RSC Chemsource/Chemspec Symposium:

The Sustainability Challenge

Munich 18-19 June 2008

Ionic Liquids:
Potential in Speciality Chemicals

Neil Winterton, Chemistry Department,
University of Liverpool
Liverpool L69 7ZD

n.winterton@liverpool.ac.uk: +(44)(0) 151-794-3606:
http://www.liverpool.ac.uk/Chemistry/Staff/winterton.html

UNIVERSITY OF LIVERPOOL

Outline of talk

- Scene-setting
- Ionic Liquids: what are they?
  why all the interest?
- Technical requirements:
  what are they good for?
  how good is the match?
- Prospects as specialities:
  where and when?
- Challenges and opportunities:
  how sustainable are they?

UNIVERSITY OF LIVERPOOL

What are ionic liquids?

- Different from conventional salts: table salt: sodium chloride:

  crystalline solid
  MPt 801 °C
  soluble in water

- Liquids comprising solely of ions:

  usually organic cations and polyatomic anions
  large asymmetric ions; diffuse charges; weak inter-ionic interactions

OILs:	organic ionic liquids
RTILs:	room temperature ionic liquids
NAILs:	non-aqueous ionic liquids
TSILs:	task-specific ionic liquids

- Arbitrarily defined, to distinguish them from 'higher-melting' salts:

  By convention: MPts <100 °C
  MPts near room temperature or below
  MPts in range typically used in reactions of organic solvents

UNIVERSITY OF LIVERPOOL

Are they so new?

Fused Salts and Their Use as Reaction Media [*]

BY DR. W. SUNDERMEYER

ANORGANISCH-CHEMISCHES INSTITUT DER UNIVERSITÄT GÖTTINGEN (GERMANY)

Apart from being of interest for physicochemical investigations, ionic liquids are a very important supplement to the non-aqueous and water-like solvents. The present discussion of the physical properties and current ideas on the structure of fused salts is followed by a report on the solubilities of gases, salts and metals. Our knowledge of fused salt baths and their use in electrochemical and electrometallurgical processes has recently been considerably expanded. Special attention is drawn to chemical reactions in fused electrolytes. Fused salts can also act as catalysts, so that they may often be advantageous reaction media for synthesis, if not the only media which can be used.

I. Introduction

Most operations in modern preparative chemistry are carried out either in or with the participation of a liquid phase, in which the mobility of the molecules is similar to that in the vapor phase, but where the density of matter is almost the same as that of a solid. However, reactions are not confined to aqueous systems and to solu- ...

... in the laboratory [1] and in industry, of reaction media which range from condensed gases to melts of predominantly covalent metal halides, and which are characterized by a slight self-dissociation, similar to that of water. Surprisingly, however, we rarely find papers describing the preparative use of ionic liquids as solvents, although the physicochemical properties of these liquids suggest that they should also be useful in fields other than electrochemistry.

...s, ionic liquids are a ...
...nts. The present disc...
...fused salts is followed...

W. Sundermeyer, *Angew. Chem. Int. Edn.*, 1965, **4**, 222

- Term 'ionic liquid' also used for 'classical' molten salts
- Low-melting salts known for >100 y
- Many important developments over last 60 y
- Explosion of interest in last 15 y
- As with studies of classical molten salts, work in ionic liquids is characterised by parallel fundamental and technical developments

UNIVERSITY OF LIVERPOOL

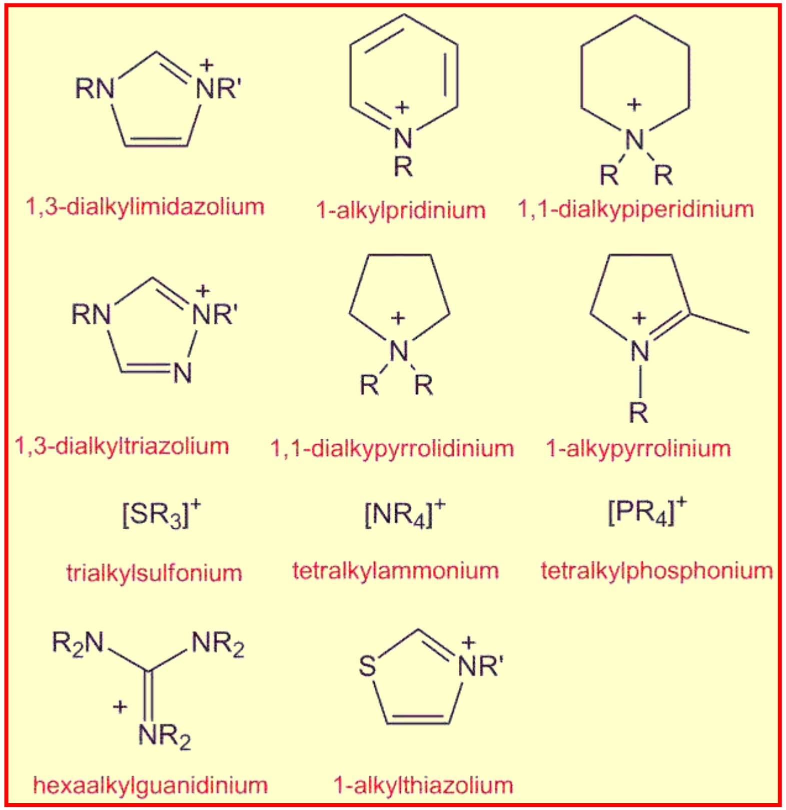
Are they so different?

