Structure in Ionic Liquids

A Dissertation in Chemistry

By

Robert Hayes

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.

1. **R. Hayes**, G.G. Warr, R. Atkin
"At the interface: solvation and designing ionic liquids"
Physical Chemistry Chemical Physics, **2010**, 12, 1709

2. **R. Hayes**, D. Wakeham, R. Atkin
" Ionic Liquid Interfacial Structure (2)"
in *Ionic Liquids UnCOILed: Critical Expert Overviews*; John Wiley & Sons, (**2012**)

3. **R. Hayes**, S. Imberti, G.G. Warr, R. Atkin
"Amphiphilicity determines nanostructure in protic ionic liquids"
Physical Chemistry Chemical Physics, **2011**, 13, 3237 (* *journal cover)*

4. **R. Hayes**, S. Imberti, G.G. Warr, R. Atkin
"Pronounced Sponge-like Nanostructure in Propylammonium Nitrate"
Physical Chemistry Chemical Physics, **2011**, 13, 13544

5. **R. Hayes**, S. Imberti, G.G. Warr, R. Atkin
"How water dissolves in Protic Ionic Liquids"
Angewandte Chemie International Edition, **2012**, 51 (30), 7468

6. **R. Hayes**, 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

7. **R. Hayes**, S. Imberti, G.G. Warr, R. Atkin
"Effect of cation alkyl chain and anion type on protic ionic liquid nanostructure"
To be submitted to *Physical Chemistry Chemical Physics*, **2013**

8. **R. Hayes**, 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

9. **R. Hayes**, 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

10. D. Wakeham, **R. Hayes**, G.G. Warr, R. Atkin
"Influence of temperature and molecular structure on ionic liquid solvation layers"
Journal of Physical Chemistry B, **2009**, 113, 5961

11. **R. Hayes**, S. Zein El Abedin, R. Atkin
"Pronounced structure in confined aprotic room-temperature ionic liquids"
Journal of Physical Chemistry B, **2009**, 113, 7049

12. R. Atkin, S. Zein El Abedin, **R. Hayes**, 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

13. R. Atkin, N. Borisenko, M. Drüschler, S.Z. El Abedin, F. Endres, **R. Hayes**, 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

14. F. Endres, N. Borisenko, S. Zein El Abedin, **R. Hayes**, R. Atkin
"The interface ionic liquid(s)/electrode(s): *in situ* STM and AFM measurements"
Faraday Discussions **2012**, 154, 221

15. T. Carstens, **R. Hayes**, 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,* **R. Hayes,*** 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

17. R. Atkin, N. Borisenko, M. Drüschler, F. Endres, **R. Hayes**, B. Huber, B. Roling
"Structure and Dynamics of the Interfacial Layer between Ionic Liquids and Electrode Materials"
Journal of Molecular Liquids, accepeted, MOLLIQ-D-13-00252, **2013**

LIST OF CONFERENCE ORAL PRESENTATIONS

1. "The Smallest Sponge: Nanostructure in Ionic Liquids"
   27th Australian Colloid & Surface Science Student Conference (27th ACSSSC)
   Roseworthy, SA, Australia, February 1st-5th 2010

2. "Amphiphilicity determines nanostructure in protic ionic liquids"
   UK Colloids 2011: An international Colloid & Surface Science Symposium
   London, United Kingdom, July 4-7th 2011

3. "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

4. "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

7. "How Protic Ionic Liquids Hydrogen Bond and dissolve in water"
   6th Congress on Ionic Liquids
   Alagrave, Portugal April 21-25th 2013

8. "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

1. "How Protic Ionic Liquids Hydrogen Bond and dissolve in Water"
   6th biennial Australian Colloid & Interface Symposium
   Noosa, QLD, Australia February 3-7th 2013

2. "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
$[Py_{n,n}]^+$	1-alkyl-1-alkylpyrrolidinium cation (n = carbon chain length)
$[C_n mim]^+$	1-alkyl-3-methylimidazolium cation (n = carbon chain length)
l_c (nm)	Alkyl chain length
v_c (nm^3)	Alkyl chain volume
Å (=10^{-10} m)	Angstrom
AIL	Aprotic Ionic Liquid
AFM	Atomic Force Microscopy
ω (°)	Average Molecular Orientation
S_N2	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
b (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
ε	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 x10^{-19} 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
$[HCO_2]^-$	Formate anion
FTIR	Fourier transfer Infrared spectroscopy
D_8-	Fully Deuterated contrast
T_g (°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
‹ r › (nm^3)	Hole (void) size
H-Bond	Hydrogen Bond
hbl (Å)	Hydrogen Bond Length
θ_{max} (°)	Hydrogen Bond Angle
H-	Hydrogeneous contrast
$[HSO_4]^-$	Hydrogen Sulphate anion
κ ($S.cm^{-1}$)	Ionic Conductivity
IL	Ionic Liquid
I ($mol.L^{-1}$)	Ionic Strength
z_i	Ion Valency
L_α-phase	Lamellar phase
LAXS	Large Angle X-ray Scattering
LJ	Lennard Jones potential
$\%_{linear}$	Linear H-bond percentage
Li^+	Lithium cation
m/z	Mass to charge ratio
T_m (°C)	Melting point
σ_D (nm)	Molecular Diameter
MD	Molecular Dynamics
M_v (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
$[NO_3]^-$	Nitrate Anion
C_iE_j	Nonionic alkyl polyglycolether surfactant (*i*=glycol units, *j*=ether units)
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser effect
NOESY	Nuclear Overhauser effect spectroscopy
OCP	Open Circuit Potential
OHD- RIKES	Optical Heterodyne-Detected Raman-Induced Kerr 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
d (nm)	Quasi-periodic repeat distance
QRE	Quasi-reference Electrodes
$g_{ij}(r)$	Radial Distribution Function for atoms i and j
RE	Reference Electrode
n_D	Refractive Index
RMC	Reverse Monte Carlo
RTIL	Room Temperature Ionic Liquid
$Al_2O_3(0001)$	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 = 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

CHAPTER 1 TABLE OF FIGURES

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* R. Crawford, 'The 2012 Good Supervisors Guide', *Abstracts of the Australian Colloids & Surface Science Student Conference*, Riverwood Downs, 6-10th February, 2012

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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.