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Ionic liquids – an overview

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ABSTRACT

A virtually unprecedented exponential burst of activity resulted following the publication, in 1998, of an article by Michael Freeman (Freemantle, M. Chemical & Engineering News*, 1998, March 30, 32), which speculated on the role and contribution that ionic liquids (ILs) might make in the future on the development of clean technology. Up until that time only a handful of researchers were routinely engaged in the study of ILs but frenzied activity followed that continues until the present day. Scientists from all disciplines related to Chemistry have now embarked on studies, including theoreticians who are immersed in the aim of improving the "designer role" so that they can tailor ILs to deliver specified properties. This article, whilst not in any sense attempting to be exhaustive, highlights the main features which characterise ILs, presenting these in a form readily assimilated by newcomers to this area of research. An extensive glossary is featured in this article as well as a chronological list which charts the major areas of development. What follows consists of a number of sections briefly describing the role of ILs as solvents, hypergolic fuels, their use in some electrochemical devices such as solar cells and lithium batteries and their use in polymerisation reactions, followed by a concise summary of some of the other roles that they are capable of playing. The role of empirical, volume-based thermodynamics procedures, as well as large scale computational studies on ILs is also highlighted. These developments which are described are remarkable in that they have been achieved in less than a decade and a half, although knowledge of these materials has existed for much longer.*

Keywords: *ionic liquids, room temperature ionic liquids, non-aqueous ionic liquids, ambient temperature ionic liquids, ionic liquid solvents, ionic liquid hypergolic fuels, volume-based thermodynamics, large scale computations on ionic liquids, ionic liquids in electrochemical devices, ionic liquids in polymerisation reactions*

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1. Introduction

Ionic liquids (IL)–otherwise referred to as: room-temperature ionic liquid (RTIL); non-aqueous ionic liquid (NAIL); ambient temperature ionic liquid (ATIL); molten or fused organic salt; low melting salt; neoteric solvent or ''designer'' solvent–have witnessed an unprecedented escalation of research activity over the last decade and a half. So rapid has been this development that there has been no time to step back and develop a systematic naming system other than to define the bare rudiments: each investigator using his own naming scheme! In order to be able to identify the chemical nature of the IL materials being studied it is necessary to be familiar with the commonest abbreviations which are currently in use for ionic liquids. Accordingly, this article begins with a table (Table 1) and Figure 1 which outlines the structural features of the cations involved. Table 1 gives details of the shorthand notation employed for the cations and anions involved in ionic liquids as are used by various workers. Standardisation is ideally required and possibly best achieved through the medium of IUPAC.

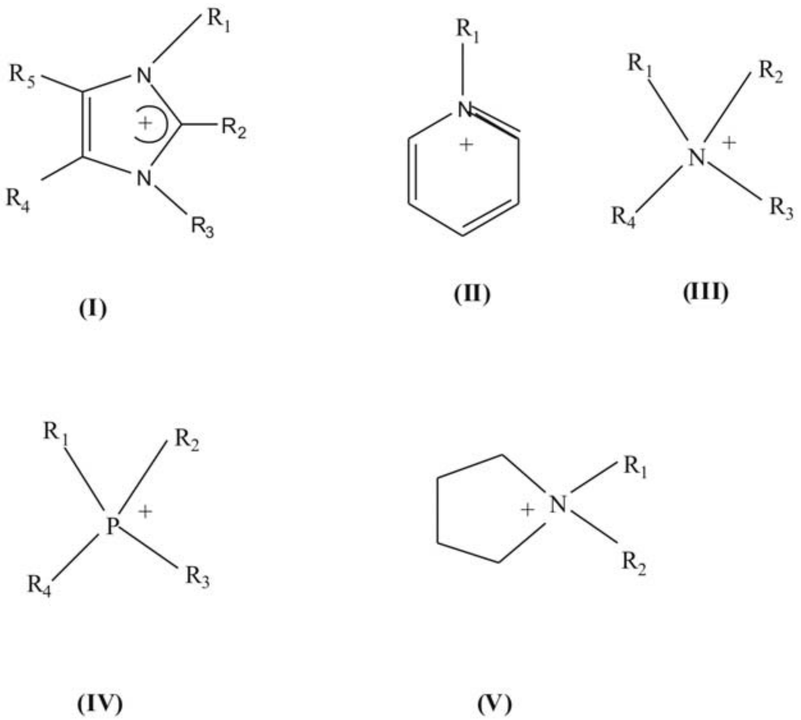

Figure 1 *Main cations involved in ILs currently being researched.*

2. Glossary

Figure 1 shows the structures of the main cations associated with current IL research while Table 1 presents a series of alternative nomenclature that are in common use for the cations and anions involved.

3. Ionic liquid properties

ILs are (arbitrarily) defined as having a freezing (melting) point, mp $<100^\circ$C (373 K)[1]. The exciting, as well as the phenomenally increasing, number of commercial and technical applications which are observed below this temperature and brought about by these potentially benign IL solvents and their properties is startling. Most ILs are in the liquid state below 67°C (340 K), although this liquid range can extend below -90°C (183 K). ILs are usually thermally stable up to 200°C (473 K) and have a liquid range of some 300°C (300 K). These liquids, which consist entirely of ions and which are held together by strong forces as a result of the

Table 1 *Glossary of names and symbols employed for cations and anions in common ILs*

Ionic liquid cation name	Equivalent cation names (not necessarily exhaustive)			
$[\text{1-methylimidazolium}]^+$ (I) $R_1 = \text{Me}$, $R_2 = R_3 = R_4 = R_5 = \text{H}$	$[\text{Hmim}]^+$			
$[\text{1-ethyl-3-methylimidazolium}]^+$ (I) $R_1 = \text{Et}$, $R_2 = R_4 = R_5 = \text{H}$, $R_3 = \text{Me}$	$[C_2C_1\text{Im}]^+$ here the C_2 refers to the ethyl substituent, whilst the C_1 refers to the Me in the 3 position	$[C_2\text{mim}]^+$ or $[\text{emim}]^+$ or $[\text{EMIM}]^+$ upper case form less usual	$[\text{EMI}]^+$	$[\text{EtMeIm}]^+$
$[\text{1-methyl-3-propylimidazolium}]^+$ (I) $R_1 = \text{Me}$, $R_2 = R_4 = R_5 = \text{H}$, $R_3 = \text{Propyl}$	$[C_3\text{mim}]^+$	$[\text{Pmim}]^+$		
$[\text{1-methyl-3-butylimidazolium}]^+$ (I) $R_1 = \text{Me}$, $R_2 = R_4 = R_5 = \text{H}$, $R_3 = \text{Butyl}$	$[C_4\text{mim}]^+$	$[\text{Bmim}]^+$	$[\text{MBIC}]^+$	
$[\text{1-methyl-2-methyl-3-butylimidazolium}]^+$ (I) $R_1 = \text{Me}$, $R_2 = \text{Me}$, $R_4 = R_5 = \text{H}$, $R_3 = \text{Butyl}$	$[C_4\text{Mmim}]^+$	$[\text{BMMIM}]^+$	$[\text{BMmim}]^+$	