- Have characteristics of salts
- Do not need the very high temperatures required for classical melts
- Can be handled like molecular solvents
- Beware of the 'almost-the-same'
- Things can be done in or with them that cannot be done with molecular solvents
- Highly research-active area

  liquid structure and dynamics; solvation phenomena; reaction medium
  catalysis; surface analysis and spectroscopy; phase behaviour
  electrochemistry; computation; physical property estimation
  materials chemistry; synthesis, purification and analysis

UNIVERSITY OF LIVERPOOL

Typical cations and anions used in ionic liquids



$[MX_n]^-$; M = Al, Ga, Fe, Cu, Zn; X = Cl, Br

$[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$

$[Al(Et)Cl_3]^-$, $[Al_2(Et)_2Cl_5]^-$, $[Al(OCH_2CF_3)_4]^-$

Cl^-, Br^-, I^-, $[F(HF)_n]^-$, $[N_3]^-$, $[SCN]^-$

$[OCN]^-$, $[N(CN)_2]^-$, $[C(CN)_3]^-$, $[B(CN)_4]^-$

$[BF_4]^-$, $[B(oxalato)_2]^-$, $B(C_6H_44\text{-}CF_3)_4]^-$

$[PF_6]^-$, $[P(C_2F_5)_3F_3]^-$, $[SbF_6]^-$

$[NO_3]^-$, $[NO_2]^-$, $[ROSO_3]^-$, $[(RO)_2PO_2]^-$

$[MeCO_2]^-$, $[CF_3CO_2]^-$, [lactate]$^-$, [amino acidate]$^-$

[*p*-$MeC_6H_4SO_3]^-$, $[CF_3SO_3]^-$

$[(CF_3SO_2)_2N]^-$

1,3-dialkylimidazolium = [rr'im]$^+$; [bmim]$^+$ (r = **b**utyl, r' = **m**ethyl) or $[C_4mim]^+$

http://ilthermo.boulder.nist.gov/ILThermo/mainmenu.uix

UNIVERSITY OF LIVERPOOL

Suppliers of ionic liquids

N.V. Plechkova and K.R. Seddon, *Chem.Soc.Rev.*, 2008, **37**, 123

ACROS	Solchemar
Bioniqs	SACHEM
BASF	DuPont
Cytec	Sigma-Aldrich
Scionix	Accelergy
IoLiTec	Chemada
Kanto Chemical Co.	Nippon Gohsei
Merck KGaA/Solvent Innovation	

- Mainly research chemicals (1-20 euro/g)
- Prices from 20-30 euro/kg for hundred ton lots of a few selected materials
- Specification and purity
- Provenance (especially synthesis route and purification method)

Characteristics relevant to industrial use

- Physical
- Chemical
- Economic
- Commercial
- Technocommercial
- Engineering
- Occupational
- Environmental
- Regulatory
- Public acceptance

Characteristics relevant to industrial use

♦ **Physical**	Viscosity	Liquid range
	Partition behaviour	Phase behaviour
	Vapour pressure	Solubility/ Solvation
♦ **Chemical**	Purity	Selectivity/Conversions
	Stability: thermal; oxidative; hydrolytic; electrochemical	
	Reactivity	QSARs
	Separability	Purifiability
♦ **Economic**	Cost	Cost/per unit of use
♦ **Commercial**	Availability	Freedom to use
♦ **Technocommercial**	IPR	Feedstock requirements
	Selection rules	Development methodology
	Disposal	Data for Life Cycle comparisons
♦ **Engineering**	Fluid flow	Heat/Mass transfer
	Recycle/recovery	Reactor requirements
	Storage	Materials compatibility
♦ **Occupational**	Toxicology	Flammability
♦ **Environmental**	Ecotoxicity	Environmental impact
♦ **Regulatory**		
♦ **Public acceptance**	Sustainability	

UNIVERSITY OF LIVERPOOL

Many applications proposed, described and patented:

- **Electrolytes:** batteries; metal deposition; electropolishing; fuel cells; solar cells; supercapacitors
- **Reaction media:** synthesis; catalysis; enzymes; nanoparticles
- **Materials synthesis:** polymerisations; gels; sol-gel; zeolites; composites
- **Solvents:** cellulose; carbohydrates; proteins; DNA
- **Analysis:** GC stationary phase; MALDI-TOF matrix
- **Processing fluids:** fuel desulfurisation; gas storage and compression; tissue preservation; fibre spinning
- **Separations:** hydrometallurgy; nuclear fuel; gas separation
- **Engineering fluids:** lubricants; heat transfer; reactive distillation
- **Additives:** plasticisers; antistatic agents; wood preservation
- **Energetic materials:** ion propulsion; propellants; explosives
- **Magnetic/optical/thermometric fluids:** mirror substrate; imaging; OLED
- **Pharmaceuticals:** synthesis; delivery; API

UNIVERSITY OF LIVERPOOL

Selected ionic liquids used in 40 applications from recent, representative or leading papers

