q H_2O for 30 min, rinsed copiously in ethanol and Milli-Q H_2O , and then dried using filtered N_2 .

The AFM fluid cell setup was adapted to perform *in situ* electrochemical force measurements. This has enabled force-distance curves to be obtained as a function of applied surface potential. The changes made were inspired by a cell design of Wanless *et al.*^[55] A thin cylindrical strip of Cu metal and 0.25 mm Pt wire were used as the counter electrode (CE) and 'quasi' reference electrodes (QRE) respectively. The CE and QRE were cleaned firstly in dilute HCl acid solution and then washed and dried as per the AFM fluid cell and o-ring components. Atomically smooth Au(111) surfaces (a 300 nm thick gold film on mica) purchased from Agilent were used as both the working electrode (WE) and the solid substrate for AFM experiments. AFM imaging of the Au(111) substrates revealed a very low root-mean squared roughness value of 0.1 nm over a 300 nm² surface area. Thus, any differences in AFM force profiles observed can be ascribed to changes in surface potential and not underlying roughness.

The CE was mounted with the o-ring in the groove of the fluid cell. This established an equipotential WE surface because the CE's effective area is relatively large and axially symmetric with respect to the WE. The QRE was located directly above the centre of the WE surface by securing the Pt wire through the outlet valve of the fluid cell. Ohmic loss was minimized by positioning the QRE to as close as possible (~2 mm) to the WE surface. The potential of all electrodes was controlled by an EG & G Princeton Applied Research Model 362 Scanning Potentiostat. The samples were held at each potential for 5 minutes prior to performing the force measurements.

The features of the force curves at a given surface potential did not alter over a 48 h period. Typical start distances for force scans were 30-50 nm from the Au(111) surface. The maximum applied force in contact was between 30 nN and 500 nN, however, no evidence of liquid structure was detected at forces greater than 30 nN in any system. Repeat experiments revealed that the number and period of the steps (oscillations) was constant. Every system and surface potential was studied over three or more separate experiments.

8.4 Results

AFM force-distance profiles for the two ILs 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate $([Py_{1,4}]FAP)$ and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([EMIm]FAP) (c.f. Table 1) is examined at five electrode potentials: open circuit potential (ocp), -1.0 V, +1.0 V, -2.0 V, +2.0 V. The IL structure in both the innermost layer and the transition zone is commented upon from the force profiles obtained. Data for ocp is discussed first as it is relatively straightforward to interpret and can be compared with previous AFM experiments using similar ILs.^[20,31] The results at ocp also provide a framework for understanding how IL structure changes at both positive (anodic) and negative (cathodic) electrode potentials, which will be addressed separately in the text. It is important to note the ocp is -0.16 V (vs Pt) for [Py_{1,4}]FAP and -0.18 V (vs Pt) for [EMIm]FAP.

Open Circuit Potential (ocp)

Figure 1A and 2A show force-separation profiles for an AFM tip approaching the Au(111) surface at ocp in [Emim]FAP and $[Py_{1,4}]FAP$, respectively. Using the data in Figure 1A as a guide, the AFM force profiles presented in this paper can be interpreted as follows. Zero force is recorded beyond ~ 5 nm, because the AFM tip experiences negligible resistance moving through the bulk as it approaches the Au(111) surface. This shows AFM is insensitive to any structure that might exist in the [Emim]FAP bulk liquid. The tip encounters the first detectable layer at ~ 4.0 nm and pushes against it. 1.0 nN force is required to rupture

this layer, and then the tip 'jumps' 0.83 nm before encountering another layer at \sim 3.2 nm from the interface. The process is repeated a further three times with layers detected at 2.4 nm, 1.6 and 0.8 nm, with the measured spacing of layers in excellent agreement with the predicted [Emim]FAP ion pair diameter (0.83 nm) determined from the bulk density (c.f. Table 1). The magnitude of the push through forces for each ion pair layer increases as the tip moves closer to the surface. Consequently the IL near surface structure is more pronounced closer to the Au(111) interface.

A key feature in Figure 1A is two small steps, 0.5 and 0.3 nm wide, detected nearest the interface. These step widths are substantially less than the [Emim]FAP ion pair dimension (0.83 nm), but their sum (0.50+0.31) is consistent with the ion pair dimension. This suggests that the steps likely correspond to anion (0.50 nm) and cation (0.31 nm) sublayers respectively. As it is likely that the Au(111) surface is negatively charged at ocp, electrostatics dictate that the 0.31 nm layer closest to the surface is enriched in cations. The next 0.50 nm step is likely an FAP anion layer, to quench the excess positive charge of surface adsorbed cations. Cation and anion sublayers are detected because the cation is attracted more strongly to the surface than it is to the anion, such that the anion is displaced first, followed by the cation at slightly higher force. For layers at wider separations, which are not in contact with the surface, the cations and anions are displaced as ion pairs.

Near surface structure is also detected for $[Py_{1,4}]FAP$ at ocp (Figure 2A). At least four ion pair layers are observed in the force profile within the transition zone. There is also evidence for a fifth, weak layer is present given the absence of data points between 4 and 5 nm. The size of these ion pair spacings is 0.9 nm, consistent with the predicted $[Py_{1,4}]FAP$ ion pair diameter (0.89 nm). Increasingly higher force is required to rupture layers closer to the interface as the IL is more structured closer to the Au(111) surface.

Table 1. Name, abbreviation, molecular structure, molecular weight (MW), density (ρ), molecular volume (MV) and ion pair diameter (D) of the ILs used in this study. D is determined from (ρ) assuming a cubic packing geometry according to the method described by Horn *et al.*^[19] Carbon atoms are shaded gray, nitrogen are blue, fluorine are yellow, and phosphorous are pink. Hydrogens are not represented.