Table 1 *Glossary of names and symbols employed for cations and anions in common ILs* (continued)

Ionic liquid cation name	Equivalent cation names (not necessarily exhaustive)		
[1-methyl-3-pentylimidazolium]$^+$ (I) $R_1 = Me$, $R_2 = R_4 = R_5 = H$, $R_3 = Pentyl$	[C_5mim]$^+$	[Penmim]$^+$	
[1-methyl-3-octylimidazolium]$^+$ (I) $R_1 = Me$, $R_2 = R_4 = R_5 = H$, $R_3 = Octyl$	[C_8mim]$^+$	[Octmim]$^+$	[Omim]$^+$
[1-n-alkyl-3-methylimidazolium]$^+$ (I) $R_1 = {}^n$alkyl, $R_2 = R_4 = R_5 = H$, $R_3 = Me$	[$C_n$mim]$^+$ here the C_n refers to the unbranched alkyl substituent of chain length *n*, whilst actual reference to the Me in the 3 position is absent	[C_nC_1Im]$^+$ here the C_n refers to the unbranched alkyl substituent of chain length *n*, whilst C_1 refers to the Me in the 3 position	[C_nMIm]$^+$
[1-*n*-alkyl-2,3-dimethylimidazolium]$^+$ (I) $R_1 = {}^n$alkyl, $R_2 = R_3 = Me$, $R_4 = R_5 = H$	[C_nC_1MIm]$^+$	[C_nMMIm]$^+$	
[1-ethanol-3-methylimidazolium]$^+$ (I) $R_1 = CH_3CH_2OH$, $R_2 = R_4 = R_5 = H$	[C_2OHmim]$^+$		
[pyridinium]$^+$	[HPy]$^+$		

Table 1 *Glossary of names and symbols employed for cations and anions in common ILs* (continued)

Ionic liquid cation name	Equivalent cation names (not necessarily exhaustive)	
$[1\text{-}n\text{-alkylpyridinium}]^{+}$ (II) $R_1 = C_n$, $R_2 = R_4 = R_5 = H$	$[C_n py]^{+}$ here the C_n refers to the alkyl substituent of chain length *n*	
$[1\text{-hexylpyridinium}]^{+}$ (II) $R_1 = \text{hexyl}$	$[C_6 py]^{+}$ here the C_6 refers to the hexyl substituent	
$[\text{butylpyridinium}]^{+}$ (II) $R_1 = \text{butyl}$	$[BuPy]^{+}$	$[BPy]^{+}$
$[\text{methyltrioctylammonium}]^{+}$ (III) $R_1 = Me$, $R_2 = R_3 = R_4 = \text{octyl}$	$[Me(Oct)_3N]^{+}$	$[N_{1\,8\,8\,8}]^{+}$
$[{}^{n}\text{pentyltriethylammonium}]^{+}$ (III) $R_1 = \text{pentyl}$, $R_2 = R_3 = R_4 = \text{ethyl}$	$[C_5NEt_3]^{+}$	$[PenEt_3N]^{+}$
$[\text{tributyl(tetradecyl)phosphonium}]^{+}$ (IV) $R_1 = \text{tetradecyl}$, $R_2 = R_3 = R_4 = \text{butyl}$	$[Bu_3(Tetdec)P]^{+}$	$[P\_{}_{4\,4\,4\,14}]^{+}$
$[\text{trihexyl(tetradecyl)phosphonium}]^{+}$ (IV) $R_1 = \text{tetradecyl}$, $R_2 = R_3 = R_4 = \text{hexyl}$	$[Hex_3(Tetdec)P]^{+}$	$[P_{6\,6\,6\,14}]^{+}$

Table 1 *Glossary of names and symbols employed for cations and anions in common ILs* (continued)

Ionic liquid cation/anion name	Equivalent cation/anion names (not necessarily exhaustive)		
[*N*,*N*-butylmethyl-pyrolidinium]$^+$ (V) R_1 = butyl, R_2 = methyl	[BMpyr]$^+$		
[*N*,*N*-pentylmethyl-pyrolidinium]$^+$ (V) R_1 = pentyl, R_2 = methyl	$[C_5MPyr]^+$		
[*N*,*N*-1-^{n}alkyl-1-methylpyrrolidinium]$^+$ (V) R_1 = ^{n}alkyl, R_2 = methyl	$[C_nMPyr]^+$		
[hydrazinium]$^+$	$[N_2H_5]^+$		
Ionic liquid anion name	Alternative anion names (not necessarily exhaustive, nor do all entries appear in this review)		
[monatomic anions]$^-$	*e.g.* chloride, Cl^- not usually enclosed in brackets		
[polyatomic anions]$^-$	*e.g.* nitrate, $[NO_3]^-$ square brackets enclose anion symbol		
[acetate]$^-$ = [alkylcarboxylate]$^-$	$[RCO_2]^-$	*e.g.* $[CH_3CO_2]^-$ acetate	*e.g.* [OAc]$^-$ alternative for acetate
[trifluoromethylacetate]$^-$	[OTfa]$^-$	$[CF_3CO_2]^-$	

Table 1 *Glossary of names and symbols employed for cations and anions in common ILs* (continued)

Ionic liquid anion name	Equivalent anion names (not necessarily exhaustive)			
[p-toluenesulfonate]$^{-}$	[tosylate]$^{-}$ alternative name	[OTs]$^{-}$ tosylate	[Ts]$^{-}$ tosylate	
[bis(trifluoromethylsulfonyl)amide]$^{-}$ [bis(trifluoromethylsulfonyl)imide]$^{-}$ [bis(trifluoromethanesulphonyl)imide]$^{-}$	[bistriflamide]$^{-}$ alternative name	[bistriflimide]$^{-}$ alternative name	$[N(SO_2CF_3)_2]^{-}$	$[NTf_2]^{-}$
[bis(trifluoroethylsulfonyl)amide]$^{-}$	$[NPf_2]^{-}$	$[N(SO_2C_2F_5)_2]^{-}$		
[bis(perfluoroethylsulfonyl)amide]$^{-}$	$[N(SO_2C_2F_5)_2]^{-}$	[beti]$^{-}$ alternative name		
[methylsulfite]$^{-}$	$[C_1SO_3]^{-}$	$[CH_3SO_3]^{-}$		
	[Fap]$^{-}$	$[PF_3(C_2F_5)_3]^{-}$		
[trifluoromethylsulfonate]$^{-}$	[Triflate]$^{-}$ alternative name	$[CF_3SO_4]^{-}$ triflate	[OTf]$^{-}$ triflate	[Tf]$^{-}$ triflate
[4-methyl-phenylsulfonate]$^{-}$	[OTos]$^{-}$			
[^{n}alkylsulfate]$^{-}$	$[C_nSO_4]^{-}$	$[C_nH_{2n+1}SO_4]^{-}$		
[dicyanamide]$^{-}$	[dca]$^{-}$	[DCA]$^{-}$	[Dca]$^{-}$	$[N(CN)_2]^{-}$

