Lewis base ionic liquids†

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Ionic liquids which are (weak) Lewis bases have a number of interesting and useful properties different to those of traditional ionic liquids, including volatility and the possibility of being distillable in some cases, a base catalysis effect in others and enhancement of the acidity of dissolved acids.

1. Introduction

Ionic liquids (IL), being salts with melting points below 100 °C, have been much discussed of late for a variety of applications.[1,2] Typically those in widespread use involve anions, such as tetrafluoroborate, hexafluorophosphate, chloride and bis(trifluoromethanesulfonyl)amide, which originate from very strong acids. These ionic liquids are typically of high thermal and electrochemical stability and very low volatility. The range of solvent characteristics attainable, including hydrophobicity, hydrophilicity, low viscosity, high conductivity and wide electrochemical window continues to expand with each new ionic liquid discovered. There is also significant interest in the development of "task specific" ionic liquids,[3] where the anion and/or cation is designed to impart specific properties to the ionic liquid, such as chirality,[4] or improved extraction or separation capabilities.[5,6]

The design and choice of ionic liquids commonly focuses on physical properties such as water-miscibility, conductivity, viscosity and solubility properties, although how the chemical structure of the ionic liquid affects these various characteristics is still poorly understood. However, there is another chemical property that imparts a variety of physical characteristics to the ionic liquids that has been little investigated; the relative acidity or basicity of the component ions. The commonplace starting point that many of the ions are inert is not always correct as one looks farther afield for task specific ions. Here we describe our recent work with a range of anions and cations having distinct Lewis acidity or basicity and discuss how these properties affect the properties and applications of the ionic liquids. We have demonstrated that ionic liquids containing Lewis base anions can exhibit a base catalysis phenomenon, which can be utilised, for example, in a variety of acetylation reactions. Further, we have investigated a range of ionic liquids using different pH indicators to determine the relative state of dissociation of acids in the ionic liquids. The ionic

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liquids can exhibit significantly different behaviours, which allows us to categorise them in terms of a relative order of anion basicities. In the case where the cation is protic, some of these basic ionic liquids also become volatile and distillable and we examine the conditions under which this can occur.

The majority of ions used in the formulation of ionic liquids can be considered in terms of the Lewis definition of acids and bases; *i.e.* whether they are capable of accepting or donating an electron pair. However, there are also a number of ions that must be considered according to the Brønsted definition; those that are able to donate or accept a proton. For example, here we also discuss a number of ionic liquids containing protonated cations. Anions that fall into this category include dihydrogen phosphate and hydrogen sulfate.

2. Classification of ionic liquids according to acidity/basicity

Neutral anions

Typical ionic liquid anions are those that can be described as "neutral" (in the acid/base sense) or "*very* weakly basic"; these exhibit only weak electrostatic interactions with the cation and thus impart advantageously low melting points and viscosities.