IL	Abbreviation	Structure	MW (g.mol ⁻¹)	ρ (g.cm ⁻³)	MV (nm ³)	D (nm)
1-ethyl-3- methylimidazolium tris(pentafluoroethyl)- trifluorophosphate	Emim FAP		556.17	1.71	0.54	0.83
1-butyl-1- methylpyrrolidinium tris(pentafluoroethyl)- trifluorophosphate	[Py _{1,4}] FAP		587.27	1.45	0.67	0.89

Interestingly, the rupture force is in every case greater for $[Py_{1,4}]FAP$ compared to [Emim]FAP. This is particularly evident for the innermost cation layers, at 18 nN and 7 nN respectively. Similar to previous findings,^[20,31] this result suggests that stronger surface-IL interactions are formed when the Coulombic charge on the ions is localized on one atom (c.f $[Py_{1,4}]^+$ cation) compared to delocalized across several atoms (c.f. $[Emim]^+$ cation).^[31] In a complementary paper, we demonstrate this mediates gold surface reconstructions in $[Py_{1,4}]FAP$, including the famous herringbone structure.^[56]

In Figure 2A, a small 0.35 nm step occurs closest to the surface. This step likely corresponds to an innermost layer enriched in $[Py_{1,4}]^+$. However, there is no small 0.5 nm anion layer detected subsequent to this; the next spacing in the profile is 0.9 nm, consistent with the size of an ion pair. This suggests a slightly different near surface structure for $[Py_{1,4}]FAP$. The longer cation alkyl chain for this IL means that solvophobic interactions become appreciable. Although the bulk structure for this IL has not been reported, a butyl chain on similar aprotic

IL cations^[53] is sufficiently amphiphilic to produce well-defined polar and apolar domains due to segregation of charged and uncharged molecular groups. At the Au(111) surface, an alternating polar and apolar layered arrangement should be maintained as solid interfaces serve to orient and align the pre-existing bulk IL structure.^[20] The data in Figure 2A suggests that the order associated with this innermost cation layer decays to the bulk morphology over ~5 nm. This is likely to follow an alternating polar-apolar arrangement of molecular groups, although significant interlayer mixing of ions is to be expected.

Significant changes in the force profiles are detected when a potential bias is applied to the Au(111) surface. There are three key changes in the force profile relating to the size of the innermost layer, the size of the transition zone and the magnitude of the push through forces. In general, the data shows that the ILs become more structured in response to an applied surface bias, particularly at negative potentials. This indicates that the electric field is inducing structure in the IL close to the interface.

Cathodic Electrode Potentials

Data at -1.0 V and -2.0 V Au(111) electrode potentials are shown for [Emim]FAP and $[Py_{1,4}]FAP$ in Figures 1B and 1D and Figures 2B and 2D, respectively. In the transition zone, steps appear sharper and better defined, and extend out over much larger distances from the interface. For [Emim]FAP, five (at -1.0 V) and six (at -2.0 V) steps are detected at negative potentials, compared to four at ocp (-0.18 V). Likewise, $[Py_{1,4}]FAP$ shows four 0.9 nm steps at ocp (-0.16 V), whereas at -1.0 V and -2.0 V five and eight layers are clearly seen. Notably, the findings at -2.0V for $[Py_{1,4}]FAP$ are the most number of layers ever detected by AFM at the solid-IL interface, indicating a high degree of structure in this system.^[20] These results demonstrate that the size of the transition zone, and consequently the extent of IL near surface structure, increases at more cathodic surface potentials; evidence of structure is first

detected in $[Py_{1,4}]FAP$ out at 7 nm for -2.0 V, but only at 5 nm for ocp (-0.16 V). A similar effect is seen in [Emim]FAP, where the onset of layering is seen at ~6 nm for -2.0 V, compared to 4 nm at ocp (-0.18 V).

In every instance, the magnitude of the push through forces for corresponding layers is higher at -1.0 V than for ocp and likewise higher at -2.0 V than for -1.0 V. The variation in force is most evident in the innermost layer. In $[Py_{1,4}]FAP$ the rupture force of the innermost layer increases from 18 nN at ocp to 28 nN at -1.0 V. An even greater change is detected for [Emim]FAP, which goes from 7.4 nN to 25 nN over virtually the same potential range. This shows that IL is more tightly bound to the surface upon applying a negative potential, leading to increased structure close to the interface.

When the electrode potential is increased from -1.0 V to -2.0 V, these innermost cation layers become so tightly bound that for both ILs the AFM tip cannot displace them from the surface. This is indicated by the size of the innermost step in Figures 1D and 2D. Steps 0.56 and 0.55 nm wide in [Emim]FAP and [Py_{1,4}]FAP are detected (respectively), consistent with the size of an anion sublayers in both cases. These anion layers detected require significantly more force to push through than any individual ion or ion pair steps at ocp. As the surface is strongly negatively charged, the innermost layer must be composed of cations, like that detected at ocp or -1.0 V. Thus, the 'zero' separation in the -2.0 V force data corresponds to at least one strongly bound cation layer which the tip cannot penetrate. Because the absolute separation between tip and surface is not known in an AFM experiment, more than one undetected, strongly bound cation layer could be present at this potential.

The structure in the interfacial (innermost) layer is influenced by the applied electrode potential. Between ocp and -1.0 V, the width of the surface-adsorbed cation layer decreases from 0.35 nm to 0.25 nm in $[Py_{1,4}]FAP$. For [Emim]FAP a similar decrease might be present but the magnitude of the change (0.03 nm) is close to the error associated with the

measurement. This indicates that the innermost cation layer flattens into a more compact orientation in response to a more negative electrode potential. Because the AFM tip is not able to probe the adsorbed cation layer for either IL at -2.0 V, it is not possible to comment on the orientation, although an even more compact flat arrangement may reasonably be expected.

Because interfacial layer structure is increased with higher cathodic potentials, the position of the subsequent steps in the transition zone can be shifted to larger tip-surface distances. This is illustrated in Figures 1A (ocp) and 1C (-1.0V) in [Emim]FAP respectively. For example, the transition zone step positions at ocp are 0.8, 1.4, 1,6, 2.4 3.2 and 4.0 nm compared to 1.2, 2.0, 2.8, 3.8, 4.6 nm at -1.0V. At the higher surface potential, more electrostatic charge needs to be compensated for by the IL, leading to stronger cation adsorption in the innermost layer. Thus, an ion pair sized step is detected in the second layer at -1.0V instead of an anion (seen at ocp), because enhanced cation adsorption induces an over screening effect whereby subsequent ion layering overcompensates the electrostatic charge of the innermost layer. It is interesting to note that this effect was by-in-large not seen in the force profiles of $[Py_{1,4}]FAP$ at cathodic potentials, which may be due to molecular effects such as the localization of charge on the cation and greater potential for solvophobic association between cation alkyl chains.

Anodic Electrode Potentials

Applying a positive potential to the electrode changes the force-distance profiles. Figures 1C & E show force-distance data at +1.0 and +2.0 V respectively for [Emim]FAP. The corresponding data for $[Py_{1,4}]FAP$ are presented in Figures 2C & 2E.

Compared to negative biases, fewer ion pair layers are detected in the transition zone at positive surface potentials. In [Emim]FAP, the first evidence of structure is observed 4.9 nm

from the surface at both +1.0 V and +2.0 V, corresponding to five ion pairs layers. $[Py_{1,4}]FAP$ is similar with four (+1.0 V) and five (+2.0 V) layers measured. This suggests that a lower level of IL transition zone structure is present at positive surface potentials.