Table 1 *Glossary of names and symbols employed for cations and anions in common ILs* (continued)

Ionic anion name		Equivalent anion names (not necessarily exhaustive)
[chloroaluminate]$^-$	*e.g.* $[AlCl_4]^-$	*e.g.* $[Al_2Cl_7]^-$
[perchlorate]$^-$	$[ClO_4]^-$	
[hydrogensulfate]$^-$	$[HSO_4]^-$	
[hexafluorophosphate]$^-$	$[PF_6]^-$	
[tetrafluoroborate]$^-$	$[BF_4]^-$	
[tris(pentafluoroethyl)trifluorophosphate]$^+$	$[(C_2F_5)_3PF_3]^-$	[FAP]$^-$
[glutamate]$^-$	[Glu]$^-$	
[dinitromide]$^-$	$[N(NO_2)_2]^-$	
[carborane]$^-$	$[CB_{11}H_{12}]^-$	
[tricyanomethyl]$^-$	[Tcm]$^-$	$[C(CN)_3]^-$
[docusate]$^-$	[Docusate]$^-$	$[R\text{-}CH_2\text{-}CH(SO_3)\text{-}R]^-$ with R-$=$ -C(O)O-CH_2-$CH(C_2H_5)(C_4H_9)$
ILs		Other synonyms

Table 1 *Glossary of names and symbols employed for cations and anions in common ILs* (continued)

Ionic liquid	Equivalent names (not necessarily exhaustive)
[emim][$CH_3CH_2OSO_3$]	[EMIES]
[C_2mim]Cl–$AlCl_3$	Refers to a RTIL binary mixture which contains one cation [C_2mim]$^+$ and two anions Cl^- and [$AlCl_4$]$^-$
[C_4MIM][CH_3O-C_2H_4O-$C_2H_4SO_4$]	ECOENG 41M
[$N(CH_3)(C_2H_4O$-$C_2H_4OH)_2(C_{13}H_{27})$][$C_1SO_4$]	ECOENG 500

charged nature of their ions, might be anticipated–and indeed are found–to exert little tendency to leave the vessel in which they are confined. They accordingly, like any typical ionic salt, exert negligible vapour pressure, and this is one of their key properties. Accordingly they are reluctant to undergo distillation, at least at normal pressures and below their decomposition temperatures. Thus ILs present an environmentally favourable alternative to traditional volatile organic solvents (VOC). Researchers have reported their tendency to resist flow, causing them to exhibit rather viscous properties (*i.e.* have higher than normal viscosities). ILs would be anticipated to be more viscous than the more traditional covalent molecular liquids, although, normally their viscosity, $\eta/\mathrm{cP} \leq 100$, making ILs workable. At the extreme, however, viscosity values of up to 500 cP can be observed[3]. These values should be compared to η values exhibited by more conventional liquids: water $\eta = 0.89\,\mathrm{cP}$, ethanol $\eta = 1.07\,\mathrm{cP}$, acetone $\eta = 0.31\,\mathrm{cP}$, however, $[\mathrm{C_2mim}][\mathrm{PF_6}]$, a fairly commonly used IL for example, has a viscosity of 270 cP. Rebelo and his colleagues[2] have, however, shown it possible to distil $[\mathrm{C_{10}mim}][\mathrm{NTf_2}]$ and $[\mathrm{C_{12}mim}][\mathrm{NTf_2}]$ at 70°C and under reduced pressure. The tenacity with which their ions bind together by virtue of their charged ions would lead one to imagine that the ions present in an IL will be more coherently bound together than they are in more usual liquids. One therefore might anticipate, and would indeed find, that the densities, ρ, of ILs would be $>1\,\mathrm{g\,cm^{-3}}$ and further, assuming that the IL in question is immiscible with water (whose density, $\rho/\mathrm{g\,cm^{-3}} = 1$), that they would form a separate lower liquid phase layer when mixed with water. They generally do so. The solubility, miscibility and immiscibility of these IL materials can differ widely and this influences their ability to be used in the role of extractants and separants. Such properties are, too, much influenced by the nature of the specific anions and cations which are present. The ILs can dissolve both ionic and covalent materials.

Naturally, consisting as they inevitably do, entirely of ions which can transport charge within the medium to a greater extent than can more conventional solvents like acetonitrile for example, the electrical specific conductivity, κ, of ILs, measured in Siemens per metre, $\mathrm{S\,m^{-1}}$, would be expected to be high, rendering them, *inter alia*, extremely useful in electrochemical applications. Sometimes, however, those ILs possessing bulky cations or anions can–by virtue of their being more viscous–often exhibit rather low conductivities (these are then measured in millisiemens per cm). Examples of the latter are found in ionic liquid

$[C_2mim][NTf_2]$ which has a low conductivity of $\kappa = 9.2\,mS\ cm^{-1}$ and in the IL $[C_6mim][NTf_2]$ for which $\kappa = 2.2\,mS\ cm^{-1}$.

Dielectric constant, ε, (or relative permittivity) depends on the nature of the molecules present in a liquid. Those having non-polar species present tend to have low dielectric constants whilst, when polar species are present, ε is much higher. Should hydrogen bonding also be in play between the species present, as is found in water for example, ε tends to be even higher. ILs, having as they do, an ability to conduct, are not usually amenable to the standard measurement techniques normally used to determine values of the dielectric constant. Values can, however, be determined using microwave dielectric spectroscopy.

A useful summary of IL properties can be found in Tables I and II of Keith Johnson's, *Interface* (Electrochemical Society journal, Spring 2007 p. 38).

4. Toxicity

As with any new class of material, the evaluation of the toxicology is of prime importance. The toxicological properties of many ILs have yet to be evaluated. ILs containing fluorinated anions tend not to be satisfactorily hydrolytically stable over long periods of time[47] and accordingly can yield toxic and corrosive HF in small quantities. Their disposal in an industrial context therefore still presents the problem in the sense that these IL and what decomposition products remain are, effectively, halogen compounds. Accordingly ILs like, for example, such compounds as [1-*n*-butyl-3-methylimidazolium][octylsulfate] (ECOENG 418), which has been styled as ''an even Greener Ionic Liquid'', are under development as halogen-free, hydrolytically stable materials[48,49]. Minor toxicity (*e.g.* LD_{50} for rats of $1400\,mg\ kg^{-1}$) has been recorded[50] for $[3\text{-hexylmethyl-1-methylimidazolium}][BF_4]$ and a lesser value for mice ($2200\,mg\ kg^{-1}$) has been found in the case of $[CABHEM][MeSO_4] = $ ECOENG 500[51]. Such evaluations continue.