[emim]Cl/AlCl$_3$	[bmpyr]NTf$_2$	[bpy]Br/AlCl$_3$
[choline]Cl/CrCl$_3$.6H$_2$O	[Hpy(CH$_2$)$_3$pyH][NTf$_2$]$_2$	[emim]OTf/[hmim]I
[choline]Cl/HOCH$_2$CH$_2$OH	[Et$_2$MeN(CH$_2$CH$_2$OMe)]BF$_4$	[Bu$_3$PCH$_2$CH$_2$C$_8$F$_{17}$]OTf
[bmim]PF$_6$	[bmim]BF$_4$	[omim]PF$_6$
[Oct$_3$PC$_{18}$H$_{37}$]I	[NC(CH$_2$)$_3$mim]NTf$_2$	[Pr$_4$N][B(CN)$_4$]
[bmim]NTf$_2$	[bmim]Cl	[bmim][Me(OCH$_2$CH$_2$)$_2$OSO$_3$]
[PhCH$_2$mim]OTf	[Me$_3$NCH(Me)CH(OH)Ph]NTf$_2$	[pmim][(HO)$_2$PO$_2$]
[b(6-Me)quin]NTf$_2$	[bmim][Cu$_2$Cl$_3$]	[C$_{18}$H$_{37}$OCH$_2$mim]BF$_4$
[heim]PF$_6$	[mim(CH$_2$CH$_2$O)$_2$CH$_2$CH$_2$mim][NTf$_2$]$_2$	[obim]PF$_6$
[oquin]NTf$_2$	[hmim][PF$_3$(C$_2$F$_5$)$_3$]	[C$_{14}$H$_{29}$mim]Br
[Me$_2$N(C$_{12}$H$_{25}$)$_2$]NO$_3$	[emim]BF$_4$	[mm(3-NO$_2$)im][dinitrotriazolate]
[MeN(CH$_2$CH$_2$OH)$_3$]	[MeOSO$_3$]	[Hex$_3$PC$_{14}$H$_{29}$]NTf$_2$
[emim][EtOSO$_3$]	[choline][ibuprofenate]	[emim]NTf$_2$
[emim][(EtO)$_2$PO$_2$]	[emim]Cl/CrCl$_2$	[Hex$_3$PC$_{14}$H$_{29}$]N(CN)$_2$

- ♦ 42 different ionic liquids: 26 different cations; 22 different anions
- ♦ 25 imidazolium salts; 13 different imidazolium cations; 7 [emim]$^+$; 6 [bmim]$^+$ salts
- ♦ 4 [R$_4$P]$^+$ and 8 [R$_4$N]$^+$ salts; 10 [NTf$_2$]$^-$, 8 halide, 4 [BF$_4$]$^-$ and 4 [PF$_6$]$^-$ salts
- ♦ [bmim]PF$_6$, [bmim]BF$_4$ or [emim]BF$_4$ used in 7/40 applications: ***but***, role of water.

- ♦ For most applications there are patents and papers, not always by same group
- ♦ Cellulose in ionic liquids: BASF has >10 patents; +10 other entities, from 1934
- ♦ Complexity of IPR

Ionic liquids in chemicals manufacture

N.V. Plechkova and K.R. Seddon, *Chem.Soc.Rev.*, 2008, **37**, 123

- Negligible vapour pressure
- Low flammability
- Large liquid range
- Ease of separation of volatile products
- Good solvency for organics and inorganics
- Novel/better/chiral chemistry

- Viscosity (mass and heat transfer)
- Stability (role of solutes)
- Separation of/from involatile products
- Recovery and recycle
- Cost/unit of use
- Commercial confidentiality

- ILs not inert: role of water
- Hydrophobic <u>and</u> hygroscopic

$$[PF_6]^- + H_2O \rightarrow [P(O)F_4]^- + 2\,HF$$

R.P.Swatloski, J.D. Holbrey and R. D. Rogers, *Green Chem*., 2003, **5**, 361

- $[P(C_2F_5)_3F_3]^-$; $[N(SO_2CF_3)_2]^-$; $[CF_3SO_3]^-$
- More hydrolytically inert but also more costly

- DuPont
  Hydroformylation, 1972
- BP
  Aromatic alkylation
- IFP
  Dimersol $\rightarrow$ Difasol
  Ni-catalysed $C_{4=} \rightarrow C_{8=}$
- Degussa
  Hydrosilylation
- Eastman Chemical
  2,5-dihydrofuran
- BASF
  Diethyl phenylphosphinite

UNIVERSITY OF LIVERPOOL

Viscosity of ionic liquids

R.A. Mantz and P.C. Trulove, Ionic Liquids in Synthesis, 2nd Edn., Eds Wasserscheid and Welton, Section 3.2, 72-88 (2008)

CATION	ANION	VISCOSITY cP (25 C)
[emim]	BF_4	32-43
	CH_3CO_2	162
	CF_3CO_2	35
	CH_3SO_3	160
	CF_3SO_3	43-45
	$(CF_3SO_2)_2N$	28-34
$[Et_3S]$	$N(CN)_2$	21
[bpy]	BF_4	103
	$(CF_3SO_2)_2N$	57

SOLVENT	VISCOSITY cP (20/25 C)
Acetone	0.3
Water	0.89
Dodecane	1.35
Acetophenone	1.6
Dimethylsulfoxide	2.0
Ethylene glycol	19.9
Conc H_2SO_4	25.4
Cyclohexanol	68
Glycerol	954

- Reduced at higher temperature
- Modified by impurities and other components
- → Supported ionic liquids; biphasic systems; rotating discs
- Reactor and process development

Ionic liquids in chemicals manufacture

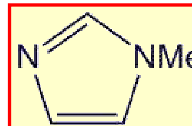
M. Maase, Ionic Liquids in Synthesis, 2nd Edn., Eds Wasserscheid and Welton, Chapter 9, 663-687 (2008)

BASF 'Basil' Process
US 2005/0020857
27 Jan 2005

$$PhPCl_2 + EtOH + Et_3N \xrightarrow{\text{xylene}} PhP(OEt)_2 + 2\,[Et_3NH]Cl$$