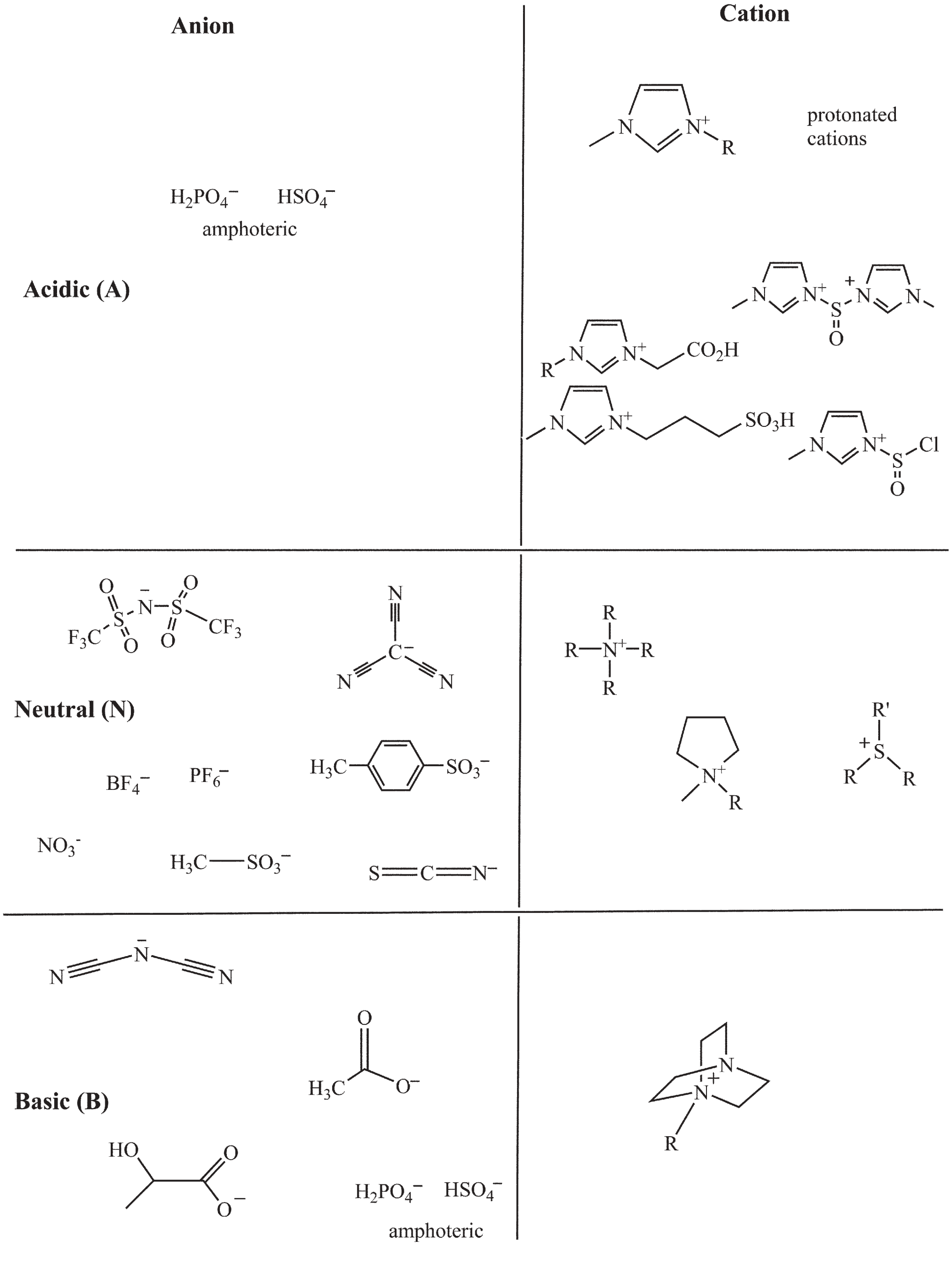

Fig. 1 Selected anions and cations categorised according to their experimentally observed Lewis acid/base properties. Acidic cations as described by Li *et al.*[7] Trialkylsulfonium cations described by Gerhard *et al.*[8]

Included in this class are anions such as hexafluorophosphate,[9–13] bis(trifluoromethanesulfonyl)amide (TFSA, also known as TFSI and $(tf)_2N^-$),[14–16] tetrafluoroborate,[9,17–19] methanesulfonate (mesylate),[20–22] thiocyanate,[23] tricyanomethide[24,25] and *p*-toluenesulfonate (tosylate)[22] (Fig. 1). Ionic liquids formed from these anions typically exhibit good thermal and electrochemical stability (electrochemical windows commonly over 4 V) and thus are often utilised as "inert" solvents in a wide range of applications.

However, as summarized in Fig. 1, there are also an increasing number of anions that do not fit into the "*very* weakly basic" category; some of which we discuss below.

Acidic cations and anions

The simplest examples of slightly acidic ionic liquids are those based on the protic ammonium, pyrrolidinium and imidazolium ions, of which many are known.[26–32] The well known $AlCl_3^-$ based ionic liquids are Lewis acidic when they contain an excess of $AlCl_3^-$. The slight acidity of the C2 proton in the dialkyl imidazolium ring is also well known and has been proposed as the source of some acid catalytic effects.[33,34]

Basic cations and anions

There are a number of ionic liquid forming anions that we can class as basic. These include the lactate,[35,27] formate,[36] acetate (and carboxylates generally) and the dicyanamide (dca) anion.[37] The dicyanamides, in particular, have become readily available because of their low viscosity, including as phosphonium salts. Since the basicity of these anions imparts different, advantageous properties to the ionic liquids, such as different solubilising and catalytic properties, as discussed below, this category of ionic liquids is likely to grow considerably in the coming years.

An alternative to the design of ionic liquids utilising a basic anion is to incorporate a basic site into the cation. This may afford more thermally stable ionic liquids than those containing basic anions, which frequently exhibit relatively low decomposition temperatures. We have thus recently reported a range of salts utilising the 1-alkyl-4-aza-1-azoniabicyclo[2.2.2]octane cation [$C_n$dabco] in combination with the TFSA anion (Fig. 2).[38]

Remarkably, the ionic liquid formed from the ethyl-substituted dabco cation is, contrary to other reported TFSA salts,[39] water soluble. This hydrophilicity is likely to reflect significant hydrogen bonding between the water molecules and the tertiary amine nitrogen of the cation. Replacement of the ethyl-substituent with an octyl group lowers the melting point of the salt by 50 °C, to produce a room temperature ionic liquid, suitable for use as a Lewis-basic solvent. With this larger substituent the TFSA salt is water-immiscible and exhibits a glass transition, crystallisation and melt at −54, −22 and 26 °C respectively. Significantly, the thermal stability of this salt is only slightly lower than other TFSA salts, such as those based on the pyrrolidinium cation, in spite of the Lewis base site. Thus, by incorporating the basicity into the cation rather than the anion of an ionic liquid it is possible to achieve an ionic liquid with the desired basic properties while avoiding problems of thermal instability.

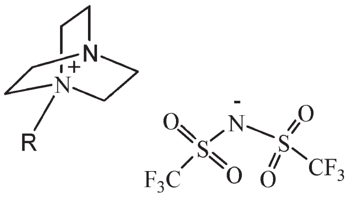

Fig. 2 1-Ethyl-4-aza-1-azoniabicyclo[2.2.2]octane bis(trifluoromethanesulfonyl)amide, [$C_n$dabco] TFSA.

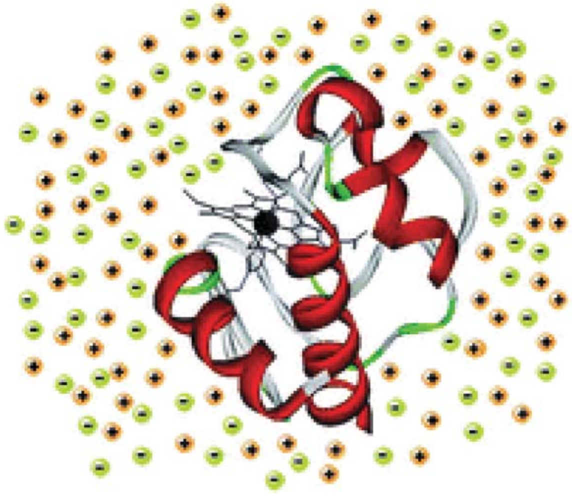

Fig. 3 Schematic representation of cytochrome c dissolved in an ionic liquid.