The innermost layers in each IL are thinner than the ion pair dimension (c.f. Table 1), and require moderately high force (~12 nN at +1.0 V and 15-18 nN at +2.0 V) to rupture. The positive potential of the surface dictates that this thin layer (0.55 nm) is enriched in anions for both ILs. This is the first time an interfacial (innermost) anionic layer at a solid interface has been detected by AFM. When the electrode potential is increased the rupture force increases, as per results obtained at negative potentials. Comparison of data obtained at positive potentials equal in magnitude but opposite in sign reveals that cations in the cathodic regime are more strongly adsorbed than anions in the anodic regime. This is likely a consequence of the FAP molecular structure in which the negative charge is somewhat shielded by the C_2F_5 groups.

Interestingly, the interfacial layer at +2.0 V (Figures 1E and 2E), becomes slightly compressible, indicated by the non-vertical data for the innermost step. This is a result of molecular flexibility imparted by the fluorinated alkyl chains. Molecular flexibility on IL ions leads to fewer ion pair layers because flexible species can pack efficiently at interfaces without layering.^[57] The present results show that FAP anions can also confer compressibility to the IL interfacial layers at high positive bias. Similar findings have previously been reported for IL cations.^[20]



Figure 1- Typical force versus distance profile for an AFM tip approaching from a Au(111) surface in [EMIm]FAP at (A) Open Circuit Potential (ocp, -0.18V) (B) -1.0 V (vs Pt) (C) +1.0 V (vs Pt) (D) -2.0 V (vs Pt) (E) +2.0 V (vs Pt).



Figure 2- Typical force versus distance profiles for an AFM tip approaching from a Au(111) surface in $Py_{1,4}$ FAP at (A) Open Circuit Potential (ocp, -0.16 V) (B) -1.0 V (vs Pt) (C) +1.0 V (vs Pt) (D) -2.0 V (vs Pt) (E) +2.0 V (vs Pt).

8.5 Discussion

The IL – electrified interface is complex. The force profiles obtained are very different to other molecular liquids or electrolyte solutions.^[58-60] The key concept developed in this study is that the IL structure in both the innermost interfacial layer and transition zone evolves with the surface electrode potential, which in some respects parallels the multilayered structure of molten salts at an electrode interface.^[61-63] However, there are some important physical and chemical differences between ILs and molten salts, which leads to subtle variation in the ELD structure. Firstly, by definition, IL ions are mobile at room temperature, meaning that they are capable of reorganizing themselves in response to changes in surface bias at ambient temperatures; no additional thermal energy is required to induce changes in IL interfacial structure. Moreover, unlike molten salts, IL anions and cations are never both spherical in geometry. The spherical shapes of molten salt ions enable them to pack like point charges in an electric field, forming neat alternating anion/cation layers that extend out from the interface. Whilst some aspects of this model are clearly retained in ILs, the unusual chemical structures of at least one, and often both, IL ions can impede neat layered packing. Further many IL cations are surfactant-like in structure, consisting of distinct charged and uncharged regions, which can produce locally layered bulk structure that becomes more pronounced at interfaces.^[20]

The interfacial layer of ions neutralises the electric field of the Au(111) surface. As a consequence, the interfacial layer should be composed of ions counter to the applied charge due to electrostatic interactions with the surface. The measured force profiles are consistent with this statement: at negative potentials spacings consistent with the cation geometry, and *vice versa*, at positive surface potentials anion sized steps are observed. The negative ocp will likely produce an interfacial layer somewhat enriched in the cation.

The electric field controls the push-through forces for the innermost layer. By enhancing the electric field strength, the ion layer is held more tightly to the interface and consequently requires higher force for the AFM tip to displace.

In a similar vein, the orientation of ions in the interfacial layer is potential-dependent. For the cation, the reduced step size suggests a flatter, more parallel ion-surface conformation is present at more negative potentials. The localization of Coulombic charge and the absence of an inflexible aromatic ring allow the $[Py_{1,4}]^+$ cation to adopt a flatter surface orientation than $[EMIm]^+$. This results in the lower relative interfacial layer thickness for $[Py_{1,4}]FAP$ at more negative potentials. In contrast, the FAP anion is a large ion with a C_3 symmetry axis through the central phosphorus atom and Coulombic charge is delocalized across numerous fluorine atoms. This serves to weaken electrostatic adsorption of anions at positive potentials compared to the $[Py_{1,4}]^+$ or $[Emim]^+$ cations. The size of the anion also means that it packs less effectively than the cations. These factors make inferring anion orientation in the interfacial layer difficult. One scenario is that the fluorinated alkyl chains anchor the anion at the surface, leading to the layer compressibility seen at +2.0 V potentials.

The orientation adopted by the ions in the innermost interfacial layer will maximise electrostatic attractions. Change in ion orientation as a function of surface charge is the origin of electrowetting phenomena in ILs,^[4,64] and will find increased significance for manipulating flow behaviour or confined structure in industrial settings.

Recent sum frequency spectroscopy (SFG) and electrochemical impedance spectroscopy (EIS) experiments suggest the IL electrical double layer is only one layer thick.^[9,10] SFG was used to examine the composition and orientation of ions in the innermost layer. SFG spectra showed that at positive potentials anions are adsorbed at the interface and cations repelled, whereas negative potentials induced the imidazolium ring to adopt an orientation more parallel to the surface plane with anions repelled. The SFG results obtained are consistent

with the structure inferred from AFM force-separation data in this study with one key difference: the IL electrical double layer must be more than one layer thick because near surface IL structure beyond the interfacial layer evolves with surface potential.

Significant structural changes are detected in the transition zone as a function of electrode potentials and thus the surface charge. The number of ion pair layers present reflects the surface charge of the Au(111) interface, with higher potentials leading to more near surface layers; the potential will oscillate sinusoidally with decreasing amplititude over the transition zone to the bulk value. This is particularly evident for cathodic surface potentials. Anodic surface potentials also yield more pronounced near surface structure than at ocp, however molecular features of the FAP anion (size, charge delocalization and poor packing efficiency) reduces its ability to template subsequent ion layers in the transition zone. Data observed at cathodic potentials suggests that the comparatively small, flexible shapes of the IL cations, as well as the localization of electrostatic charge, enables the $[\text{Emim}]^+$ and $[\text{Py}_{14}]^+$ species to pack efficiently at the electrode interface and template multiple ion pair layers into the transition zone. These trends are consistent with recent systematic capacitance measurements^[11] which show a thicker double layer is generated at higher surface potentials. The magnitude of the push through forces increases substantially in the transition zone when a surface bias is applied, revealing the layered arrangement becomes significantly more ordered. This finding will impact upon applications including Lithium batteries^[65] and dye

sensitized solar cells,^[3] where the approach of dissolved Li^+ ions or the redox couple (respectively) to the electrode interface could be impeded by increased solvent structure close to the interface. The increased capacitance of ILs containing Li^+ (compared to the neat IL) has been suggested to be related to the well known extension of the cathodic stability limit of these systems upon Li^+ addition,^[66] however this may also result in low deposition rates once

the Li^+ ions present in the inner layer are consumed and the Li^+ ions must diffuse to the electrode surface from the bulk electrolyte.

