Ionic liquids: Some of their remarkable properties and some of their applications

Owen J. Curnow

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140 (email: *owen.curnow@canterbury.ac.nz*)

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Introduction

Ionic liquids are a fascinating class of materials which, although they have been known about since 1914,[1] have only come to prominence over the last decade or so. Commercially, electrochemical applications (e.g., non-volatile electrolytes for batteries) represent just one area in which there is significant interest. Publications and patents have grown dramatically since 2000[2] (there have been over 15,000 papers and well over 1,000 patents on ionic liquids!) and there are now many books on the topic.[3,4] The somewhat arbitrary definition of an ionic liquid (IL) is that it is a salt [R]X with a melting point below 100 °C. It would be tempting to define them as those that are liquids at room temperature (these are called room temperature ionic liquids (RTILs)); however, in practice even salts with melting points above 100 °C are potentially useful. Most commonly, an IL consists of an organic cation $[R]^+$ and an inorganic anion X^-. Figure 1 illustrates the most commonly used cations.
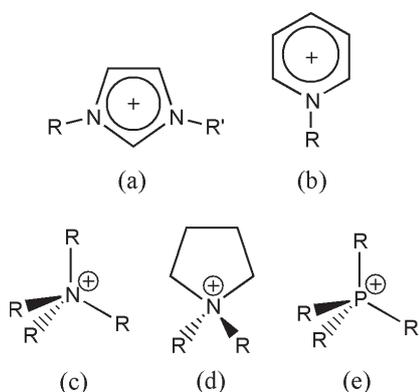

Fig. 1. Common classes of cations used in ILs: (a) imidazolium, (b) pyridinium, (c) ammonium, (d) pyrrolidinium and (e) phosphonium.

There are several factors that make ILs particularly interesting and potentially useful. As salts, they have almost no vapour pressure. Not only does this inhibit their release into the environment, but it also provides for interesting new applications. An example is fine control for jet propulsion in space (having essentially no vapour pressure, the ejection of liquid can be easily controlled), as well as applications more relevant on earth (discussed below). ILs also conduct electricity and this, coupled with their low volatility and high electrochemical stabilities (especially the imidazolium salts), makes them of interest for battery applications, dye-sensitised solar cells and a host of other related applications. Additionally, it is relatively easy to tune the properties of an IL by either changing the substituents on the cation or exchanging the anion; there are many thousands of readily prepared ILs. Inter-

estingly, ILs are usually very good solvents – some can even dissolve up to 20% by weight of cellulose, normally a difficult-to-dissolve structural polymer. Generally, they are very similar in terms of their solvation properties to common polar organic solvents such as dichloromethane, ethanol and acetonitrile. However, while you can make ILs that are soluble in water but immiscible with non-polar solvents such as hexane, you can also make ILs that are immiscible with water but soluble in, or even miscible with, hexane!

Historical background

Despite the relatively long time since the first publications about ILs, two very early reports on ionic liquids and their properties have been key to the progress made in the last decade or so. The first IL was, in fact, reported in 1914 by Paul Walden using the reaction of ethylamine with nitric acid to give ethylammonium nitrate ,which has a melting point of just 14 °C.[1] This IL is now recognised as belonging to a class of ILs termed protic ionic liquids (PILs) owing to the presence of a hydrogen-bonding NH group.

$$EtNH_2 + HNO_3 \longrightarrow [EtNH_3]^+ + NO_3^-$$

Non-protic ammonium salts $[NR_3R']X$ are readily prepared by alkylation of tertiary amines NR_3 with alkyl halides R'X:

$$NR_3 + R'X \longrightarrow [NR_3R']^+ + X^-$$

In 1934, a US patent described the use of halide salts of nitrogen-containing bases as solvents for the dissolution of cellulose and uses of these solutions.[5] Examples included 1-ethylpyridinium chloride (prepared from pyridine and chloroethane). Today, significant resources are being put into the dissolution and regeneration of cellulose using ILs, as cellulose-derived materials are structurally strong, biodegradable and environmentally friendly.[6,7] This is potentially of great benefit to the New Zealand economy because of our significant cellulose resources. The anion is important in the dissolution process: chloride and acetate anions, for example, are able to break up the cellulose interactions due to their hydrogen-bonding ability.