A further advantage to this basic cation is the ability of the tertiary amine nitrogen to interact with metal cations, assisting in the solubilising of metal salts into the ionic liquid. For example, [C_8dabco]TFSA can dissolve $Cu(NO_3)_2$, which is insoluble in other TFSA ionic liquids. This is of considerable interest in areas such as coordination chemistry and for use of ionic liquids as media for metal-catalysed reactions.

Lall *et al.*[40,41] have also included the 1,4-diazabicyclo[2.2.2]octane ring in a range of polyammonium salts, in combination with the phosphate anion. These "liquid ionic phosphates" are reported to be liquid at or near room temperature.

Amphoteric anions

There are a small number of ionic liquid anions that fall into the interesting class of "amphoteric anions", with the potential to both accept and donate protons depending on the other substances present. The hydrogen sulfate (HSO_4^-) and dihydrogen phosphate ($H_2PO_4^-$) anions are simple examples of such anions.

Fraga-Dubreuil *et al.*[42] have reported the utilisation of ionic liquids incorporating these anions, in combination with imidazolium cations, as catalysts for a range of esterification reactions (see also base-catalysis discussion). The hydrogen sulfate anion has greater Brønsted acidity than dihydrogen phosphate and this is reflected in a greater rate enhancement of the esterification reactions investigated. Similarly, ionic liquids utilising these two anions have been used to catalyse the Mannich reaction[28] and the tetrahydropyranylation of alcohols.[30] Gilbertson *et al.*[43] have also reported the use of dihyrogen phosphate for the synthesis of imidazole functionalised polynorbornene derivatives, for use in high temperature fuel cells.

Our group has recently reported the significant benefits of using dihydrogen phosphate ionic liquids for protein solubilising and stabilization.[44] Cytochrome c can be dissolved in butylmethylimidazolium dihydrogenphosphate, butylmethylpyrrolidinium dihydrogenphosphate or choline dihydrogenphosphate, containing 10–20 wt% water to render them liquid and aid solubility, up to a final concentration of 37 mg mL^{-1} (Fig. 3). This is a significant improvement in solubility compared to previous reports of attempts to dissolve proteins in ionic liquids.[45–48] Further, the secondary structure of the cytochrome c is retained in the ionic liquid, whereas in previous reports the secondary structure of the protein is lost on dissolution, which can result in loss of activity.

Thermal and IR analysis of the dissolved cytochrome c shows that the thermal stability of the protein is dramatically increased in the dihydrogenphosphate mixtures. In aqueous buffer the protein chain can be seen in the IR spectra to unfold as the temperature approaches 80 °C, whereas in choline dihydrogenphosphate this only starts to occur above 100 °C, and is still less significant at 130 °C than it is as 75 °C in the aqueous solution. In buffered aqueous cytochrome c solutions, the protein remains denatured on returning to room temperature after heating to 80 °C, whereas in the choline dihydrogenphosphate system the protein returns to room temperature almost unchanged after being briefly heated to 110 °C. It is interesting to note that this stabilisation is not observed when the dihydrogenphosphate salts are used as dilute aqueous solutions; it appears that a high concentration of the salt, with only a small amount of water, is necessary to effect the protein stabilisation.

Thus, these ionic liquids are clearly beneficial for use with cytochrome c and it appears that the nature of the anion is a key factor. The dihydrogenphosphate anion offers both hydrogen donor and acceptor sites, in addition to providing a proton activity similar to that in neutral water. The interesting properties of this anion in its ionic liquid will undoubtedly prompt further investigations into the use of other biocompatible anions and cations and the utilisation of these ionic liquids with many other protein types.

3. Acid and base solutes in ionic liquids

One of the important and very revealing properties of any solvent is the way that it responds to the presence of an acidic or basic solute. The state of an acid or base compound, such as acetic acid or ammonia, in an ionic liquid solvent is a strong function of the acidity/basicity of the ionic liquid itself. Here we describe a number of experiments designed to elucidate this important behaviour in a broad range of ionic liquids. It appears that some ionic liquids can turn a strong acid into a weaker acid, while other ionic liquids turn weak into strong. These results suggest a means of classification of ionic liquids with respect to their acid/base properties as discussed further below.[49]

In traditional solvents, acids and bases are categorized in terms of *Brønsted* acidity, which relates to the ability of the acid, HA, to donate a proton to a molecule of the solvent, S: $HA + S \rightleftharpoons A^- + HS^+$.

The equilibrium constant for this reaction, K_a, is a measure of the acidity of the acid, but it clearly also has a dependence on the basicity of the solvent, S. The more general *Lewis* definition of acidity and basicity involves simply the ability of the molecule to accept or donate electrons. The role of the solvent can be to act as the predominant base and thereby to form HS^+ (*e.g.* H_3O^+ in water).