The AFM data presented in this study is consistent with an oscillatory potential distribution at the electrode interface with a period equal to the ion pair diameter and an amplitude that decreases with distance from the surface. The force data does not contradict Kornyshev's theory of lattice saturation behaviour at high negative potentials,^[18] but no evidence of this was observed in capacitance measurements at the $[Py_{1,4}]FAP - Au(111)$ interface in a complementary paper.^[56] It is possible that the increased number of ion pair layers detected in the transition zone supports an overscreening effect where individual ion sublayers overcompensate for the charge of the previous layer, particularly for [Emim]FAP. Thus, with greater bias applied to the Au(111) surface, more electrostatic charge needs to be compensated for by the IL, leading to the increased number of layers.

Because the transition zone is composed of multiple ion pair layers a diffuse layer in the Gouy – Chapman – Stern sense cannot form in ILs. This casts doubt on the applicability of GCS models^[21] for describing the structure at IL-electrode interfaces. The oscillatory nature of the ion arrangements means that successive ion pair layers near the surface cannot be considered as a discrete region that responds uniformly to changes in applied surface potential. Instead, ion pair layers respond as a function of their separation from the interface as small planes of charge over which the potential decays sinusoidally.

To our knowledge, this is also the first time structural, oscillatory forces^[67] at the solid liquid interface have been directly measured as a function of electrode potential. Whilst spectroscopic^[68,69] or scattering^[70,71] studies in aqueous systems have suggested that the near surface liquid structure changes in response to an applied potential bias, detection via surface force measurements has been made difficult by the presence of strong electrostatic and van der Waals DLVO forces, both of which are effectively screened in the IL.

8.6 Conclusions

AFM was used to examine the IL electrical double layer structure at a Au(111) electrode surface. Ion arrangements vary significantly as a function of applied potential, with more structure detected at higher voltages. The force-separation data obtained can not be explained by a Stern–Gouy–Chapman double layer model as there is no diffuse layer in the conventional sense. The data suggests a capicitative double layer is present in ILs, with an oscillating potential decay profile and a very small separation distance between each plane of charge.

The innermost layer is enriched in ions that interact electrostatically with the surface. This layer contracted and became harder to displace as the surface potential was increased. Multiple ion pair layers were detected extending from the Au(111) surface. The number of layers depends on the applied potential, with larger applied potentials leading to more layers. This points to a templating effect at the IL-interface: higher surface potentials result in stronger electrostatic interactions with the innermost layer. This produces a more enriched, more tightly bound and more compact ion layer closest to the surface. This in turn induces neater packing in the next ion layer, and so forth, resulting in increased structure. The smaller size, localization of Coulombic charge, and reduced distance between the plane of ion-Au(111) surface charges mean that surface-adsorbed cations can induce more near surface structure than surface-adsorbed anions. This shows the degree of structure at IL-electrode interface can be tuned by surface potential and by the molecular structure of the IL ions.

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CHAPTER 9

C9: Effect of dissolved Lithium Chloride on the ionic liquid – Au(111) electrical double layer structure

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9.1 Abstract

The electrical double layer at ionic liquid (IL) – Au(111) interfaces is composed of alternating ion layers. Interfacial layering is markedly weaker when small amounts of LiCl are dissolved in the IL for all potential between -2V and +2V (vs Pt). This means that models developed for pure IL electrical double layers may not be valid when solutes are present.

9.2 Introduction

Ionic liquid (IL) electrochemical research is complicated by the absence of a comprehensive model for the structure of the electrified solid – IL interface.^[1] While the electrical double layer is well-described for aqueous systems,^[2-4] descriptions for IL systems are still developing,^[5,6] and to date have focussed on pure liquids; the effect of dissolved solutes on interfacial IL nanostructure and the double layer has received scant attention.^[7] In this paper the effect of dissolved LiCl on IL interfacial nanostructure at an electrode surface as a function of potential is probed. These results will enhance our understanding of the electrical double layer in IL systems. The system examined models some of the more promising IL based electrochemical applications, including electrodeposition^[8] and Li-batteries,^[9] where adsorption of ions to the solid surfaces, and the near surface liquid nanostructure, play key roles in determining performance.

The IL-electrode interface is more complex than aqueous systems.^[10] For instance, solventsolvent interactions are considerably different in ILs. Because ILs are pure liquid electrolytes, the ionic atmosphere is not diluted by neutral solvent molecules. This leads to highly effective charge screening in ILs, with calculated Debye lengths of order of the size of individual ions. Moreover, unlike inorganic electrolytes, the electrostatic charge is usually not localized on one atom and so the system cannot be modelled as a continuum of spherical point charges. In general, IL ions are large and asymmetric, with the charge delocalized over one or more functional groups. Compared to inorganic salts, this changes the cohesive interactions in ILs by both weakening electrostatic attractions/repulsions and introducing the potential for other types of ion-ion interactions common to molecular solvents^[11] or surfactant mesophases,^[2] eg. H-bonding^[12] or solvophobic^[13] interactions.

Compared to aqueous electrolytes, ion-surface interactions are also considerably different in ILs. Many computational papers have shown that ion-surface interactions are strong in ILs

and are driven by electrostatic attractions (via charged groups) or van der Waals forces (via uncharged groups) between ions and the surface respectively.^[6,14-17] Notably, because the concentration of ions is high and relatively uniform in ILs, the ion-surface interactions are not strong enough to induce distinct regions of ion excess and ion depletion close to the interface analogous to Stern and diffuse layers in classical theories for aqueous electrolytes. Instead, experimental measurements reveal ILs display ion layering at solid surfaces,^[18-22] including at charged electrode interfaces.^[10,23-27] In some respects, this is reminiscent of solvation layers for molecular liquids^[2] or simple ABABA-type ion layering in pure molten inorganic salts at solid interfaces.^[28,29] IL surface layering depends on both surface-specific and bulk factors.^[21] The bulk contribution is derived from the IL ion amphiphilicity, which promotes selfassembly of charged and uncharged molecular groups, often in sponge-like nanostructures;^[30,31] the interface acts to orient and align this nanostructure into layers. Surface-specific effects refer to the competition between overscreening and lattice saturation. In Kornyshev's model,^[5] the ions arrange into layers of counter ions, co-ions, counter ions etc., where each successive layer away from the interface forms a net negative (or positive) plane of charge that overcompensates the potential of the underlying layer. If the electrode is sufficiently polarized, multiple layers of the same ion type may be required to quench the electrode's surface charge.