5. ILs: the key milestones in the chronology of development

Freeman[4] has presented a useful chronological account (up until 2008) of the development of ILs which we have here annotated further to cover developments of more recent importance. Briefly, the story begins in 1961 when the term ''ionic liquid'' was first coined during a Faraday Society Discussion Meeting by Bloom[5] although, in this context, he referred to the pure molten alkali metal halide *salts* and not to the ionic liquid *liquids* which are the subject of this review. The simple difference is one of phase (solid as opposed to liquid). Both contain predominantly pairs of ions (discrete cations and anions).

Major milestones in the identification and researching of key ILs can (following Freemantle) be acknowledged to be, in chronological order:

1961: First Faraday discussion held in Liverpool entitled "*The structure and properties of ionic melts*". The meeting dealt with molten inorganic salts.

1963: First real synthesis of an ionic oil, triethylammonium dichlorocuprate, $[Et_3NH][CuCl_2]$ which exists at 25°C and so is an example of a room (ambient) temperature ionic liquid [ATIL or RTIL] by Yoke *et al.*[6]

1970: Bockris and Ready[7] publish their text *Modern electrochemistry* containing a Chapter entitled "ILs" (Chapter 6) which discussed tetralkylammonium salts and alkali metal halides and silicates.

1976–8: Oysteryoung *et al.*[8,9] identify [1-butylpyridinium][Cl] = $[C_4py][Cl]$, a salt which when mixed with $AlCl_3$, forms molten systems at room temperature for a wide range of $[C_4py][Cl]:[AlCl_3]$ composition ratios.

1982: Wilkes *et al.* reported[10] an important new class of RTILs in the dialkylimidazolium chloroaluminates.

1992: Wilkes *et al.* developed[11] the use of the 1-ethyl-3-methylimidazolium cation = $[emim]^+$ partnered with the $[PF_6]^-$ and $[BF_4]^-$ anions as ILs which are stable in air and *nearly* moisture-stable.

1996: Bonhöte and Grätzel[12] synthesised [dialkylimidazolium]$[NTf_2]$, which are hydrophobic ILs.

In parallel with these developments came a realisation of the technological importance of ILs as highlighted in:

1964: Gordon[13] makes reference to low melting quaternary ammonium salts as potential organic reaction media.

1972: Parshall[14] reports the first instance of homogeneous catalysis in molten salt media at low temperatures.

1976: Oysteryoung *et al.*[8] reported Friedel–Crafts alkylations at *room temperature* in molten salt media.

1981: Knifton[15] uses $[PH_4]^+$-containing ionic liquids in order to convert CO/H_2 into glycol, $HO.CH_2.CH_2.OH$.

1982: Poole *et al.*[16] demonstrated [ethylammonium] [NO_3] in use as the stationary phase in GLC.

1984: Magnuson *et al.*[17] first introduced IL-enzyme systems.

1990–5: Chauvin's group[18,19] performed catalytic dimerisations using molten salts as well as isomerisations and hydrogenation reactions using ILs as media.

1996: Commencement of the use of ILs in a large scale (1500 metric tons p.a.)

Commercial process synthesis. (Isomerisation of 3,4-epoxy-1-butene into 2,5-dihydrofuran was traditionally carried out in liquid media. The process needed to handle a solvent with a high-boiling point, produced side products not easily distilled away which destroyed the effectiveness of the catalyst. [PR_4][I] (R = alkyl) an ionic liquid used in conjunction with a Lewis acid , R_3Sn, provided the Texas Eastman Division with a system having low toxicity, markedly increased selectivity and provided a catalyst which did not distil off with the product.)[20]

1997: Ken Seddon[20] promotes the idea of ILs and clean technology.

1998: *Chemical Engineering News* promotes[4,21] the notion of "designer" as IL solvents and the route to clean technology. The article[21] really triggered interest in RTILs as can be seen in Table 1 and led to a flurry of scientific activity in the area.

1999: ILs Laboratory (QUILL = Queen's University IL Laboratory) established in Belfast.

1999: ILs become commercially available (see www.solvent-innovation.com).

1999: Although not immediately equated to IL development, work by Christe *et al.*[23–26] investigating the $N_5{}^+$ cation and compounds such as [N_5] [N_3] as potential propellants and HEDM (high energy density materials) place polynitrogen materials in the forefront as candidates for the green explosives of the future, many of which may be adapted and delivered as hypergolic [*i.e.* spontaneous ignition of one chemical when contacted by another] ILs in the future.

2000–date: Theoretical chemistry begins to play a role in the investigation[26–28] of ILs.

2005: First Conference on ILs takes place in Salzburg.

2005: The conference "Molten Salts 7" devoted a specific session to ILs.

2005–date: Emel'yanenko, Verevkin, Heintz, Voss, K., Schultz and others[30–36] at the University of Rostock (North Germany) begin a systematic experimental determination of standard thermochemical data for ILs and related materials[37]. This initiative will serve to create an ever expanding thermochemical database so essential for a newly emerging area of chemistry, especially since there are no historic data recorded for these materials within existing thermochemical tables.

2008: Possibly most important IL development in 21st century so far, was the discovery by Chambreau, Schneider, Rosander, Hawkins, Vaghjiani and colleagues[38,39] at the Edwards Air Force Base, U.S.A. that selected ILs can behave as fuels and undergo hypergolic reactions when exposed to conventional oxidising agents. Ionic liquids possessing the $[\text{dicyanamide}]^- = [N(CN)_2]^-$ anion are, for example, shown to have hypergolic properties[40], *e.g.* [the bipropellant system of fuming HNO_3 and IL, 1-methyl-4-amino-1,2,4-triazolium] $[N(CN)_2]$.

2011: Volume based thermodynamics, VBT[41–43] is applied to study the thermochemistry of $[\text{emim}][ClO_4]$[44]. This paper outlines some of the questions raised surrounding the needed reparameterisation of VBT to suit the IL media. A Warwick–Freiburg–Munich–Rostock initiative (involving this author and Professors Krossing, Klapötke, Verevkin and researchers) has been launched (July 2011) to further explore this topic.

6. Escalation of studies on ILs

Table 2 gives an indication of just how studies on ILs have escalated since 2008.

Table 2 *Escalation of studies on ILs, post 1888*

Year	Number of papers published on ILs
1888	1
1998	240
1999	277
2000	353
2007	8,000
2008	10,500
2010	14,000

7. Preparation of ILs

Figure 2 gives a schematic to indicate how some ILs can be prepared.