The exact values of acid dissociation constants, K_a(IL), in any given ionic liquid are unknown at present and are not easily measurable by direct means. Given the large number of ionic liquids now known, this data gap is enormous. Some progress towards understanding the relative magnitude of K_a values can be achieved by asking the question: Is the ionic liquid anion more or less basic than water? Given that the anion is often intentionally chosen in most ionic liquid chemistry to be at the extreme of the *very* weakly basic anions, the answer to this question is certainly, in those cases, yes. The corresponding conjugate acid is therefore much more acidic than the hydronium ion. Since the anion is a weaker base than water, one might immediately expect that an acid dissolved in such an ionic liquid would exhibit a lower degree of dissociation, α, than in water. Thus the Brønsted acidity of a solute acid is expected to be lower (K_a smaller) in such ionic liquids than in water—*these ILs turn strong acids into weaker acids.*

On the other hand, some of the basic anions in Fig. 1 are more basic than water and therefore can be expected to act as stronger proton acceptors than water. An acid dissolved in an ionic liquid containing such an anion may then exhibit a higher degree of dissociation than in water. Thus the Brønsted acidity of a solute acid may be higher (K_a larger) in such ionic liquids than in water. The extent to which this is the case is a matter of the relative acceptor strength of the ionic liquid anion and the conjugate base of the solute acid. *Such basic ionic liquids turn weak acids into stronger acids.*

This understanding can be investigated further by using acid solutes which have spectroscopic signatures that are sensitive to their state of protonation, *i.e.* indicator acids of the type

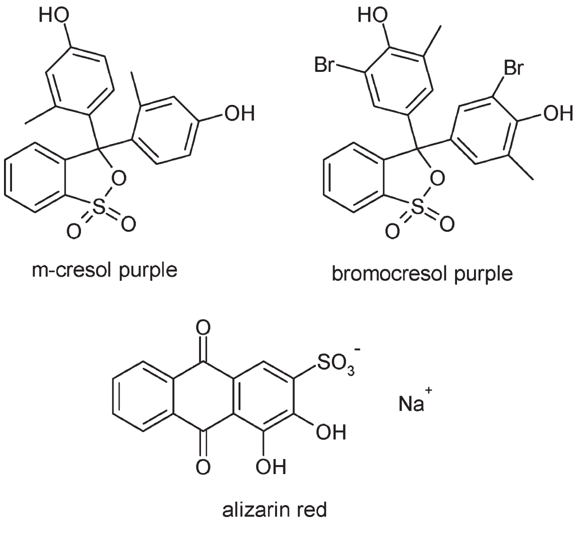

Fig. 4 Acid/base indicators used.

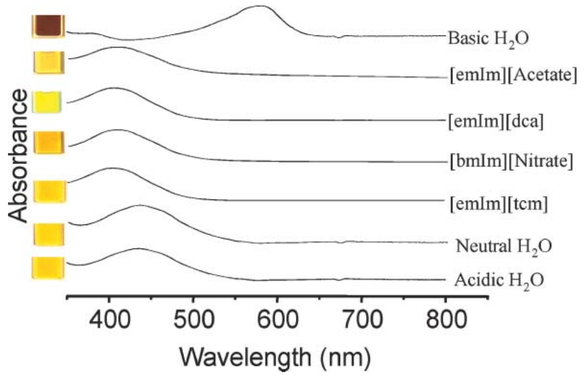

Fig. 5 Visible spectroscopy of *m*-cresol purple in various ionic liquids and aqueous solutions. Concentration ~1.0 wt% in all cases. (Not shown: bmimPF$_6$, emimTFSA and bmimBF$_4$ also produce spectra equivalent to acidic water).

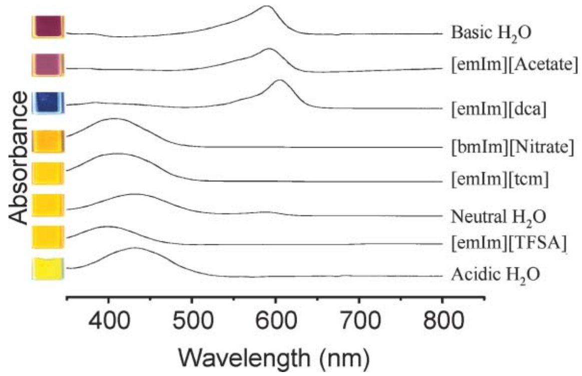

Fig. 6 Visible spectroscopy of bromocresol purple in various pure ionic liquids and aqueous solutions. Concentration ~1.0 wt% in all cases. (Not shown: [emim][PF$_6$] and [emim][BF$_4$] produce spectra equivalent to the TFSA case).

shown in Fig. 4. Thomazeau *et al.*[50] have also recently reported a study of TFSA and BF_4^- ionic liquids based on this concept. Fig. 5 shows the visible spectrum of the weak organic acid, *m*-cresol purple, in water and in a number of ionic liquids in which it is soluble.

m-Cresol purple was chosen as a typical probe indicator acid because of its strong degree of colouration in both acid and base forms, the acid form being a straw yellow colour and the base form a deep purple. This difference is dramatically observed in the visible spectra of the acid (λ_{max} = 440 nm) and base forms (λ_{max} = 600 nm) (Fig. 5). In pure water this acid, at the concentration involved, is expected to be only approximately 0.02% dissociated into the base form at room temperature. Thus the base form is almost completely absent from the spectra of the indicator acid in pure water.

Equally, the base form is not observable in any of the solutions of the indicator acid in the ionic liquids shown. Notably, in the acetate, dicyanamide (dca), tricyanomethide (tcm), nitrate, PF_6^-, TFSA and BF_4^- ionic liquids the indicator acid appears to be as little dissociated as it is in acidic water. Thus we estimate that the degree of dissociation of this acid is very small (<1%) in all of these ionic liquids and hence all act similarly as solvents with respect to this acid.