- Solid $[Et_3NH]Cl$ product
- Difficult separation
- Inefficient process

$$PhPCl_2 + EtOH + 2\ \text{1-Meim} \rightarrow PhP(OEt)_2 + 2\,[MeimH]Cl$$



1-Meim

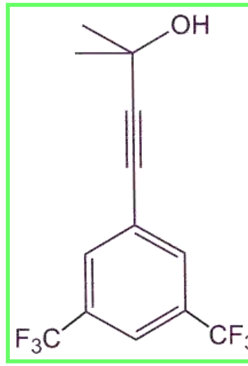
- [1-MeimH]Cl product (MPt 75 °C)
- Separate liquid phase
- Ease of recovery
- 8×10^4-fold increased s.t.y.
- Eco-effciency analysis

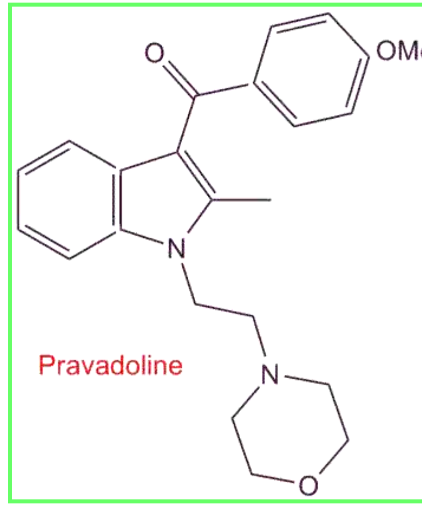
UNIVERSITY OF LIVERPOOL

Ionic liquids and pharmaceuticals

W.L. Hough and R.D. Rogers, *Bull. Chem. Soc. Jpn.*, 2007, **12**, 2262; Rogers *et al.*, US 2007093462 (26 April 2007)

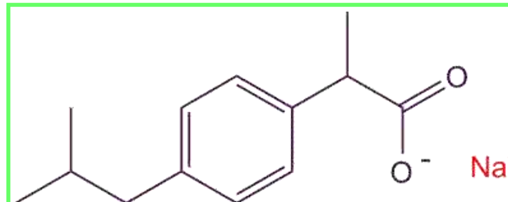
- Use in synthesis:
  - Seddon/QUILL: [bmim]PF_6/pravadoline
    M.J.Earle *et al., Green Chem.*, 2000, **2**, 261
  - Central Glass: $[Bu_3P(CH_2)_2C_8F_{17})]OTf$
  - Chiral synthesis
    A. Winkel *et al., Synthesis*, 2008, 999



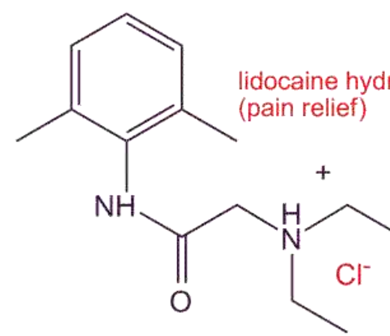


Pravadoline

- Delivery by controlled release:
  - [rmim]PF_6 (r = C_4, C_6; C_8)
    V. Jaitely *et al., Int. J. Pharm.*, 2008, **354**, 168



sodium ibuprofenate
(anti-inflammatory)



lidocaine hydrochloride
(pain relief)

- Liquid active pharmaceutical ingredients (API)
- Avoid polymorphism of crystalline solids
- Many pharmaceuticals are salts: Na[A]; [B]Cl
  - Sodium ibuprofenate (anti-inflammatory)
  - Lidocaine hydrochloride (pain relief)
- Convert to liquids with benign counter-ion?

Ionic liquids in electropolishing

A.P. Abbott *et al.*, *Phys. Chem. Chem. Phys*., 2006, **8**, 4214

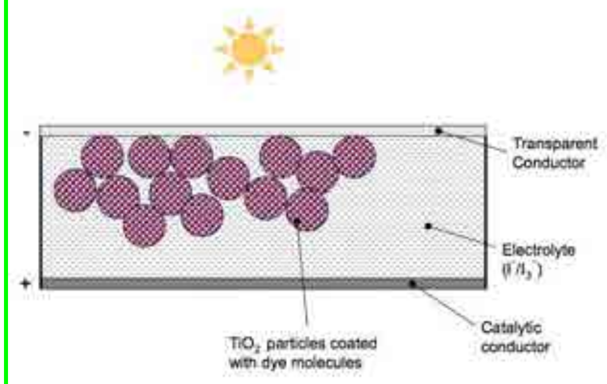
- Stainless steel: controlled dissolution
- Conventionally use mixed H_2SO_4/H_3PO_4 as electrolyte
- Viscosity improvers: glycerol
- Deep eutectics: choline chloride + 2HBD: urea (FPt 12 °C); malonic acid (FPt 3 °C); phenol (FPt -30 °C)
- $[Me_3NCH_2CH_2OH]Cl$ + 2 ethylene glycol ($HOCH_2CH_2OH$)
- Improved current efficiency
- Negligible gas evolution
- Medium relatively benign/non-corrosive
- Improved finish
- 1300 L scale, Anopol Ltd, Birmingham, UK
- Operated for >1 y
- Recycle and recovery

UNIVERSITY OF LIVERPOOL

Ionic liquids as electrolytes in dye-sensitised solar cells

M. Gorlov and L. Kloo, *Dalton Trans.*, 2008, 2655

- Negligible volatility
- Good solvency
- High electrochemical stability
- Good thermal stability
- Low viscosity preferred
- Hydrophobicity
- Light-to-electricity conversion efficiency, η, up to 11% at 100 mW/cm^2 sunlight
- First generation studies
- Long-term stability



[hmim]I
[hmmim]I
[pmim]I
[hmim]IBr$_2$
[aeim]I
[C$_{12}$mim]I
[MeBu$_2$S]I
[iBuHex$_3$P]I
[Me$_2$Hex$_2$N]I
[bpy]I
[bpy]IBr$_2$
[emim]OTf
[emim]NTf$_2$
[guan]SCN
[emim]SCN
[aeim]NTf$_2$
[emim][N(CN)$_2$]
[emim][C(CN)$_3$]
[emim][B(CN)$_4$]

UNIVERSITY OF LIVERPOOL

Ionic liquids as electrolytes in super-capacitors

T.Sato, G. Masuda and K. Tagaki, *Electrochim. Acta*, 2004, **49**, 3603; Nisshinbo Industries Inc.