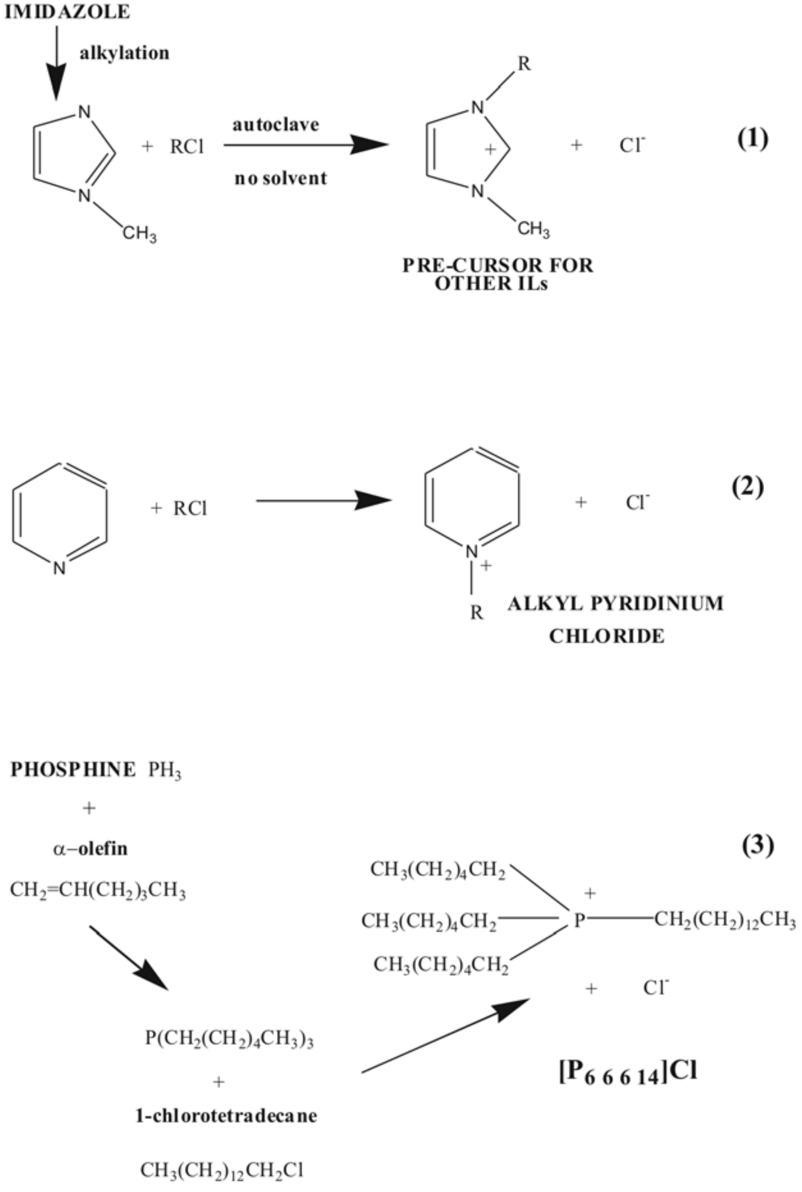

Figure 2 *Some preparative schemes for synthesis of ILs.*

8. Current, most frequently studied, ILs

Table 1 lists the cations and anions which are found in the ILs currently being studied, the most frequent of which are imidazolium-based ILs [$C_n$mim] [anion]. These have been studied, having variation of the alkyl chain length, such that $1 < n < 16$ and also, occasionally, having functional groups (CN, OR, OH, SO_3H) introduced into the $C_n$alkyl chain.

9. Applications of ILs

Rhodes has recently, in this journal[45], briefly reviewed ILs from the point of view of their green future, including some fascinating applications which include use of ILs as fluid bases for mirror coatings of telescopes[46]. Noting that the high vacuum conditions found on the Moon, which often quickly destroy coatings on astronomical instruments, would be less prone to do so in the case of IL fluid–based coatings because of the low vapour pressures of the ILs themselves. The potential of ILs for use as alternatives to detergents for cleaning up oil spillages is innovative and for [C_4mim]Cl as a non-aqueous electrolyte for the recovery of spent uranium is also featured.

In what follows we highlight a number of further applications of IL in some detail and then mention briefly some further potential uses. The coverage is by no means exhaustive and indeed the list lengthens almost by the day. As space is limited, the coverage here is selective and the topics chosen are to some extent fairly arbitrary although an attempt has been made not to overlap with the topics recently covered by Rhodes[45].

It is worthwhile commenting too that, already, a few processes which have employed IL technology have come and gone, as commercial and chemical needs and market forces fluctuate. A salient example is the Eastman Chemical Company synthetic plant for the production of 2,5-dihydrofuran which ran very successfully for 8 years. This process employed an IL as a co-catalyst for the isomerisation of 3,4-epoxy-1-butene which gave the target product. The effective role, assumed by the IL used, was to produce a stable, selective and miscible co-catalyst system that was cheap (and so avoided the previous need to use of high boiling solvents which, themselves, created a number of unwanted side reactions).

We now turn to consider some key areas of ionic liquid development.

9.1 ILs in their role as important solvents

Although theoretically able to deliver a whole range of both physical and chemical properties the concept of ILs as being ‘‘designed’’ solvents has not really materialised as yet. The wealth of data on solubility and miscibility characteristics, and indeed thermodynamic properties[37], necessary to tailor make ILs to return given target properties are still being assembled. The process of finding alternative solvents in the form of IL has, at least to date, rather been a trial and error procedure. It is the trends that are now becoming evident and these are used to inform choices.

The wide ranging solubilisation and miscibility properties of ILs as led by the studies of Patell *et al.*[57] uncovered the remarkable property of $[AlCl_4]^-$ anion-containing ILs liquids of being able, with microwave inducement, to dissolve kerogen–a fossilised material which is present in sedimentary rock deposits and which is used for used for geochemical dating. Until 2002, the only known solvent for kerogen was hydrogen fluoride, which rendered geochemical dating exercises particularly hazardous. Accordingly with the advent of this new discovery, dating techniques have been rendered much more straightforward.

Despite their expected polarity, due to the composition which is made up of discrete ions, which might be thought to confine their solubilising characteristics to that of polar solutes, ILs can usually dissolve both polar and non-polar materials. In essence, ILs provide the possibility of invoking, within solution, a whole spectrum of interactions. These include ionic interactions, hydrogen bonding interactions, dipolar and dispersion induced forces and indeed furnishing a medium for aromatic solvation too.

Blanchard *et al.*[61] have recorded the solubilities of organic solutes in $[C_4mim][BF_4]$ at room temperature as are listed in Table 3.

Table 3 *Solubility of organic solutes in $[C_4mim][BF_4]$ at room temperature*

Solute in $[C_4mim][BF_4]$ at room temperature	Solubility/mole fraction of solute dissolved
Acetophenone	Miscible
Aniline	Miscible
Solid Phenol	0.69
Benzene	0.66
Hexanol	0.26
Cyclohexane	0.21
Nbu-O-Et	0.06
Solid Benzamide	0.04
Hexane	Immiscible

Examples can be found of ILs of differing types in respect of their coordinating ability and their inherent miscibility (which increases with temperature) with water. Complex bi- and indeed multi-phasic systems can be conceived owing to the range of properties exhibited. Thus ILs containing anions which are basic, such as $[C_n mim][NO_3]$ or $[C_n mim]Cl$, will tend to coordinate well with ions in solution, in contrast to ILs like $[C_n mim][NTf_2]$ $[C_n mim][BF_4]$ or $[C_n mim][PF_6]$ containing anions which coordinate rather weakly. Strongly acidic anions when present in ILs (*e.g.* $[Al_2Cl_7]^-$) provide non-coordinating environments and hence metal salts are poorly soluble within these systems.