As a second example of this behaviour we used bromocresol purple (Fig. 4) as the probe acid. This is a slightly stronger acid than *m*-cresol purple, being about 0.2% dissociated in pure water. Fig. 6 shows the visible spectra of the acid in a variety of ionic liquids and aqueous solutions. In this case, the acid remains substantially undissociated in the TFSA, PF_6^-, BF_4^- ionic liquids as well as the nitrate and tricyanomethide ILs. However, in the acetate ionic liquid, only the absorption spectrum of the base form is observed, indicating almost complete dissociation in that medium. The spectrum of the indicator acid in the dicyanamide ionic liquid shows strong absorption from the base state as well as a weak absorbance in the region of the acid form. The visual appearance of this sample is also more intermediate in colour than the acetate case. It appears therefore that the acid is not completely dissociated in the dicyanamide case. Notably in both the acetate and dicyanamide cases the acid is more dissociated (a stronger acid) than it is in pure water. Thus the acetate and dca ionic liquids turn this relatively weak aqueous acid into a stronger acid in the ionic liquid.

This indicator acid thus shows varying degrees of dissociation depending on the chemical properties of the anion in the ionic liquid. The PF_6^-, BF_4^-, TFSA, tcm and nitrate ionic liquids are all weaker proton acceptors than the bromocresol purple anion. On the other hand, the acetate and dicyanamide anions are sufficiently proton accepting to fully or partially deprotonate, respectively, the bromocresol purple. This observation begins to allow an ordering of anions according to their basicity.

A third example utilizes a still stronger indicator acid, Alizarin red S (Fig. 4). This acid is approximately 0.5% dissociated in pure water. Here we see a still greater spread in the colour and spectra of the indicator in the various ionic liquids (Fig. 7). The nitrate, dicyanamide and acetate ionic liquids show the distinct spectrum of the base form of the indicator. λ_{max} shifts still further to longer wavelengths in basic water due to the second deprotonation of the molecule at the much higher pH reached in the aqueous system. This spread in behaviours indicates that the proton accepting tendency of the indicator anion now lies intermediate amongst the ionic liquids, allowing us to further rank their proton acceptor tendencies. Despite the spreading out of the different ionic liquids, the TFSA ionic liquid remains, not surprisingly, a

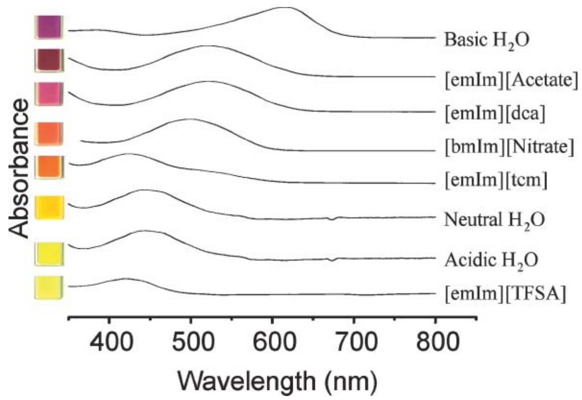

Fig. 7 Visible spectroscopy of Alizarin red S in various pure ionic liquids and aqueous solutions. Concentration ~1.0 wt% in all cases.

relatively very poor proton acceptor. The BF_4^- and PF_6^- ionic liquids behave similarly.

Table 1 lists the acid dissociation constants, pK_a^{aq}, for these and a number of more familiar acids, in water, as well as the acids of the anions used in the ionic liquids studied here. By making the assumption that *at least the relative order of* pK_a *values is similar* in any given ionic liquid to the order in water then we can estimate the α values for the ionic liquid media. This assumption allows for the different, as compared with water, nature of the interactions that certainly exist between the dissolved species HA, HS^+, A^- and the solvent ionic liquid species. It assumes that the shift in pK_a caused by this second order effect is approximately the same for all of the acids. The first order effect arises from the relative basicities of the two competing bases, the ionic liquid anion and the conjugate base of the probe acid. There is almost certainly a further strong second order effect arising from the ionic nature of the solvent but this is not easily resolvable from the first order effect. Nonetheless, this ionic solvent effect should be relatively the same for all the ionic liquids and therefore not strongly alter the relative order of pK_a values. We use emimBF_4 and emim acetate as two archetypal examples of a weakly basic and a basic anion respectively to estimate effective acidity of an acid HX in an IL containing anion S^-, from the following processes:

$$HX + H_2O \rightleftharpoons X^- + H_3O^+ \quad pK_a^{aq}(HX) \tag{1}$$

$$HS + H_2O \rightleftharpoons S^- + H_3O^+ \quad pK_a^{aq}(HS) \tag{2}$$

$$HX + S^- \rightleftharpoons X^- + HS \quad pK_a^{IL}(HX) \tag{3}$$

$$pK_a^{IL}(HX) = pK_a^{aq}(HX)/pK_a^{aq}(HS)$$

Therefore, the extent of dissociation α of an acid in an ionic liquid can be approximately calculated in principle from knowledge of the pK_a^{aq} value of the acid in water and also the pK_a^{aq} for the conjugate acid (HS) of the ionic liquid anion (S^-) in water. These calculations (Table 1) can only be approximate because of the as yet unquantified second order effects discussed above.