- $[Et_2N(Me)CH_2CH_2OCH_3)]BF_4$
- Sealed for life device
- Claimed high power and energy density
- Electric buggy:
  - recharges in 1 minute
  - can travel 10 km before recharging
- Railway electrical propulsion:
  - no overhead cables
  - no third rail

UNIVERSITY OF LIVERPOOL

A lot of excitement and promise, but:

- How to find the exact (or optimal) match to your needs from such a plethora of choice?
- Will it be available and at the right price?
- Optimum choice is usually circumstance-specific
- ILs are rarely ‘drop-in’ substitutes

- Provenance: synthetic route
- Reactivity: not just water and hydrolytic stability
- Involatility: both a strength and weakness

New analytical methods
Contaminants and their removal
Separation of involatile products
Removal *from* products
Recovery and recycle

- Toxicity and ecotoxicity
- Are they ‘green’? Life-cycle assessments
  Sustainability

UNIVERSITY OF LIVERPOOL

Ionic liquids and toxicity

- Few ILs studied in depth: database growing
- Generally considered safe cations and anions

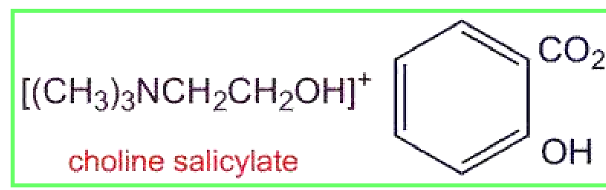
  chloride; lactate, acetate, dioctylsulfosuccinate

  amino acid derivatives (H. Ohno)
  choline chloride: ([$Me_3NCH_2CH_2OH$]Cl; MPt *ca* 300 °C; Vitamin B4)

  choline saccharinate (MPt 69 °C)[(a)]
  choline acesulfamate (MPt 25 °C)[(a)]
  choline salicylate (MPt 50 °C)[(b)]

- But will these particular products meet your needs?

(a) P. Nockemann, *et al*, *J. Phys. Chem., B*, 2007, **111**, 5254



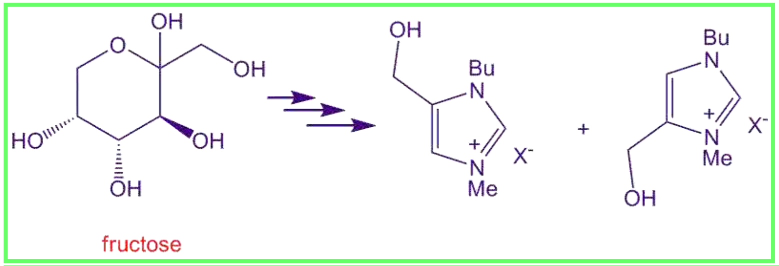
(b) R.H. Broh-Kahn, *et al.*, US Patent 3069321 (1962)

Ionic liquids: are they 'green'?

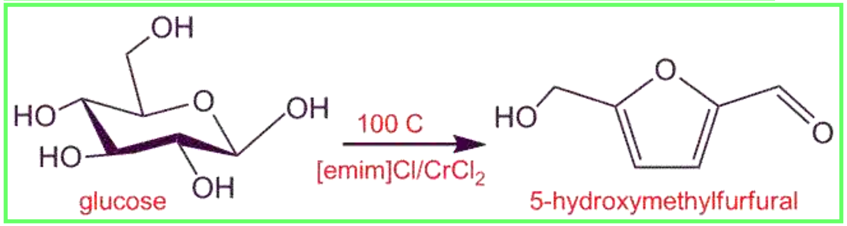
- Generic claim cannot be sustained: non-volatility just part of the story
- Individual IL claims to be proved: for each ion; co-operative effects?
- Ecoimpact[(a)] eco (aquatic) toxicity; sorption/bioaccumulation; biodegradation; photodegradation

- Life Cycle Analysis:[(b)] [bmim]BF_4/Diels-Alder reaction: > water; $LiClO_4$/Et_2O
  issues of separation, stability and recycle
  imidazolium *v*. ammonium?

- IL from sustainable/renewable precursors:[(c)] fructose to IL



- IL for sustainable processing[(d)]
  Cellulose in ionic liquids[(e)]
  HMF in [emim]Cl + catalyst[(f)]



(a) B. Jastorff *et al., Green Chem.*, 2005, 7, 362.
(b) Y. Zhang *et al., Environ. Sci. Technol.*, 2008, **42**, 1724; D. Kralisch *et al., Green Chem.*, 2005, **7**, 301.
(c) S.T. Handy *et al., Org. Lett.*, 2003, **5**, 2513; G. Imperato *et al., Eur.J.Org.Chem.*, 2007, 1049.
(d) J. Ranke *et al., Chem. Rev.*, 2007, **107**, 2183.
(e) O.A. El-Seoud *et al., Biomacromolecules*, 2007, 8, 2629.
(f) H. Zhao *et al., Science*, 2007, **316**, 1597.