The OH- and OR- derivatised ILs have been found to be useful as solvents for sugars, cellulosic and lignin materials and amino acids, as well as for triglycerides. Cellulose is, for example, an important and *the* most abundant global biodegradable and biorenewable resource in existence. In fact, as Rhodes points out[45], it is our greatest potential carbon resource in order to replace fossil materials. It is used for the manufacture of fibres, membranes, tissues, paper, polymers, coatings and medical products but is extremely resistant to aqueous dissolution or to dissolution by the more conventional organic solvents (which then require disposal). Because of this, there are many current restrictions on its wider use. Whilst the current dissolution routes for cellulosic materials can involve safety, energy and environmental disadvantages, the potential has been noted whereby 1-alkyl-3-imidazolium acetates and chlorides show ability to dissolve cellulose with both ease and efficiency. Among examples are included: $[C_4mim]Cl$ [52], $[Amim]Cl$[53], $[C_2mim][HCOO]$[54], $[C_n mim][anion]:[C_n mim][CH_3COO]$, $n = 2$ and 4[55,56].

9.2 ILs in their role as extractants and separators of chemicals from aqueous and organic media

Because of their properties, ILs have important applications as solvents in the industrial arena[58,59]. ILs can be utilised effectively for the purposes of increasing the volatility difference between components that one wishes to separate by fractional distillation. This is particularly true for water- containing mixtures (*e.g.* alcohol–water) in view of the affinity which many ILs have for water. ILs can, for example, remarkably increase the volatility of the component with the lower boiling point, thus eliminating azeotropic behaviour. As an example we can cite the case where $[C_4mim][BF_4]$ is employed for the separation of ethanol–water azeotropes[60]. Jork *et al.*[60] also discuss selectivity of ionic liquids for use in solvent extraction procedures. Tailoring of ILs to perform with more and more specific liquid–liquid equilibria is almost certainly likely to result in numerous further applications emerging.

10. ILs in their role as hypergolic fuels and propellants

Hydrazine and its derivatives are currently selected as the fuels of choice for propellant systems for rockets. However, a number of undesirable complications in their use include their rather high vapour pressures which, in turn, introduce the need for careful management as well as a requirement to maintain complex handling procedures (particularly in view of their known carcinogenic and toxic properties) and being vigilant towards the attendant safety precautions. More specifically, fuels of the past have invariably been toxic being mixtures of hydrazine hydrate, methanol and water or triethylamine, aniline, toluidine systems with oxidisers being selected from among liquid oxygen, IRFNA (inhibited red fuming nitric acid–consisting of *ca* 83% NA + 14% N_2O_4 + *ca* 2% H_2O + 0.6% HF), WFNA, hydrogen peroxide and N_2O_4. The research history[62–75] in this area is littered with many abortive attempts at designing both the fuels and the oxidisers. This is what makes the discovery of the possible role of ILs as replacement fuels such a major milestone. Several improved factors that ILs introduce in this context make them well able to help trim budgets as regards the design and operation of space vehicles. ILs provide the likelihood of rich, exciting and varied, future research possibilities for use as monopropellants, bipropellants, heat and light sources, *etc.* and this field is just opening up. Much of the research is likely to be classified in the first instance. Bipropellants combine an oxidiser (*e.g.* liquid O_2) and a fuel (*e.g.* kerosene) and require separate tanks in order to store the propellant components. This, of course, requires separate pumps and controllers for delivery and is accordingly more expensive than the monopropellant delivery devices that ILs are heralding.

An exciting discovery, reported in 2008, was that ILs composed of dicyanamide, $N(CN)_2{}^-$ anions were capable of instantaneous ignition when contacted with 100% nitric acid as an oxidiser. Their low volatility, long liquid range, good chemical and thermal stability present the clear possibility that these systems might indeed be able to supersede hydrazine systems as mono- and bipropellants. A further advantage is that these IL systems could function under a range of conditions.

Hypergolicity is an historical term used to describe the *spontaneous* reaction of one chemical (the fuel or reducing agent) when contacted with another (the oxidiser). The reaction can take place within liquid–liquid, solid–solid or liquid–solid media. The importance of the discovery that ILs can serve in this capacity is destined to lead on to greener explosives, propellants and fuels which are far easier to manipulate. The result is also likely to herald modification and simplification of the design restrictions which currently apply to the design of propellant delivery systems for rockets and satellites. The fact that ILs can perform in this role means that control is then vested solely in their *chemistry* and not in any subsidiary initiation procedures previously necessary. These hypergolic reactions are virtually instantaneous and so they require no elaborate delivery, ignition systems or devices. Thus a droplet of IL (as for example 1-methyl-4-amino-1,2,4-triazolium dicyanamide) hitting the surface of WFNA (white fuming 100% nitric acid) leads to ignition of between 15 and 31 milliseconds–contrast this with the previous ignition target time goal of 50 milliseconds which had to be achieved using peripheral ignition devices!

Significant research has taken place recently on new green monopropellant formulations[76] with promising results, and currently in Europe there are a number fully developed showing improved physical properties and better performance than hydrazine as well as being 10% denser than classical bipropellant systems. These new propellants are safer and more environmentally friendly and full flight evaluation is imminent.

Monopropellants are liquids which consist of a single compound including both fuel and oxidiser[77]. Once contacted with a catalyst such as Shell-405, Ir/Al_2O_3 they react hypergolically[78]. The target for current research in our Munich laboratories (and elsewhere) is the development of new monopropellants which are non-toxic and which exhibit at least equivalent and possibly enhanced performance over hydrazine and having decreased sensitivity enabling their use as rocket propellants. ILs, or at least ''energetic'' ILs (EILs), can nicely fulfil this role. Indicative of candidates to serve as EILs are the thermodynamic property of possession of a high and positive standard enthalpy of formation, $\Delta_f H^\circ(\mathrm{IL,\ l}) \gg 0$ coupled with a high density.

This criterion enables theoretical studies to be made in advance of experimentation and the acquisition of thermodynamic data for IL materials is proceeding at a tremendous pace–as has recently been indicated in a recent review by the author[37]. In addition to the experimental work, volume-based thermodynamics, VBT[41−44] is currently under further development so as to adapt it to be specifically applicable to ILs. Since only long-range Coulombic interactions are treated currently in VBT if we are to encompass ILs within the theory we need to incorporate dispersion (R^{-4}, R^{-6} and R^{-8}) interactions within the theory. Izgorodina[80] has suggested that the α parameter [in equation (4) of the VBT equation] should vary for ILs depending on the symmetry of the ion packing in the crystal structure.