We thereby see from Table 1 that acids behave as slightly weaker acids in emim BF_4 than they do in water. Applying the same ideas to ionic liquids of anions from acids further up this list, for example in emim mesylate, we can predict that some acids that we expect to be moderately strong in water, *e.g.* trifluoroacetic acid, will in fact behave as moderately weak in the emim BF_4 ionic liquid. In other words, an acid will remain more protonated in an ionic liquid bearing an anion whose conjugate acid lies above it in this list.

On the other hand, emim acetate is able to act as a stronger acceptor for protons than water or any of the acids above acetic acid in the list. In contrast to the neutral ionic liquids in Fig. 1, this ionic liquid can produce strongly dissociated solutions of the solute acid. The anions S^- in these ionic liquids thus act as Brønsted bases to promote the dissociation of the dissolved acid. The sheer concentration of S^- available (activity approaching 1) also forces the position of this equilibrium towards the right. From these observations it appears that what we commonly think of as relatively "weak acids" can in fact behave as "strong acids" in basic ionic liquids, depending on their relative positions in Table 1.

Bases in ionic liquids

The state of a base in an ionic liquid can be described in an analogous way. Thus, in both the neutral and basic types of

Table 1 Acid dissociation constants and degrees of dissociation for various acids in water and ionic liquids

Acid	Formula	pK_a^{aq}	Calculated α in H_2O (0.1 M)	Predicted α in emiBF_4 (0.1 M)	Predicted α in emiacetate (0.1 M)
Trifluoromethane sulfonic acid	CF_3SO_3H	*ca.* −13	1	1	1
Perchloric acid	$HClO_4$	*ca.* −10	1	1	1
Hydrogen iodide	HI	*ca.* −7	1	1	1
Hydrogen bromide	HBr	*ca.* −6	1	1	1
Tricyanomethane	$CH(CN)_3$	*ca.* −5	1	1	1
TFSA acid	$HN(CF_3SO_2)_2$	*ca.* −4	1	1	1
Hydrogen chloride	HCl	*ca.* −3	1	1	1
Toluenesulfonic acid	CH_3PhSO_3H	*ca.* −2.8	1	1	1
Methanesulfonic acid	CH_3SO_3H	*ca.* −2	1	1	1
Nitric acid	HNO_3	*ca.* −1.5	1	1	1
Thiocyanic acid	HSCN	−1.85	1	1	1
Hydronium ion	H_3O^+	−1.74	–	1	1
Tetrafluoroboric acid	HBF_4	−0.44	0.97	—	1
Trifluoroacetic acid	CF_3COOH	0.0	0.92	0.8	1
Benzenesulfonic acid	$C_6H_5SO_3H$	0.7	0.7	0.5	1
Phosphoric acid	H_3PO_4	1.97	0.28	0.2	1
Hydrofluoric acid	HF	3.45	0.06	0.04	1
Formic acid	HCOOH	3.75	0.04	0.02	1
Acetic acid	CH_3COOH	4.75	0.01	0.008	—
Dicyanoamine[a]	$HN(CN)_2$	5.1	0.009	0.005	0.8
Alizarin red S	$C_{14}H_7NaO_7S$	5.7	0.004	0.002	0.7
Carbonic acid	H_2CO_3	6.4	0.002	0.001	0.4
Bromocresol purple	$C_{21}H_{16}Br_2O_5S$	6.4	0.002	0.001	0.4
Metacresol purple	$C_{21}H_{18}O_5S$	8.3	<0.001	<0.001	0.05
Hydrocyanide	HCN	9.3	<0.001	<0.001	0.02
Water	H_2O	14	10^{-7}	$<10^{-7}$	7×10^{-6}

[a] As measured from a 0.1 M aqueous solution of sodium dicyanamide

IL, a base such as ammonia or an amino group will remain in its base form and be available, as such, chemically. In principle then, these IL are solvents that are able to deliver the base in its simplest form to a reaction. This fact has consequences in biochemical applications, since bases such as dopamine, which would exist under physiological conditions in the protonated form, may not be so in an ionic liquid. However, recognizing (below) the role of water, presents a partial solution to this problem.

In the case of weakly acidic ionic liquids, corresponding to those which display distinct proton donor (or, in general, Lewis acid) properties, the same type of considerations apply. A base will remain unprotonated in such an IL depending on the relative acidities of the IL cation and the protonated solute base.

The role of trace water in ionic liquids

Given the almost ubiquitous presence of water in ionic liquids under normal laboratory conditions, it is of interest to inquire into the role of small amounts of water in the acid/base discussion above. Water contents may be low from a purity point of view (say $< 0.5\%$w/w) but may nonetheless be present at molar concentrations close to the concentration of the dissolved acid or base. As an active proton acceptor, water will thus dramatically increase (to the extent of the amount of water present) the degree of dissociation of an acid in a neutral ionic liquid, as compared to the pure ionic liquid. Similarly, the state of a base will be altered by the presence of water in a neutral ionic liquid. Water will be at least partly dissociated, producing OH^- in a basic ionic liquid.