In this manuscript we examine how the structure of the IL-electrode interface changes with 0.05 wt% dissolved salt (LiCl) using Atomic Force Microscopy (AFM) force curve measurements. Dissolved solutes have a strong influence on the double layer structure in aqueous systems^[2] and are known to alter the interfacial (electro-)chemistry of ILs even at very low concentrations.^[32] We present force curve data for three Au(111) surface electrode potentials – open circuit potential (ocp), -2.0 V, and +2.0 V (all versus Pt reference electrode) – and compare the results to our previous investigation^[26] with the same IL (1-hexyl-3-

methylimidazolium tris(pentafluoroethyl)-trifluorophosphate, [HMIm]FAP) at the pure IL-Au(111) electrode interface.

9.3 Materials & Methods

Custom-made ultrapure samples of 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HMIm]FAP) was purchased from Merck KGaA (EMD), with all detectable impurities are below 10 ppm. Analytical grade Lithium Chloride was purchased from Sigma-Aldrich. Prior to use, the IL and LiCl samples were separately dried under vacuum for 48 hours at 100 °C. This led to water contents in the electrolyte solutions undetectable by Karl Fischer titration. 0.05 wt% LiCl solutions were prepared using an analytical balance, with the resultant solution heated at ~60°C and sonicated for several hours in a sealed vial to ensure complete dissolution. A concentration of 0.05 wt% was chosen as it represents approximately half the saturation concentration (0.93 wt %) of this salt in [HMIm]FAP. AFM force measurements were conducted exactly as describe previously.^[32,35]

9.4 Results & Discussion

Figure 1A-C shows force v separation profiles for an AFM tip completely immersed in [HMIm]FAP + 0.05 wt% LiCl (blue) approaching the Au(111) electrode surface at three different surface electrode potentials; A: ocp, B: -2.0 V, C: +2.0 V (versus a Pt quasi-reference electrode). Corresponding data for pure [HMIm]FAP (green) is also presented.26 Comparison between the data sets allows the effect of LiCl addition on IL interfacial structure to be commented upon, as it highlights differences both as a function of distance from Au(111) interface (intra-profile) and surface electrode potential (between profiles). As results for the pure [HMIm]FAP have already been discussed,^[26] the focus of this manuscript is the [HMIm]FAP + 0.05 wt% LiCl data.



Figure 1- Typical force versus distance profiles for an AFM tip approaching a Au(111) surface at different surface electrode potentials in [HMIm]FAP + 0.05 wt% LiCl (blue) and pure [HMIm]FAP (green). Data for (A) Open Circuit Potential (ocp, -0.11 V) (B) -2.0 V (vs Pt) (C) +2.0 V (vs Pt) is presented

The form of the force curve data in the presence and absence of LiCl is similar, with stepwise profiles recorded as the tip pushes up against, and then ruptures, successive ion layers. This indicates a layered ion arrangement at the Au(111) interface. However, at all potentials investigated, the addition of LiCl reduces the force required to rupture near-surface layers, implying that near surface ionic liquid structure is weakened. This is most notable at ocp, where the interaction between the surface and the AFM tip changes from repulsive in the absence of electrolyte, to attractive when 0.05 wt % LiCl is present. Applying a potential to the surface increases the strength of surface layering, and repulsive forces are measured again, but the rupture force for layers is always lower than in the absence of electrolyte. One consequence of the reduced strength of interfacial layering is that the steps in the force profile are less clear, and the spacing between steps is not as consistent as for the pure liquid. Nonetheless, inferences about the effect of added LiCl on interfacial structure may be drawn. For [HMIm]FAP + 0.05 wt% LiCl at ocp, as the tip moves towards the surface an attractive force is measured from 3.5 nm to 0.3 nm. The force then becomes repulsive, as the tip pushes against the layer in contact with the surface until a force of ~2.5 nN is reached, and this layer is ruptured. Even though the tip-surface interaction is attractive, the presence of steps in the force profile confirm that a layered interfacial structure is retained. The spacing between steps in the force data is considerably more scattered (± 0.2 nm) in the presence of LiCl than for pure [HMIm]FAP. This finding, in conjunction with weakened forces, suggests that dissolved Li⁺ and/or Cl⁻ ions weaken the IL's interfacial layering.

Comparison of the step positions in Figure 1A elucidate how IL interfacial structure changes at ocp with added LiCl. The presence of steps at ~0.3 nm and ~0.85 nm in both the presence and absence of LiCl indicates that the IL ion arrangement is similar in the first two ion layers. These dimensions approximately correspond to the size of the $[HMIm]^+$ cations (~0.3 nm) and ion pair (~0.85 nm). This indicates that the counter-ion (cation) is enriched and the co-

ion (anion) is depleted (repelled) at the surface. This surface layer is weakly bound, and the AFM tip is able to displace it and move into contact with the Au(111) surface. Although there are steps in the force curve at wider separations, they are difficult to detect because of the attractive interaction and cannot readily be associated with the ion dimensions, consistent with weak structure.

The AFM data for negative (-2.0V: Figure 1B) and positive polarizations (+2.0V: Figure 1C) are quite different compared to ocp. At both positive and negative potentials, the forces are repulsive in every instance. This means that the interfacial structure is stronger at these potentials than at ocp, consistent with previous results for pure ILs as potential is raised.^[23,26] However, the layer rupture forces are reduced compared to those obtained for the pure liquid at the same potentials, meaning that surface structure is reduced. Thus, there are two competing effects: LiCl acting to reduce interfacial structure and the increased surface electrode potential favouring it. Steps consistent with cation-enriched (~0.3 nm) and anion-enriched layers (~0.5 nm) are detected nearest the surface, at negative and positive surface the surface charge. The innermost steps appear slightly smaller than for pure [HMIm]FAP. This may be due to increased local concentration of Li⁺ cations or Cl⁻ anions in these layers reducing the average step size. Force data was also obtained at +1.0 V and -1.0V but the data was much less consistent in terms of both the step spacing and push through forces, so is not presented. This variability is consistent with weaker interfacial structure.