$$U_{\mathrm{POT}} = 2I[\alpha V_{\mathrm{m}}^{-1/3} + \beta] \tag{4}$$

VBT, when treating some ILs, particularly protic ILs, because it currently does not adequately model the hydrogen bonding between the ions, may well generate lattice energies, U_{POT}, which are unsatisfactory and this in turn could, in turn, influence some thermodynamic predictions made. It is not any failure on the part of VBT that makes it currently not quite suitable for ionic liquid treatment since it was devised to handle thermodynamics of *ionic solids* originally. What is proposed, therefore, is that we mount an initiative in order to study the application of VBT to ILs. The key objective will be to retain the simplicity of form (and consequent ease of use by non-specialists) and for this purpose a team is being assembled consisting, *inter alia*, of Jenkins (Warwick and Munich), Klapötke (Munich), Stierstorfer (Munich), Krossing (Freiburg), Beichel (Freiburg), Eiden (Freiburg), Verevkin (Rostock) and a number of other colleagues. Despite these limitations, VBT *has* been applied in the preliminary study of conductivity and viscosity[83,84] by Krossing and the findings reveal that the viscosity η and conductivity, σ are, for example, linearly correlated to the formula unit volume, V_{m} by the relationships (5) and (6) of the form:

$$\eta = a \exp(bV_{\mathrm{m}}) \tag{5}$$

$$\sigma = c \exp(-dV_{\mathrm{m}}) \tag{6}$$

where a, b, c and d and constants which were *anion* dependent and average errors were believed to be 26 cP and 0.2 mS cm^{-1} respectively. Other studies have followed a similar volume-based approach[85,86] and discussed the effect of impurities, particularly on transport properties[87].

In addition large scale, fully *ab-initio* computational approaches are being developed for ILs as indicated in the next section.

11. ILs treated using Large-scale, fully *ab-initio* calculations

A thorough overview of current theoretical approaches, including VBT[41–44], for the study of thermodynamic properties such as melting point and enthalpy of vaporisation and of transport properties such as conductivity and viscosity has been published recently by Izgorodina[80].

Her article is a critical review and usefully discusses strategies for enhancing the predictive power, as well as the versatility, of the current methods. Izgorodina points out the immense task ahead involved in synthesising and validating the estimated 10^{19} ILs potentially available, noting that this would take centuries! Furthermore, by no means all, but indeed only a small fraction of these ILs will be lead to actual useful and practical applications by virtue of the need for them to possess the appropriate combination of suitable properties. What better justification then can there be than the above to drive an initiative for theoreticians to develop robust (as well as more approximate, but indicative) computational approaches to investigate essential properties of these interesting materials?

The task ahead is by no means simple, indeed the influences caused by various substitutions of cations or anions within the ILs has been shown to influence thermodynamic and transport properties in a highly complex and not always obvious manner[81,82]. This observation places stringent requirements on the evolving theoretical approaches, namely that any methodology developed such be adequately and thoroughly tested.

Molecular dynamics has been employed to simulate ILs and their transport and thermodynamic properties[88,89]. The technique used is one which represents the potential energy of the system in an analytical form (denoted as the force field). Each term in the force field is determined by the types of interaction likely to be found within the liquid treated. Some of the parameters are evaluated by using gas phase treatments to model interactions and this enables some specific ionic IL interactions to be neglected in some cases. Again hydrogen bonding interactions can prove to be the most difficult to include satisfactorily in such calculations. Adopting Car–Parrinello Molecular Dynamics (CPMD)[90] procedures can avoid the necessity for parameterisation since the force field is replaced by an actual quantum mechanical calculation (*ab initio* Molecular Dynamics). The latter approach has advantages over conventional MD calculations, these being that:

- local structures are better modelled
- versatility is introduced (no prior knowledge of experimental data is required).

Gordon[91] has also produced a review of fully *ab initio* approaches and of those hybrid approaches which combine quantum and molecular mechanics (QM/MM). A useful critique of the future of molecular simulations of ILs is provided within Izgorodina's review[80].

12. ILs in electrochemical devices

Electrochemical devices of one kind or another offer enormous potential towards the creation of alternative sources of energy, driven, of course, by depletion of natural energy resources such as coal and oil and also by pending climate change caused by CO_2 pollution. The nature of the electrolytic components used in these devices is such as to cause them to have to satisfy a number of criterion which include:

- exhibiting negligible vapour pressure and therefore low volatility;
- showing high conductivity;
- possessing low viscosity;
- having high electrochemical stability;
- possessing a low melting point (although the development of solid electrolytes in solar cells suggests, perhaps, that this last criteria is less important).

From our earlier discussion it will be clear that ILs satisfy most, if not all of these properties. ILs certainly are found to surpass, performance-wise, traditional electrolytes and they are rapidly replacing these electrolytes in many areas involving high efficiency energy storage and generation. Such applications include solar cells (DSSCs–dye sensitised solar cells) and lithium batteries as is described below.

ILs in dye sensitised solar cells–DSSCs

This has been an active area of research since 2003 when Graetzel *et al.*[92] and his co-workers reported that ILs, when used as electrolytes in DSSC devices, gave comparable conversion rates of solar to electricity generation ratios as did conventional solar cells. DSSC cells are photovoltaic and involve a dye (often a ruthenium bipyridyl complex) activated by light which mimics photosynthesis (*i.e*. adopts a similar role as chlorophyll does in plants)[93,94]. Graetzel *et al.*[92] initially employed an electrolyte consisting of lithium iodide mixed with [C_2mim][dca] and [C_3mim]I. ILs really need to possess low viscosities for use in such cells as these and accordingly, since ILs involving I^- and I_3^- ions have high viscosities and impose performance limitations, other IL electrolytes were sought. For example, [C_3mim]I has a high viscosity of some 880 cP. Accordingly, [C_2mim][SeCN], having a viscosity of only 25 cP at ambient temperature, when used as an electrolyte was demonstrated[95] to achieve a conversion efficiency of near 8% and higher. By the end of the decade, Graetzel and his co-workers were achieving conversion ratios of up to 9.5% and stability of up to 40 days, using a modified ruthenium bipyridyl dye, an electrolyte involving an IL, [C_3mim]I and the organic solvent 3-methoxypropionitrile.

ILs in lithium batteries

Among rechargeable energy delivery systems, lithium batteries have the highest energy-density ratio. Their anode is usually graphitic in nature and the cathode involves a transition metal Li oxide material such as $LiNiO_2$ or $LiCoO_2$ with an electrolyte which is a mixture of ethylene carbonate (employed in order to prevent the electrolyte from suffering reduction by creating a passive film over the graphite anode) and an electrochemically stable Li salt (such as $LiPF_6$) dissolved in, for example, dimethyl carbonate acting as an organic solvent. The latter however can present both a safety risk (volatility and hence ease of flammability) and also affect adversely the temperature range over which such batteries can be used. Since ILs maintain their fluidity over a considerable temperature range and also are much less flammable than typical organic solvents, they have been candidates to replace the organic solvent media in Li-ion batteries. Thus, for example, the IL [C_2mim][Tf_2N] when used as solvent for the Li salt electrolyte with an intercalation promoter (such as vinylene carbonate) added in small amounts provides us with a battery[96] whose performance at least equals the more traditional systems. A complex and reversible intercalation process involves the Li ions being incorporated and then released from within the (layers of) graphite electrolyte.