4. General and specific base catalysis in ionic liquids

The distinction of different ionic liquids as Lewis/Brønsted acids or bases clearly also indicates potential applications of these materials as either acid or base catalysts. Much of the early research into the use of ionic liquids centred on their use as reaction media for catalytic reactions, where they were simply an alternative to conventional molecular solvents.[51] While this use of the ionic liquid as the reaction medium often results in increases in rate and/or reactivity, there are clear advantages to completely removing the need for the added catalyst, which are often expensive and non-recyclable, by using the ionic liquid both as the reaction media and the catalyst. There are many reports on the use of ILs as Lewis acid catalysts; the original chloroaluminate ionic liquids have been widely used.[52–54] More recently, there has been a number of air and water stable acidic ionic liquids that have also been used in catalytic applications.[55–60]

We have recently discussed the use of basic ionic liquids as catalysts in the context of the base catalysed acetylation of alcohols including glucose.[61] This is a widely used means of protecting alcohol groups which is conventionally performed using acetic anhydride and a base catalyst in a traditional solvent. There are a wide range of solvents and catalysts commonly utilised for the *O*-acetylation reaction of carbohydrates; for example pyridine is a commonly used solvent/catalyst, despite considerable safety concerns. Using dicyanamide ionic liquids we showed that a range of alcohols and carbohydrates can be rapidly acetylated using acetic anhydride (Ac_2O), with no additional base catalyst in some cases. These observations originated in our work with glucose, which is soluble in dicyanamide and acetate ionic liquids to greater than 10 weight percent at room temperature. Disaccharides (*e.g.* sucrose) and trisaccharides (*e.g.* raffinose) are less soluble than glucose, but their solubility is significantly improved with gentle heating. The products of the acetylation reactions were also completely soluble in the dicyanamide ionic liquids and were precipitated from solution at the end of the reaction by addition of water. To minimise the volume of ionic liquid used, the reaction can be carried out using beyond-saturation solutions of the saccharide, which then forms a completely homogeneous solution as the reaction proceeds to give the more soluble product. No partially-acetylated products were produced using the dicyanamide ionic liquid. Illustrative reaction conditions, yields of the fully acetylated products and their anomeric ratios are summarized in Table 2.

The advantages of using the dicyanamide ionic liquid over conventional molecular solvent/catalyst systems for the acetylation reaction of α-D-glucose are illustrated in Table 3 by the reactions using triethylamine as catalyst in bmimdca as solvent, as compared to dimethylformamide (DMF), acetone or acetonitrile. The dca reactions are significantly faster and higher yielding than in the conventional solvents. The anomeric ratio is shifted towards 50 : 50 in the presence of the dca anion as compared to the high *β* content that is typical of triethylamine. When the acetylation is performed in emidca with pyridine as the catalyst, the reactions proceed in good yields, but without the complete α anomeric selectivity obtained when using this catalyst in a conventional molecular solvent. The presence of the additional *β* anomer indicates that the dicyanamide anion is playing a competitive catalytic role in

Table 2 α-D-Glucose acetylation with a range of added catalysts in a range of solvents

Solvent (equiv.)[a]	Catalyst (equiv.)	Ac_2O (equiv.)	Temp, $T/°C$	Time/h	Yield (%)	Anomeric ratio α : β
DMF (10)	Et_3N (5)	5	Room temp.[b]	24	88	28 : 72
Acetone (10)	Et_3N (5)	5	Room temp.	48	75	11 : 89
Acetonitrile (10)	Et_3N (5)	5	Room temp.	48	69	8 : 91
bmim dca (10)	Et_3N (5)	5	Room temp.	0.2	95	60 : 40
bmim dca (2)	Et_3N (5)	5	Room temp.	0.1	97	17 : 83
bmim dca (2)	Et_3N (5)	5	0	4	80	58 : 42
bmim dca (10)	pyridine (10)	10	50	0.2	98	95 : 5
bmim dca (1)	pyridine (0.5)	5	0	4	83	75 : 25
none	emim dca (0.5)	5	50	0.2	92	46 : 54

[a] Molar equivalents. [b] Room temperature is approximately 25 °C.

Table 3 *O*-Acetylation of a range of alcohols and carbohydrates with no added catalyst

Substrate	Solvent (equiv.)[a]	Ac_2O (equiv.)	Temp, T/°C	Time/h	Yield (%)
α-D-Glucose	bmim dca (2)	5	Room temp.[b]	0.2	89
α-D-Glucose	bmim dca (2)	5	50	0.1	98[c]
β-Me-Glucose	bmim dca (2)	4.5	Room temp.	0.2	92
N-Acetyl neuraminic acid	emim dca (2)	5	Room temp.	24	72
Sucrose	bmim dca (4)	8	Room temp.	24	93
Raffinose	emim dca (6)	11	Room temp.	24	90
2-Naphthol	emim dca (2)	1	Room temp.	24	85
t-BuOH	emim dca (2)	1	Room temp.	24	91
Cyclohexanol	emim dca (2)	1	Room temp	0.5	90
α-D-Glucose	bmim TFSA (2)	5	Room temp.	24	0
α-D-Glucose	emim acetate (2)	5	Room temp.	1	95

[a] Molar equivalents w.r.t. substrate. [b] Room temperature is approximately 25 °C. [c] Anomeric ratio 48 : 53

the reaction, which becomes more significant at lower pyridine concentrations. Thus, the dicyanamide ionic liquid is clearly not simply a neutral solvent in this reaction. This is further exemplified by the final entry in Table 2, in which only a very small quantity of emimdca is required to fully acetylate the glucose, suggesting that the dicyanamide ion itself is acting as a regenerating catalyst.

Thus in Table 3 we summarize a number of acetylation reactions in which the dca IL is used, as both solvent and catalyst. Glucose and a range of other compounds containing a variety of primary and secondary hydroxy groups of varying reactivity have been acetylated, as well as simple alcohols such as tertiary butyl alcohol, to demonstrate the generality of this reaction to aromatic and aliphatic alcohols.