At this stage, the precise mechanism by which LiCl reduces interfacial structure is unclear. At 0.05 wt%, the mole ratio of LiCl to [HMIm]FAP is 1:138, which would seem to be too low to markedly change the bulk IL nanostructure, and consequently the surface structure. i.e. it is unlikely that LiCl is evenly distributed throughout the liquid, but rather is concentrated at the surface. This seems probable, as both the Li^+ cation and the Cl⁻ anion are smaller and harder

than their IL counterparts, so will be more strongly attracted to a polarized surface. Enrichment of LiCl near the electrode surface could reduce the interfacial forces in three ways. Firstly, the near-surface LiCl concentration could be sufficiently high to markedly reduce the strength of interfacial IL nanostructure, perhaps by swelling and weakening the electrostatic domains. Alternatively, interfacial LiCl could change the IL's Hamaker constant in the vicinity of the surface, such that a stronger attraction results at close separations. This need not necessarily lead to a reduction in near surface nanostructure, but cannot be ruled out. Finally, and in our view most likely, either the Li⁺ or Cl⁻ is preferentially adsorbed to the electrode surface (depending on potential), impeding surface-IL contact. This disrupts the templating effect of the surface on the IL,^[23] and the strength of interfacial nanostructure is reduced. Further experiments using different salts and ILs are already underway to elucidate which of these factors is of greatest importance.

9.5 Conclusions

The force data provides no evidence of Li underpotential deposition, or gold dissolution due to the presence of chloride in the anodic regime, which has been reported in similar ILs at the Au(111) interface.^[33] However, this cannot be excluded. Underpotential deposition would mean that a Li⁺ cation attracted to the surface would not serve merely to balance the surface charge, but rather would be deposited and incorporated into the electrode. The form of the force data at -2.0V and +2.0V did not vary appreciably over the course of an experiment, which suggests that if underpotential deposition (or gold dissolution) is occurring it is not sufficiently rapid to significantly affect the Li⁺ or Cl⁻ concentration appreciably. STM studies are currently underway that will resolve these issues. Nonetheless, these results demonstrate that interfacial IL nanostructure can be controlled via addition of low concentration of inorganic electrolyte, providing a simple method of tuning IL interfacial forces.

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CHAPTER 10

C10: Discussion, Future Directions & Conclusions

[All proceeding Chapters are self-contained and have separate discussion and conclusions. The findings from key Thesis Chapters (7 & 8) are examined below. Paragraphs that closely resemble, or taken directly from these previous chapters are highlighted with "‡‡"]

10.1 Discussion & Future Directions

In the last forty years, nanoscience and nanotechnology has developed rapidly as scientists have gained precise control of matter down to the atomic level.^[1] This has seen an enormous number of nanostructures and nanomaterials characterised in the literature, that show many interesting chemical, physical, electronic, thermal or optical properties.^[2] Despite these successes, the synthesis of modern nanomaterials remains challenging due to the unique operating conditions e.g. tiny length / time scales and high surface-to-volume ratio of components. In general, this has seen nano-processes often resulting in lower efficiencies or prone to deviations from expected behaviour compared to macroscopic chemical processes. Currently, synthetic nano-reactors^[3,4] are being explored to bridge this efficiency gap, because they provide a reasonably well-defined nanospace or cavity in which reactions can occur. Other workers have focused on self-assembled phases,^[5] which exploit the polar / apolar domains of surfactant amphiphiles formed in an aqueous media. However, scaling up these systems for controlled mass nanofabrication has not been achieved, and so they cannot be easily integrated into existing macroscopic technologies and devices.

The results in this Thesis highlight the potential for PILs to be used as self-assembled nanoreactors, as has been suggested for aprotic ILs by other researchers.^[6] Unlike nanoreactors^[3,4] and self-assembled phases,^[5] no complex encapsulation techniques or critical ion concentrations are required to induce self-assembly in PILs (or aprotic ILs); the bicontinuous phase forms spontaneously in the pure liquids, and the structure is quite robust to high water content.^[7] Because the PILs can build up tuneable H-bond networks in the polar domains, this will be useful in cases where proton transfer is the rate determining step in the reaction/process mechanism. However, in order to fully integrate ILs into the nanotechnology revolution, better understanding of ion dynamics is required. This will enable the relationships between structure, dynamics, and property to be made.

All the PILs examined here self-assemble in the bulk to form bicontinuous nanostructure of of polar and apolar domains. This is seen in both long-range snapshots and in short-range nearest-neghbour arrangements derived from EPSR models, as well as in the existence of the nanostructure peak (Peak 1) in the raw neutron scattering data. The repeat spacing of the PIL nanostructure depends weakly on anion type, but increases and segregation becomes better defined with increasing cation alkyl chain length. This is due to the different, competing roles of ion-ion interactions and volume effects.^{‡‡}

It is possible, although unlikely, that structure at longer length scales is present in the bulk for the PILs. We have recently acquired neutron diffraction on the NIMROD instrument at ISIS to test this hypothesis. This instrument provides subatomic resolution over a wider q-range than SANDALS ($0.02 - 100 \text{ Å}^{-1}$), corresponding to the interatomic through to the mesoscopic distances. Analysis of this data is ongoing.

Coulombic interactions are the most important factor in ion self-assembly as the force is at least an order of magnitude stronger than other ion-ion interactions.^[8] In the bulk, it enforces an electroneutral distribution of positive and negative charges, thus lowering system energy. However, the high ionic concentration (~10 M) and dielectric constants (~20-30)^[9] of PILs leads to Debye lengths smaller than PIL ions.^[10] This means that, Coulombic interactions are weaker and felt over shorter distances in the bulk compared to ions in a vacuum.‡‡

Coulombic interactions lead to the formation of a polar domain. This is observed in every PIL because (1) cation charged groups selectively solvate the anion's charged groups (and vice versa) and (2) uncharged groups are expelled from this region. The localization of Coulombic charge on the ions assists in polar domain formation, leading to strong charge-charge correlations. This is is not always the case in ILs; a popular strategy to lower IL melting point is delocalising charge over a large molecular volume. This reduces cohesive interactions between charged groups, and thus a weaker tendency to self-assemble.‡‡

Solvophobic interactions^[11] aggregate and align cation alkyl chains expelled from the polar domains. This produces a well-defined apolar domain in the bulk. In every PIL, the arrangement of alkyl chains in the apolar domain is locally flat, like a bilayer, but with some interdigitation. Similar to the hydrophobic effect in water,^[12] solvophobic interactions are entropy-driven and increase in strength with cation alkyl chain length. Thus, the structural effect of switching from $EA^+ \rightarrow PA^+ \rightarrow BA^+$ is to promote ion self-assembly and form a larger, more distinct apolar domain. This leads to leading to the variation in Peak 1 observed in the neutron diffraction data, corresponding to more robust PIL nanostructure.^{‡‡}