It was quite some time before more advances were made in IL technology. In the 1970s and 80s, chloroaluminate anion mixtures $Cl^-/[AlCl_4]^-/[Al_2Cl_7]^-$ were described for use as battery electrolytes;[8] firstly using pyridinium cations, but then using the more electrochemically stable imidazolium cations. Unfortunately, these are very water-sensitive materials and the area remained quiet for a few more years after these electrolytes were developed.

Wilkes and Zaworotko presented a landmark paper in 1992 on air- and water-stable imidazolium-based ionic liquids.[9] The significant change was the use of water- and air-stable anions such as acetate, nitrate and $[BF_4]^-$. Consequently, we now had stable salts that are liquid at room temperature, as well as having a wide electrochemical window (this defines how easily they are oxidised and reduced). Since then, a wide variety of anions have been developed. Interestingly, although the focus in the IL literature is often on the cation, it is usually the anion that is most influential in determining the properties of the ionic liquid. Varying the alkyl chain lengths on the organic cation, for example, is usually used to fine tune the properties, whereas changing from a hydrophilic anion (such as nitrate) to a hydrophobic anion (such as $[PF_6]^-$) leads to a large change in solubility and other properties. Figure 2 shows a selection of anions with which many chemists would be unfamiliar, but which are now commonly used for producing ILs.
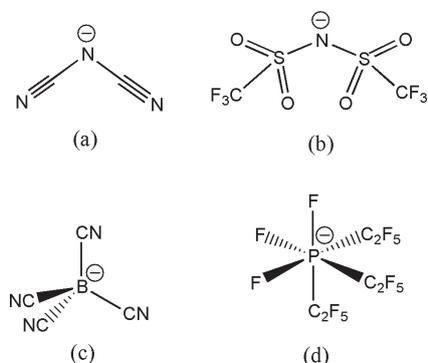

Fig. 2. Common anions used for ILs: (a) dicyanamide (DCA), (b) bis(trifluoromethanesufonyl)amide (TFSA, TFSI or NTf_2^-), (c) tetracyanoborate and (d) tris(pentafluoroethyl)trifluorophosphate (FAP).

Melting points and viscosities

The reason for using such exotic anions is a desire for low melting and low viscosity materials, since these are ILs that are easy to handle (transfer, stir, etc.) and have high conductivities (making them useful for electrochemical applications). The factors affecting melting point and viscosity are complex and, quantitatively speaking, poorly understood. The most common technique to lower the viscosity is to reduce the molecular weights of the ions; however, this generally raises the melting point owing to the increased ionic attractions. Consequently, there is a balancing act required to obtain the lowest viscosity ILs without the melting points being too high. As the ions get smaller and ionic attractions increase; this can be counteracted by using ions with delocalised charges to spread out the charge and reduce the electrostatic attractions. The imidazolium and pyridinium cations, as well as the anions like those shown in Fig. 2, are, therefore, well-suited for preparing RTILs. Additionally, decreasing the symmetry (imidazolium cations) reduces crystallinity, and so also lowers the melting points, as does increasing the conformational flexibility of the ions (compare FAP and TFSA to DCA and $[B(CN)_4]^-$, or *n*-propyl to isopropyl). Symmetry and shape also play a role in determining the viscosity of a liquid; remarkably, these factors are especially poorly understood.

So what are the viscosities of typical ILs? This is certainly one aspect that often concerns scientists when considering whether or not to use an IL. Compared to water with a viscosity of 0.83cP at 25 °C, a viscosity of 32cP for 1-ethyl-3-methylimidazolium TFSA ([EMIM]TFSA) seems high.[10] However, you should compare it to olive oil at about 80 cP, 10W40 motor oil at about 250 cP, and tomato sauce at about 75,000 cP! Also, viscosities decrease significantly as the temperature increases (Fig. 3[11,12]) and even a small increase above room temperature is greatly beneficial.
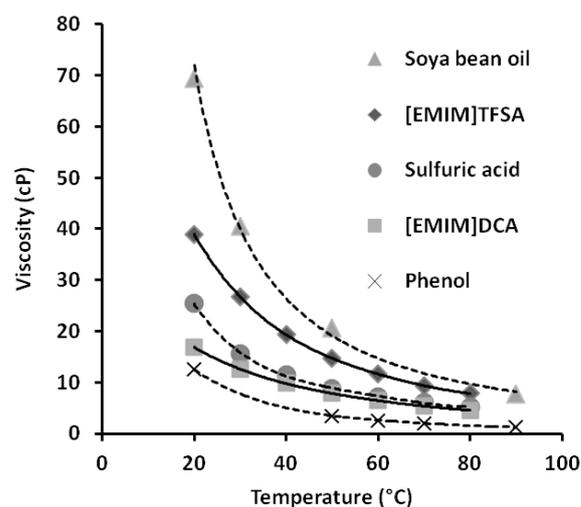

Fig. 3. Plot of viscosity versus temperature for [EMIM]TFSA, [EMIM]DCA and some common liquids.