UNIVERSITY OF LIVERPOOL

Purification, recovery and recycle of ionic liquids

'Ionic liquid recovery and recycle is the big unsolved challenge'
P.E. Rakita, 'Ionic Liquids as Green Solvents: Progress and prospects', ACS Symp. Ser., *2003,* ***856,*** *p32*

- Large-scale recovery and reuse:
  - No general method
  - Difficult to separate non-volatile components
  - Need to retain critical properties and to avoid loss of performance
  - Cost *v*. Benefit (*cf* distillation of cheaper molecular solvents)
  - For 20x cost of molecular solvent need better than 20x > efficiency of use

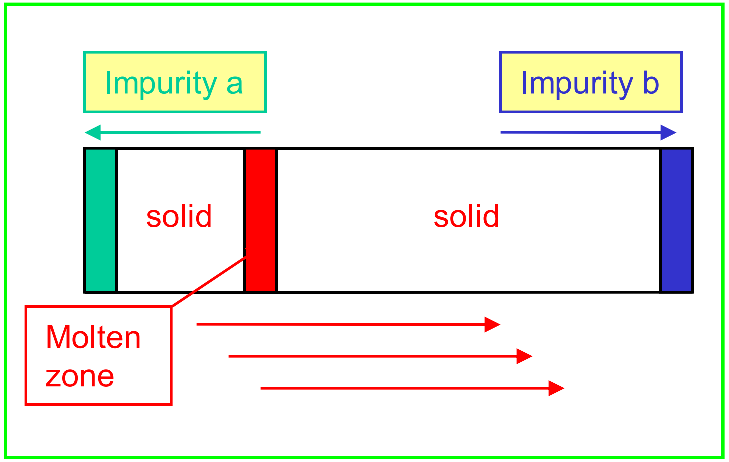
- Distillation: Most ILs have negligible vapour pressure
  [emim]NTf_2: 300 °C/0.1 mbar distils at 0.12 g h^{-1}
- Decomposition: 'Distillable' ionic liquids: $[Me_2NH]_2CO_2$
  Protic IL: neutralisation and re-formation ([1-MeimH]Cl)
  Carbene formation
- Extraction: Use of molecular solvents; supercritical fluids
- Chromatography: Use of molecular solvents; introduces particulates
- Nanofiltration:
- Crystallisation: From solution
  Melt crystallisation (Sulzer, WO2008031246; 20 Mar 2008)
  Zone-melting

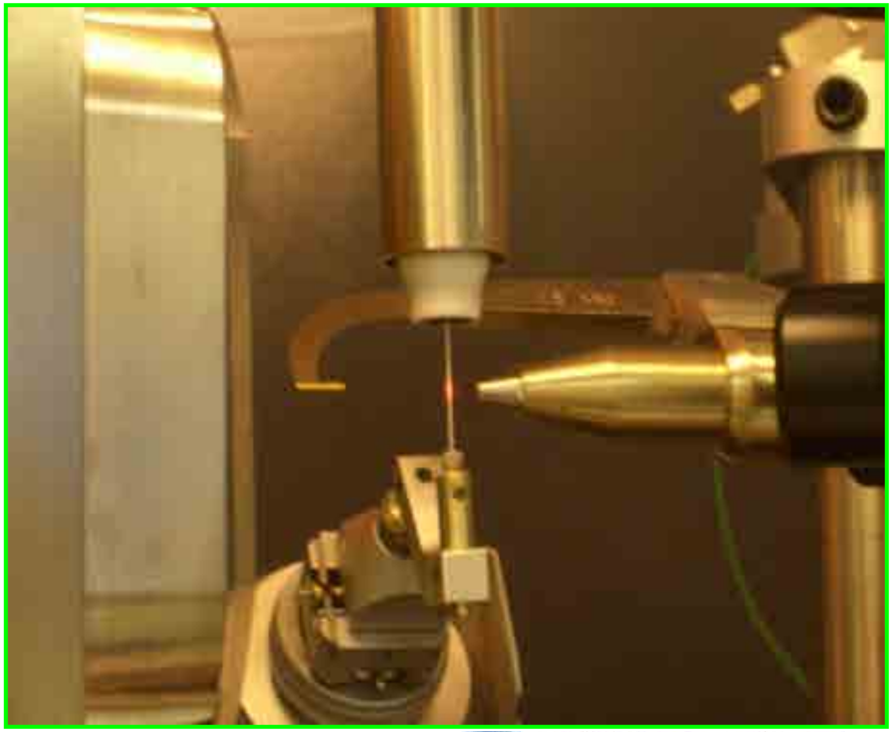
Purification and recovery of ionic liquids by zone-melting

Optical Heating and Crystallisation Device®

Developed by Roland Boese[a,b]
OHCD purchased from Bruker
Fitted to Bruker APEX CCD diffractometer

(a) V. R. Thalladi et al, *J. Am. Chem. Soc.* 1998, **120**, 8702. b) R. Boese, *et al*, *Angew. Chem. Int. Ed.*, 2003, **42**, 1961.