13. ILs in polymerisation

Not surprisingly ILs have been trialled as media for polymerisation reactions. In 2000, my colleague, Dave Haddleton at Warwick[97] demonstrated the first example of (rapid) living radical polymerisation within IL media and showed how products could then be relatively easily extracted into toluene–with no catalytic contamination taking place either. They used the IL, $[C_4mim][PF_6]$, as a solvent for the living free radical polymerisation of methyl methacrylate and catalysed the polymerisation by means of a copper(I) salt. Termination within living polymerisations is characteristically either non-existent or incredibly slow to occur. Within such systems therefore, can be achieved the synthesis of multiply branched functionalised macromolecules whose molecular architecture can be particularly finely controlled and accordingly narrow molecular weight distributions are thereby achieved. Moreover other polymerisations were investigated by others and co-polymerisations and ring-opening polymerisations can be achieved within IL media. Commercially, $[C_4mim][PF_6]$ is known to be an efficient plasticiser for poly(methyl methacrylate)[98].

14. ILs in other guises

In this final section, in order to ensure, albeit briefly, that a reasonably full picture is provided in this review of the full scope of the potential presented by these remarkable ILs, we give now snapshot glimpses of further uses and applications. For further information on these topics resort should be made to the wider literature.

ILs can be utilised as a replacement for formalin, used to preserve tissue[99]. Drugs for the treatment of HIV and similar viruses are based on natural nucleosides but these materials are poorly soluble in conventional organic solvents. The search for new drugs is much hampered by the fact that better solvents (like DMSO and DMF, for example) are themselves toxic. ILs are proving to be much superior solvents and the reactions carried out within them are faster and, moreover, the actual amount of solvent needed is then cut down by factors of 8–10[100].

> IL cations present in the IL structure have been related to antimicrobial activity[101].

Conventional liquid-in-glass thermometers have limitations in their use and in the range of temperature they cover. ILs $[TEMA][CH_3SO_4]$ and $[P_{6\,6\,6\,14}][Tf_2N]$ have both been proposed[102] as thermometric liquids and they extend the range, the former being stable between −81°C to 200°C and the latter between −76°C and 400°C. The colourless liquids can easily be made visible by dye addition.

> ILs can make useful lubricants[103], because of their low flammability. They are safe to use in confined spaces like tunnels and mines.

> ILs are virtually incompressible and can be used within a cylinder as a compressant. If the IL selected is completely immiscible with a gas under compression, one can do away with seals and lubrication[104].

> ILs have been use in several instances for mass spectroscopy, specifically for ESI-MS and MALDI-MS applications.

It has proved possible to exploit the various physical properties of ILs and their solubility for the development of sensors for gas detection (*e.g.* ammonia in the detection of food deterioration, medical diagnosis and automotive applications).

Promotion of enzyme catalytic and biotransformation reactions have featured widely in IL research although the extent of their use in the biotechnology area has yet to be fully determined. Much research here is ongoing.

Numerous organic reactions have benefited from the involvement of ILs and some of these are listed alphabetically by name: Aldol Condensation; Baeyer–Villager Oxidation; Baylis–Hillman reaction; Beckmann rearrangement; Diels–Alder reaction; Friedel–Crafts reaction; Grignard reaction; Heck reaction (one of most widely studied in respect of ILs); Knoevenagel Condensation; Mannich Reaction; Michael Addition; Robinson Annulation; Sonogashira coupling; Stille coupling; Suzuki cross-coupling; Swern oxidation; Ullmann coupling; Wacker oxidation and Wittig reaction. In terms of general (unnamed) reactions, the following have seen ILs used as solvents/catalysts: aromatic nitration; alkylation; cracking; cycloaddition; debromination; dimerisation; electrophilic reactions; epoxidation; esterification; etherisation; halogenation; hydroformylation; hydrogenation; hydrosilylation; nucleophilic reactions; olefin metathesis; oligomerisation; oxidation and peptide synthesis, although this list is not exhaustive.

> Photochemical reactions can be carried out, and often electron transfer processes are assisted by virtue of the polar nature of ILs.

> Chemical synthesis of peptides has been achieved in ILs[105].

> Catalytic oxidation of alcohols, aldehydes, alkanes and olefins can be carried out in ILs[106,107].

> In 2000, it was demonstrated that ILs can be used to prepare porous materials such as silica aerogels using $[C_2mim][Tf_2N]$ as solvent[108].

Further areas where ILs can contribute include nuclear chemistry, the control of the physical and chemical properties of nanoparticles and microspheres, aspects of coordination chemistry and the study of organometallic compounds and, of course, in catalytic aspects of chemistry.

Other fascinating features of ILs is the fact that they essentially consist of a separate cation and an anion species. Such duality of composition means that the possibility exists to ‘‘build in’’ to either one of these ions present appropriate, chemical, biological or physical properties. This idea in itself will, undoubtedly, lead to much more sophisticated as well as efficient drug delivery systems which are increasingly specific in their purpose and targeted organ. In itself this represents an entirely new realm of chemistry for the future. It heralds major initiatives and influences on pharmaceutical developments.

In summary then, these IL materials can offer advantages across all major science areas including materials science, electrochemistry, organic, inorganic, bio and materials chemistry. They are often readily reclaimable following their use in solvation or catalytic processes. They also present us with a novel opportunity to study chemistry within a liquid medium at temperatures below 100°C.

To date, less than 1600 ILs have been characterised, it has been estimated that at least 10^{19} seem possible. They remain thermally stable at temperatures higher than more conventional covalent solvents as well as possessing a wider range of solubility than do ordinary solvents and are often much more miscible, offering examples of both hydrophobic and hydrophyllic solvents. In this sense, they offer us new types of media in which to carry out reactions.

As well as exhibiting catalytic activity for many chemical reactions, they find use as replacements for conventional toxic solvents. They can be used to avoid and prevent chemical pollution.

Chirality can sometimes be induced within them, enabling their use to provide asymmetric synthetic targets. Racemate resolution is sometimes achievable using chiral ILs.

There are, inevitably, occasional downsides since, for example, some ILs can react with water and consequently may need manipulation in a dry N_2 box. Others (*e.g.* [diethylimdazolium] $[PF_6]$) can undergo hydrolysis in water to produce hazardous hydrogen fluoride under certain conditions!

Aprotic ILs are composed of non-protonated cations coupled with anions and these represent the more usually encountered materials although protic ILs are exemplified by [1-methylimidazolium][BF_4] = [Hmim][BF_4] or ethylammonium nitrate [$EtNH_3$][NO_3], being the first example of an organic salt having a melting point less than 100°C. Sometimes, if during synthesis incomplete proton transfer is observed then the latter ILs may contain molecular as opposed to ionic species but this is usually only in small amounts.

Once, having achieved creation of individual ‘‘designer’’ ILs there follows then an almost infinite possibility to create yet further ‘‘designer’’ properties by mixing of these liquids in a whole range of ratios. Watch this space as more fascinating properties and applications reveal themselves ..!!

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