The solvophobic interactions provides the additional stabilising force that sequesters the polar and apolar groups, counteracting the electrostatic repulsions in the polar domain. This is in keeping with Tanford's idea of two "opposing forces"^[12] in aqueous amphiphile self-assembly. Interestingly, the concentration of polar/apolar interfaces in PILs is exceptionally high, and repeats every ~1 nm (depending on the position of Peak 1). This is just above the critical radius for a stable amphiphile self-assembly.^[13] This indicates that PIL nanostructure with an ethyl group may be the smallest example of amphiphile self-assembly. The absence of tail-tail correlations in methylammonium PILs^[14] is consistent with this.‡‡

Such amphiphilic nanostructure invites comparison with the self-assembly of conventional amphiphiles in water and other polar solvents. We have previously described PIL

nanostructure as analogous to bicontinuous microemulsions, or more closely corresponding to L₃ (sponge) phases [Appendix 4]. Surfactant self-assembly phases are described by the preferred curvature of the molecules at an internal interface that separates polar from nonpolar regions, which is most commonly represented by the dimensionless surfactant packing parameter. This is usually expressed as the ratio of hydrophobic chain volume to the product of the chain length and the area occupied at the interface, v/a_0l . In this description, the shape of the nonpolar domains falls into certain ranges yielding spheres (direct micelles) if $v/a_0l <$ 1/3; locally cylindrical if $1/3 < v/a_0l < 1/2$, planar (bilayer) if $1/2 < v/a_0l < 1$, and so on. Bicontinuous microemulsions and sponge phases have interfaces with near-zero mean curvature, so their packing parameters typically lie in the range $v/a_0l \sim 1$.^[48,49] While nonpolar volume and length are well-defined geometrical quantities, a_0 must often be obtained indirectly and describes the area occupied by the polar part of the surfactant.

For ionic liquids it is convenient to re-cast this parameter as the ratio of preferred areas of the non-polar and polar fragments of our PILs packed into their respective domains: a_{alkyl}/a_{polar} , where $a_{alkyl} = v/l$ assuming the nonpolar moieties pack at liquid hydrocarbon density, and a_{polar} simply replaces a_0 . Both preferred areas can be calculated from liquid densities, and from bond lengths and angles, or from molecular modeling packages.

Despite the large changes in cation and anion structure among the PILs examined here, the packing parameters vary little. These are listed in Table 5. All packing parameters are near 1, so should yield similar, bicontinuous structures with near-zero preferred curvature. All are certainly well away from conditions where discrete aggregates like direct or reverse micelles would be expected in these PILs.

This approach yields a simple "average curvature" description of observed PIL nanostructures, and suggests routes towards the design of new nanostructures by changing polar and nonpolar packing constraints. For example, secondary ammonium cations or

divalent anions would both be expected to increase a_{alkyl}/a_{polar} by increasing valkyl at constant l and a_{polar} , driving the structure first towards a network of polar tubes and then to discrete polar droplets. Adopting another approach, we have reported previously that the dissolution of 50 %w/w water into EAN changes does not simply swell the native L₃-sponge of pure EAN, but changes it into a locally cylindrical mesh of nonpolar domains.^[35] This is consistent with the expected increase in preferred polar area at constant a_{alkyl} , and consequent reduction in packing parameter.

For a given a_{alkyl} : a_{polar} ratio, it is likely that the polar/apolar interface is subject to an areaminimisation constraint as per classical L_3 -sponges.^[16] This would tweak ion arrangements to fulfil the requirement of constant mean curvature in the bicontinuous phase. On a related note, more rigorous theoretical treatment of the PIL sponge structures, and how their topology and nodal surfaces compare to classical bicontinuous phases^[17,18] has not been performed herein. This is important for understanding the underlying physics of non-aqueous self-assembly eg. curvature and bending energy of the nanostructures.

In general, the importance of H-bonding towards PILs structure has been overstated. Evans *et al.*'s hypothesis of 3D H-bond network in EAN^[19] is widely accepted in the literature^[20-26] and is consistent with established models of structure in molecular protic liquids.^[27-36] However, this has lead to the belief in some quarters that all PILs can build up H-bond networks structures.^[20-25,37-55] Moreover, many studies continue to emphasize the similarity of PIL H-bond networks to that found in water^[26,56-62] or other protic solvents.^[63] It is common to find statements such as "*PILs can build up hydrogen bonding networks similar to water molecules due to their protic nature and general solvent properties*"^[58] in reference to ion arrangements.

The results in Thesis show that whilst a 3D H-bond network forms in the PIL bulk, it is quite different to water and confined to within the polar domain of the self-assembled

nanostructure. Even for anions with different capacity to H-bond, there is no discernible effect of bulk structure; the overriding effect of electrostatic, solvophobic interactions and volume changes is stronger than any differences in H-bonds. In some respects, this is analogous to well-established concepts of H-bonding in protein folding,^[64] as H-bonds do not control self-assembly, but form between adjacent donor and acceptor sites in the nanostructure. This shows that H-bonds are accommodated between ions as best they can, but are not the principle drivers of structure.

Interestingly, some studies still ignore H-bonding in PILs^[65-70] and or treat these solvents as unstructured media^[71-79] of uniform polarity. This reflective, at least in part, of the classical view of liquids as an 'unstructured' homogeneous state of matter.^[80]

The EPSR models highlight that PIL H-bonds are important for understanding solvent properties. Trends in melting point, glass transition temperature, ionic conductivity and viscosity can be correlated with the nature of H-bonds in the PIL. This has far reaching implications for solvent selection as the nature of H-bonds present in the nanostructure is reflective of PIL behaviour; whether the H-bonds are strong or weak correlates with the strength of the cohesive interactions and thus PIL properties. For some time now, ILs have been touted as 'designer solvents' due to the promise that macroscopic properties can be tuned by variation in ion structure. The results suggest can be achieved by greater understanding of PIL H-bonding, and ways to control it via ion self-assembly. This is similar to widely used approaches in crystal engineering,^[81] where chemists modify the strength/geometry of H-bonds to achieve desired physical properties. For example, distorting the H-bond network may be advantageous where PILs are required as solvents, with melting points below room temperature. In other cases, a less constrained H-bond network is desirable as it will facilitate faster proton transfer in the bulk. This will become increasingly important as PILs are explored as electrolytes for hydrogen fuel cells,^[82,83] pharmaceutical compounds^[84] and CO₂-capture^[85] where liable protons are key to process efficiency.