Only works if crystalline phase separation occurs

Ultrapurification of ionic liquids by zone melting

[emim]Cl (MPt 85 °C); [emim]Br (MPt ~70 °C)

A.Koenig and P. Wasserscheid, Proc. 13th Int. Workshop Ind. Crystallisation, Sept 2006, Delft, pp79-84

UNIVERSITY OF LIVERPOOL

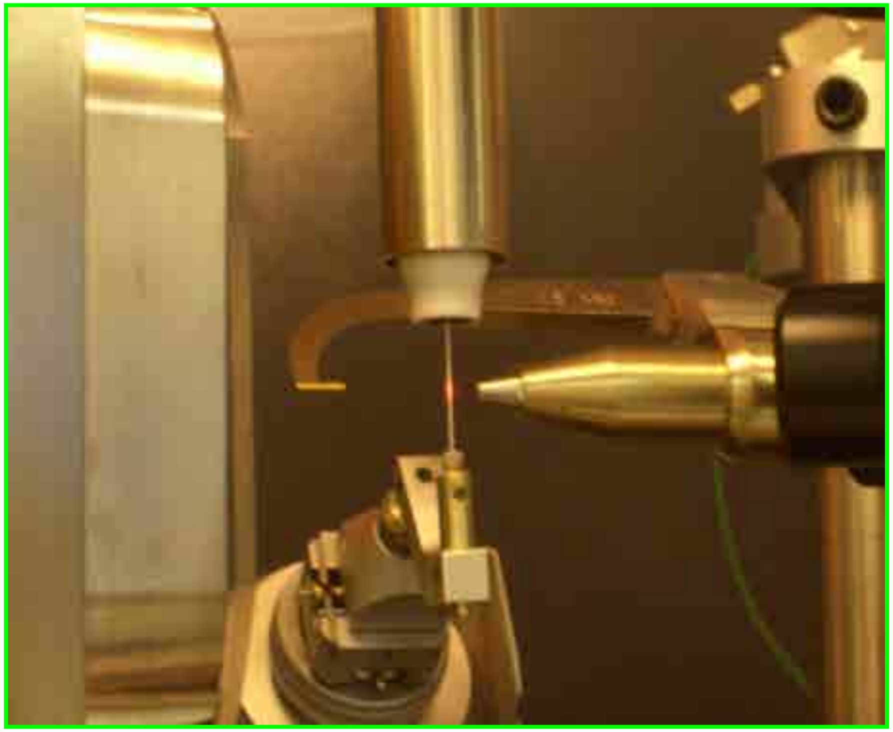
Purification and recovery of ionic liquids by zone-melting

Optical Heating and Crystallisation Device®

Developed by Roland Boese[a,b]
OHCD purchased from Bruker
Fitted to Bruker APEX CCD diffractometer

(a) V. R. Thalladi et al, *J. Am. Chem. Soc.* 1998, **120**, 8702. b) R. Boese, *et al*, *Angew. Chem. Int. Ed.*, 2003, **42**, 1961.

- Ionic liquids used not especially pure
- Characterise phase-behaviour by DSC
- ~1 mg sealed in glass capillary (3 cm × 0.5 mm)
- Form polycrystalline mass by cooling in flow of cold nitrogen (Oxford Cryosystem)
- Melt 1 mm deep column using IR laser
- Move melt zone along capillary (2-24 h)
- Adjust laser power/speed of scan
- Repeat until single crystal obtained
- Temperature of melt zone not known

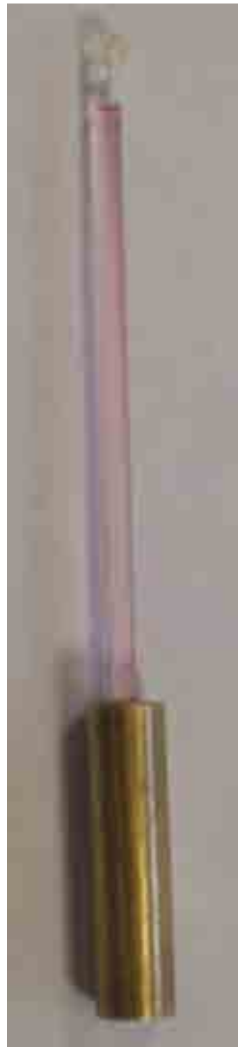


UNIVERSITY OF LIVERPOOL

Purification and recovery of ionic liquids by zone-melting

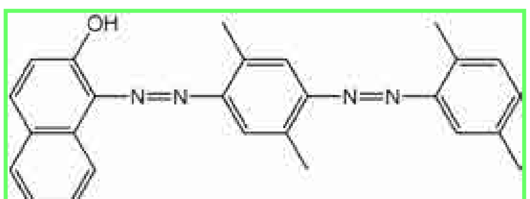
Effect of impurities and glass formation

[bmim]CF_3SO_3
+ Oil Red O
before scan
in OHCD



[bmim] CF_3SO_3
+ Oil Red O
after 3 scans in
OHCD at 10 mm h^{-1}

Separation not seen on similar treatment of Oil Red O in [bmim]BF_4



Oil Red O: λ_{max} = 518 nm

UNIVERSITY OF LIVERPOOL

Purification and recovery of ionic liquids by zone-melting

Glass-formers:

- [bmim]BF_4
- [bmim]OAc
- [bmim]SCN
- [bmim]$N(CN)_2$
- [omim]NTf_2
- [hmpip]NTf_2

New crystal structures:

[emim]OTf	*-25.7 °C*
[emim]NTf_2 (I)	*-25.7*
[emim]NTf_2 (II)	
[bmpyr]NTf_2	*-10.8*
[hmim]NTf_2	-10
[hpy]NTf_2	*- 3.6*
[bmim]NTf_2	-2
[emim]BF_4	*-1.3*
[bmim]PF_6	*+1.9*
[bmpyr]$P(C_2F_5)_3F_3$	+2
[bmim]$MeOSO_3$	+5
[bmim]OTf (I)	*+6.7*
[bmim]OTf (II)	
[hmpyr]NTf_2	+9
[pmpyr]NTf_2 (I)	+12
[pmpyr]NTf_2 (II)	
[pmpip]NTf_2	+12
[bmim]$MeSO_3$	+73