Another interesting aspect to consider when optimising the melting point is that while lower molecular weights raise melting points, so do higher molecular weights. This is, of course, attributed to the increasing van der Waal's interactions. Thus, there is frequently an optimum alkyl chain length for low melting points.

The liquidus range – the temperature range at which a compound is liquid

Given that ILs are essentially non-volatile (none have measureable boiling points at atmospheric pressure), the upper level of their liquidus range is determined by their thermal decomposition temperature (this is often reported as the onset decomposition temperature as the temperature is raised by 10 °C/min); the weight loss is measured by Thermal Gravimetric Analysis (TGA). It can often be more than 400 °C in an inert atmosphere. However, generally of more relevance to practical applications is ILs' isothermal decomposition behaviour, i.e., how quickly an IL decomposes at a fixed temperature. Unfortunately, these measurements are relatively time-consuming and so are not usually reported. Practical upper limits for the liquidus range of ILs are more typically about 250 °C. Nonetheless, that still gives ILs a very large useful liquidus range compared to common molecular liquids. Whereas the alkyl chain length affects the melting point, the upper limit of the liquidus range is most affected by the anion, as decomposition temperatures decrease with increasing nucleophilicity of the anion.

A brief and incomplete discussion of applications

The variety of potential applications for ILs is quite incredible.[2,4] It seems that almost any process involving a liquid or solvent can use ILs. Here, I briefly summarise only a few that I think are interesting and/or important. A partial list of applications already in use, but not discussed further here, includes: the gas company Linde has liquid pistons in which ILs act as functional fluids for the compression of gases; the Swiss company Novasina uses ILs as sensor electrolytes; BASF uses the BASIL process to prepare the photoinitiator precursor alkoxyphenylphosphines on the multi-tonne scale; ionikylation is a process for the alkylation of four-carbon olefins with isobutane – Petrochina operate a 65,000 tonne per year plant; the Difasol process is an add-on to the Dimersol process to dimerize short chain alkenes into branched alkenes; and the company Air Products uses ILs instead of pressurised cylinders as a transport medium for reactive gases such as trifluoroborane, phosphine and arsine.

### Electrochemical applications

These are generally considered the most commercially important. This is because of the inherent conductivity of the ILs, as well as their non-volatility. Typical electrochemical applications are in dye-sensitised solar cells, fuel cells, electro-optics, lithium-ion batteries and electrolytes for metal plating. An important requirement here is that the liquid is stable to a wide range of redox potentials, i.e., it has a wide electrochemical window. Electrochemical windows vary significantly: they can be as large as 6 V but are typically 3–5 V. This compares to 2.4 V for water and 5.0V for acetonitrile.

Applications in chiral syntheses

There have been few applications in chiral syntheses, though research in the area is very active.[13] It is relatively easy to make a chiral ionic liquid (CIL) in which either or both the cation and anion are chiral. Alkylation of amino acids, for example, generates ammonium CILs when combined with appropriate anions (Scheme 1[14]) while deprotonation of an amino acid and combination with an appropriate cation generates ILs in which the anion is chiral (Scheme 2[15]). There are many other inexpensive sources of chirality for ILs.[19]
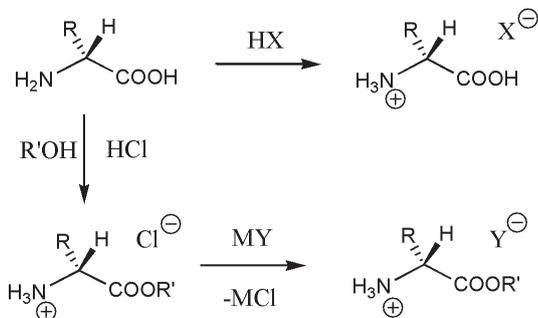
Scheme 1. Generation of ILs with chiral cations.
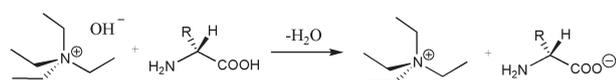
Scheme 2. Generation of ILs with chiral anions.