We cautiously suggest that line tension^[8,86-88] may be present in the PIL nanostructure, similar to that for bicontinuous microemulsions.^[89] In bicontinuous microemulsions, line tension is associated with the film of surfactant aggregates adsorbed at the oil-water interface, which keeps the two components locally well-sequestered. Whilst a molecular film is absent in PILs, a well-defined polar/apolar interface is formed, and stabilised by interactions on either side of the amphiphile. Thus, if present, line tension may act in a similar manner, leading to the bulk correlation peak. More information about ion dynamics is required to test this hypothesis and relate it to (Helfrich) spontaneous curvature^[90].

The recent explosion of interest in ILs for electochemistry requires development of a comprehensive model for the IL electical double layer. Likewise, use of ILs in electrochemical devices demands in-depth knowledge of ion arrangements under working conditions. The AFM experiments performed herein directly probe the IL electical double layer structure *in situ*, and show how it evolves at different surface potentials. This is important because previous experimental evidence have relied on capacitance measurements^[91-99] which yield averaged, macroscopic structural information and there is considerable variation in published capacitance data.

The AFM data presented in this work are consistent with an electrical double layer model that forms an oscillatory potential distribution, with a period equal to the ion pair diameter and amplitude that decreases with distance from the surface. The force data do not contradict Kornyshev's theory of lattice saturation behaviour at high negative potentials,^[100] but no evidence of this was observed in capacitance measurements at the $[Py_{1,4}]FAP-Au(111)$ interface in a complementary work (c.f Appendix 5). It is possible that the increased number of ion pair layers detected in the transition zone supports an overscreening effect where individual ion sublayers overcompensate for the charge of the previous layer. Thus, with greater bias applied to the Au(111) surface, more electrostatic charge needs to be compensated for by the IL, leading to the increased number of layers.^{‡‡}

This the first time structural, oscillatory forces have been directly measured as a function of electrode potential.^[101] While spectroscopic^[102,103] or scattering^[104,105] studies have demonstrated changes in near surface water structure with applied surface potential, detection via surface force measurements has been made difficult by the presence of strong electrostatic and/or van der Waals DLVO forces, both of which are screened in the IL.## The AFM results have broader implications for other surface-dependent technologies. For instance, it suggests ILs may be suitable for precision boundary lubricants on electrical contacts^[106] or surfaces prone to contact electrification.^[107] This is because a tuneable selfreplenishing boundary layer can be created at the solid-IL interface, switching from cationenriched (at negative potentials) to anion-enriched (at positive potentials). Notably, conventional lubricants for electrical contacts (polytetrafluoroethylene) are expensive and electrically insulating. Use of ILs can overcome this as they can be made relatively cheap and are electrically conducting at ambient temperatures. Recently, we demonstrated of control of nanoscale friction by an IL at the Au(111) interface, c.f. Appendix 9. Future work should be directed to other conductive surfaces including graphite,^[108] which has been known to facilitate superlubricity.^[109]

10.2 Conclusions

Solvophobic nanostructure in PILs is a consequence of electrostatic attractions between the ions and packing constraints. Attractive electrostatic interactions between cations and anions produce polar domains, from which alkyl groups are excluded. This is because mixing alkyl chains into the polar domain would push cation and anion charge centres apart, which is not energetically feasible, i.e. it is the strength of electrostatic attractions that drives solvophobic assembled of the cation alkyl chains. **‡**

The primary evidence for a solvent nanostructure is seen in the neutron diffraction spectra. The pronounced low q peak in the d_3 -PIL diffraction spectra is consistent with twice the PIL ion pair dimensions, indicating long range correlations in the bulk. As the cation alkyl chain length is increased the low q peak shifts to lower q (larger distances) and shell plots indicate that ions occupy better defined positions. This indicates that longer alkyl chains lead to larger and better defined nanostructure. Conversely, changing the anion species for the same cation does not have a significant effect.‡‡

The observation that PIL nanostructure is of amphiphilic (solvophobic) origin invites comparison with aqueous surfactant structures. These are frequently rationalised using the critical packing parameter, which reveals the preferred curvature of the molecules at an internal interface separating polar and non-polar regions. In PILs, nanostructure can be analysed in a similar fashion by considering the areas of the non-polar and polar fragments packed into their respective domains. While there is substantial variation in the structures of the cations and anions employed in this work, there is little diffrence in the PIL packing parameters, which are all close to 1. This is the reason that all these PILs produce low curvature bicontinuous structures; ion-ion interactions *partition* groups into two subvolumes, the area ratio of which defines a packing geometry for how they connect and *fill* space.^{‡‡}

Atomic Force Microscopy (AFM) has been used to examine aprotic IL ion arrangements close to the at the Au(111) electrode surface. The electrical double layer structure was found to be consistent with a capicitator-like structure, with very small separation between planes of charge. The data is not consistent with models that imply a monolayer of adsorbed counterions, or those that advocate an adsorbed ion layer plus an electrostatically bound diffuse layer. Structure is shown to vary significantly as a function of applied potential, with more structure detected at higher voltages. The force-separation data obtained are inconsistent with a Stern–Gouy–Chapman double layer model as there is no diffuse layer in the conventional sense. The data suggests a capacitor-like double layer is present in ILs, with an oscillating potential decay profile and a very small separation between plane of charge. This indicates that the IL electrical double layer structure is much more complicated than for aqueous solutions.^{‡‡}

The innermost layer is enriched in ions that interact electrostatically with the surface. This layer contracted and became harder to displace as the surface potential was increased. Multiple ion pair layers were detected extending from the Au(111) surface. The number of layers depends on the applied potential, with larger applied potentials leading to more layers. This points to a templating effect at the IL-interface: higher surface potentials result in stronger electrostatic interactions with the innermost layer. This produces a more enriched, more tightly bound and more compact ion layer closest to the surface. This in turn induces neater packing in the next ion layer, and so forth, resulting in increased structure. Interestingly, this structure can be weakened via the addition of small quantities of LiCl. The effect of other dissolved materials, (eg. H₂O-sensitive salts for metal and semi-conductor electrodeposition,^[110,111] ruthenium dyes for DSSCs,^[112] gel or polymer electrolytes for batteries^[113]) have not been investigated. This suggest that most of the fundamental characterization of IL interfacial structure in electrochemistry has yet to be performed.‡‡

Surface-adsorbed cations can induce more near surface structure than surface-adsorbed anions. This shows the degree of structure at IL-electrode interface can be tuned by surface potential and by the molecular structure of the IL ions. Thus, IL interfacial structure/ can be designed for electrochemical interfaces, which will be important in many future areas of IL research.‡‡

Future force work should investigate how lateral structure is affected by applied potential and dissolved electrolytes. Alternatively, other complementary techniques may be used such as neutron reflectivity. This technique is well-disposed to structure at buried solid-liquid interfaces using H/D isotopic substitution, and does not subject the ions to confinement as per AFM.

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