- IL purification by zone-melting is possible
- But not in all cases: glass formation
impurity effect on phase behaviour
- Multiple scans necessary
- Limit to cases where costs are justified
- Low cost method of IL purification still required

A.R. Choudhury *et al., CrystEngComm.*, 2006, **8**, 742.
A.R. Choudhury *et al., J. Am. Chem. Soc.*, 2005, **127**, 16792.
K. Matsumoto *et al., Sol. State Sci.*, 2006, **8**, 1250
S.M. Dibrov and J.K. Kochi, *Acta Cryst.*, 2006, **E62**, o19
A.R. Choudhury, W.A.Henderson, S. Parsons et al., unpublished

[Me_3NH]Cl.4HCl (MPt -54 °C); [Me_2SH]Cl.4HCl (MPt -80 °C)

D. Mootz *et al., Angew.Chem.Int.Edn.*, 1989, **28**, 169; D. Mootz, *et al., Zeit. anorg. allgem. Chem.*, 1992, **615**, 109.

Potential uses of ionic liquids

- **As speciality products in their own right:**
  - many producers and suppliers; large range of products
  - disposal? lease-products?
  - no front-runner; few broad-spectrum products; ‘slot-in’ replacements?
  - registration, purity and specification
  - many modest-sized end-using customers with different needs

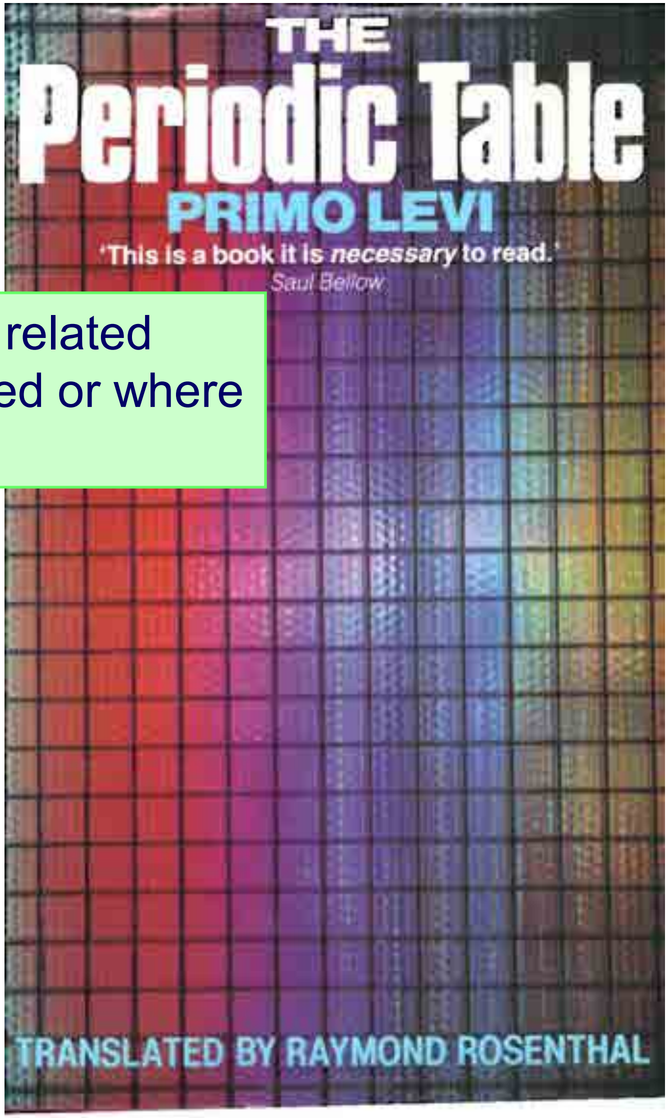
- **As reaction/processing media:**
  - for producing and processing of specialities
  - will require process and reactor engineering development
  - impact on unit costs; cost/unit of effect
  - is multiple-reuse possible?
  - single-use processes?

- **As additives; in hybrid materials; in composites or devices:**
  - novel effects; high value
  - fewer customers
  - electrochemical/mechanical/optical device manufacturers as customers
  - ionic liquid formulated or incorporated into (multicomponent) product
  - single use or multiple re-use?
  - sealed-for-life systems

LIVERPOOL

The ‘almost-the-same’

Primo Levi, The Periodic Table, 1975



- Be aware of developments and opportunities in related areas in which organic salts have long been used or where related developments are taking place:

- Inorganic low-temperature molten salts
- Phase-transfer catalysts
- Liquid clathrates
- Ionic liquid crystals
- Cationic and anionic surfactants
- Supporting electrolytes
- Zwitterions
- Deep eutectics
- Functionalised polymers
- Gelled/polymer electrolytes
- Membranes (*eg* Nafion)
- Ion exchange resins

UNIVERSITY OF LIVERPOOL

Ionic liquids: Conclusions

- Dynamic, fascinating and rich research area

- Exciting potential; endless possibilities; risky exploitation; fast moving
- Complex IPR
- Few new fully-commercialised large-scale developments announced

- Complexity of choice or opportunity to tune properties: pessimist or optimist?
- Costs *v.* benefits
- Databases incomplete
- Provenance/product/performance spec: interaction between supplier/user

- Profitable developments will arise
- Can contribute to sustainability of chemical technology

- Reaction medium for specialties: contacting and recovery
- Low cost general method for ionic liquid re-purification still needed

- High-value sealed-device applications not requiring recovery

UNIVERSITY OF LIVERPOOL