Depending on the mechanism of the process, it may be advantageous to use a CIL to enhance enantioselectivities. This area is clearly of much significance to the pharmaceutical industry. I should note that chiral molecular solvents, on the other hand, are rare and very expensive. Surprisingly, there has been very little work on combining CILs with chiral organometallic catalysts which are often used in the pharmaceutical industry to introduce chirality.

Potential lubricants

As potential lubricants, ILs usually have much greater thermal stability than petroleum-based oils. However, owing to their greater expense, they are most likely to be used as additives or in specialty high temperature applications. The ionic nature of ILs has an interesting and useful impact on their properties as lubricants. For example, the use of phosphate or sulphate anions with hydrophobic cations generates a system in which the anion interacts with the two metal surfaces that are trying to come into contact while the cations are sandwiched in between (Fig. 4).[16] This results in less friction and less wear and tear on the two surfaces.
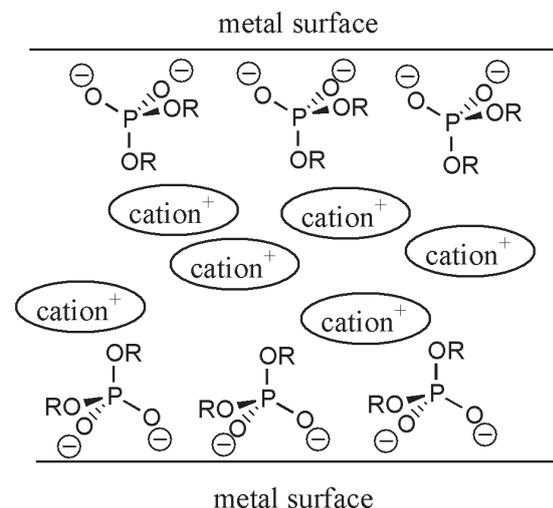

Fig. 4. A phosphate IL between two metal surfaces.

Chromatography

 ILs can be used as the stationary phase for GC and HPLC columns. Their non-volatility as well as the ability to tune the properties of the IL, most notably to introduce chirality, give them ideal properties for these applications.

Microwave chemistry

It is well known that water and other small polar molecules readily absorb microwaves. Remarkably, ILs absorb microwaves to a much greater extent than water.[17] Whereas water may take a minute or so to boil in a conventional microwave, an IL will reach the same temperatures in a matter of seconds. The high liquidus range of ILs means that very high temperatures can be reached very quickly. I suspect that many applications that take advantage of this property are still to be realised.

Catalysis

As well as providing a new class of solvents, ILs also provide a new method called supported ionic liquid phase catalysis (SILPC).[18] In this method, a thin layer of IL is

adsorbed on small particles of alumina, for example, and this is then placed in an organic medium in which the IL is insoluble. An organometallic catalyst is dissolved in the thin layer of IL. The large interfacial area between the IL and the organic solvent means that organic substrates are able to readily access the catalyst and the products can quickly return to the organic phase for subsequent separation (see Fig. 5). It can be viewed as a homogeneous version of heterogeneous catalysis!
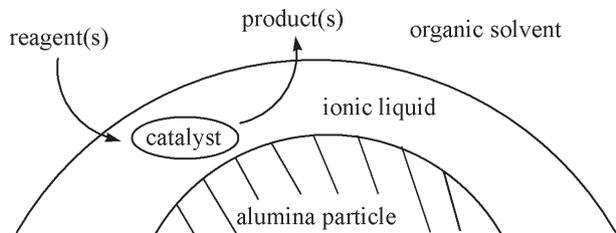

Fig. 5. Schematic of supported ionic liquid phase catalysis (SILPC).

Biochemical applications

Early investigations suggested that ILs are poor solvents for enzymes, as the enzymes were rapidly denatured. However, subsequently it was found that many enzymes are, in fact, stable in ILs when the IL is carefully chosen, and there is now a lot of highly-competitive research in this rapidly growing field.[19]

The cost

Another factor affecting the take-up of IL technology is, of course, their cost. Fortunately, costs have decreased significantly in recent years as demand has led to larger multi-ton production runs. For the research chemist, there is now a large variety of affordable ILs in fine chemical catalogues.

How green is green?

One of the attributes commonly applied to ILs is that they are "green solvents". Regrettably, this is somewhat of an over-statement. Like many materials, they certainly have aspects to them that can be taken advantage of to enhance the 'greenness' of a process. For example, they are essentially non-volatile, and this hinders their release into the environment; also, they can be easy to recycle and reuse. However, they are not intrinsically green. Not only is it relatively trivial to design highly toxic ILs, but toxicity studies on ILs in general are still at an early stage. Perhaps more of an issue is that, should an IL be released into the environment, their non-volatility and high stabilities can make them difficult to remove.

Our research at Canterbury

At Canterbury, we have developed a new class of ILs based on the triaminocyclopropenium (tac) cation, $[C_3(NR_2)_3]^+$.[20] These simple cations are readily prepared from pentachlorocyclopropane (or tetrachlorocyclopropene) and a secondary amine (Scheme 3).

The ammonium by-product can be removed by a number of methods, depending on the amine. Ammonium salts of volatile amines can be removed *in vacuo* after neutrali-

sation with base, whereas other ammonium salts require crystallisation or solvent extraction procedures for their removal. Conversion of the chloride salts to other anions is generally quite easy, although removing the last of the chloride can be problematic in some instances. Anions of strong aqueous acids (HBr, HBF_4, HNO_3, etc.) can be introduced by addition of the aqueous acid followed by extraction of the IL with an organic solvent. When the acid is not readily available, addition of the corresponding group 1 or silver metal salt followed by organic extraction is usually the favoured procedure.
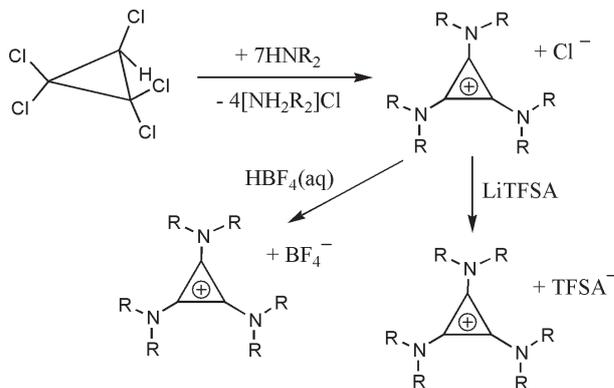
Scheme 3. Synthesis of tac ILs.

Despite the ring strain of the three-membered ring, these cations are incredibly stable: they can be heated to reflux in water; some salts have thermal decomposition onset temperatures (T_d) as high as 400 °C; and they have good electrochemical windows with low reduction potentials. The reason for this stability is the charge delocalisation on the three carbon and three nitrogen atoms, as well as the aromaticity of the 2π-electron cyclopropenium system.

The ILs presented in Table 1[20] have very good T_d values and acceptable melting points. The viscosities are typical of many ILs; unfortunately, they do not approach those of the least viscous ILs (Fig. 3). Our ability to manipulate specific properties of these ILs gives us enormous potential to target specific applications.

Table 1. Data for selected tac ILs.

Compound	T_m (°C)	T_d (°C)	Viscosity at 20 °C (cP)	Viscosity at 60 °C (cP)
$[C_3(NEt_2)_3]BF_4$	27	377	210	29
$[C_3(NEt_2)_3]TFSA$	23	393	95	20
$[C_3(NPr_2)_3]BF_4$	81	397	–	–
$[C_3(NPr_2)_3]TFSA$	34	409	220	32
$[C_3(NBu_2)_3]BF_4$	34	373	–	90
$[C_3(NBu_2)_3]TFSA$	7	400	230	38
$[C_3(NBuMe)_3]BF_4$	n.o.	374	360	40
$[C_3(NBuMe)_3]TFSA$	n.o.	386	105	20

Summary

My last four or five years as a researcher in ionic liquids have been quite fascinating. As a synthetic organometallic chemist who was used to purification by distillation or crystallisation, dealing with ILs that will neither distil nor crystallise (rarely, anyway) has frequently proven to be a challenge! Fortunately, of the one hundred or so ILs

that we've now produced, only a handful have not (yet) been successfully purified. The future of ionic liquids is very bright and getting brighter. Increasingly, ILs find themselves in significant commercial applications and the costs of ILs continue to decrease. And I haven't even mentioned the chiral-magnetic-luminescent or hypergolic ILs!

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