The suggested base-catalysis role for the basic IL anion in this reaction was further confirmed by the observations (Table 3) that bmimTFSA, which we describe as a "neutral" ionic liquid, demonstrates no catalytic effect for this reaction at all, with no acetylated product obtained. On the other hand, the use of emim acetate, another distinctly basic ionic liquid, produces high yields. The acetate anion is chemically quite different from dicyanamide but still clearly demonstrates effective catalysis of the *O*-acetylation of glucose, with 95% product yield obtained within an hour. The clear involvement of the basic anion thus suggests a mechanism analogous to that operative in the presence of an added base such as pyridine. A possible mechanism is shown in Fig. 8. The small size of the dca anion compared to Et_3N and pyridine may explain the lack of anomeric selectivity in its action.

These observations we believe demonstrate the existence of a *specific base catalysis* mechanism in these basic ionic liquids *i.e.* catalysis arising from basic ions from or, in this case comprising, the solvent itself. Presumably, mixtures of these basic ionic liquids with neutral ionic liquids would therefore create a *general base catalysis* effect (*i.e.* wherein the reaction rate is proportional to the concentration of the basic ion). Further, as the basicity of ionic liquids is to some extent "tuneable" by judicious choice of anion, the base catalysis effect of the ionic liquids may also be controllable.

There are a number of other reports of the use of ionic liquids for acetylation reactions[33,62–66] but no others that utilise an ionic liquid as a *base* catalyst. Of particular relevance here, Gholap *et al.*[33] reported the use of ultrasound to promote the acetylation of alcohols in a range of different ionic liquids utilising the 1,3-di-*n*-butylimidazolium cation. The authors directly relate the rate of the acetylation reaction to the Lewis/Brønsted acidity of the ionic liquid used. It was proposed that the C2 hydrogen interacts with the oxygen of the acetic

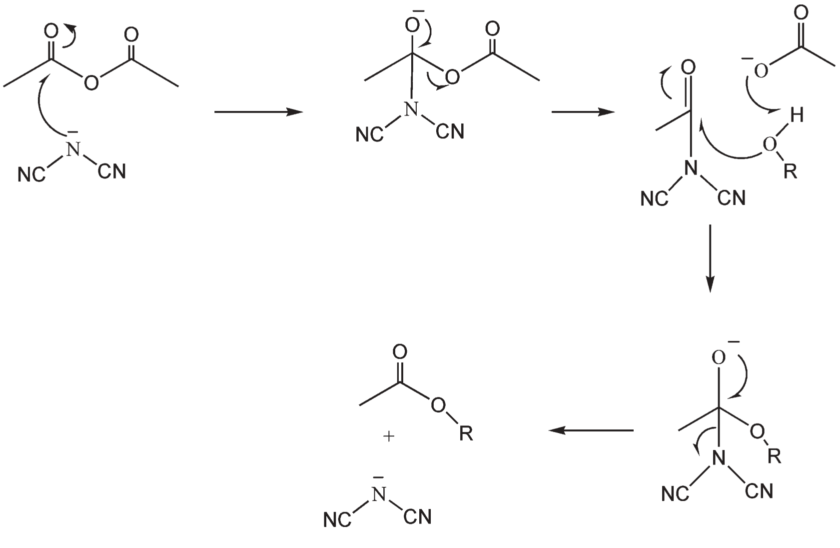

Fig. 8 Proposed mechanism for the role of the dicyanamide anion in the base-catalysed acetylation reaction.

anhydride and facilitates the generation of the reactive acetyl cation. Thus, the rate of reaction is increased with increasing acidity of the ionic liquid. The role of the acidic imidazolium proton in this reaction was further indicated by the poor performance of the reactions in ionic liquids where the 2-position is substituted and in non-imidazolium ionic liquids.

Perhaps one of the most significant uses of the acetylation of alcohols is in cellulose chemistry. There is significant commercial interest in the processing of cellulose, with derivatised products having applications in industries including paper, polymer, fibre and paints. The use of ionic liquids to dissolve and acetylate cellulose has been reported.[67–69] Thus, demonstration of the successful use of imidazolium dicyanamide and acetate ionic liquids for the acetylation of alcohols including glucose clearly indicates a potentially important area of future work. Application of this general base catalysis concept to cellulose processing, and expansion of the number of basic ionic liquids that can be used to effect this catalysis, has significant commercial interest.

5. Distillable ionic liquids

Ionic liquids are often described as having virtually zero vapour pressure, as well as being chemically and electrochemically stable. However, these properties are not completely ubiquitous among the broad family of low melting organic salts; in fact high chemical and electrochemical stability and low volatility is mainly a feature of the combination of *very* weakly basic anions and fully substituted quaternary nitrogen or phosphorous based cations (*i.e.* no active protons). Further, in some applications of ionic liquids the lack of volatility is a distinct disadvantage, since it restricts the methodologies available for the handling, purification, removal and recycling of the IL. For example, recent work in our laboratories on electroconductive polymers has demonstrated the production of useful materials by electropolymerization in ILs, but the removal of the IL after the process is difficult.

Here we describe a number of examples from a general family of ionic liquids which are volatile and which can be distilled under relatively normal conditions of pressure and temperature. The liquids have in common a weakly basic anion, a cation from a tertiary amine and an exchangeable proton. The effect of these two features is to potentially allow the removal of the neutral acid and base species separately from the liquid by distillation, since these exist in equilibrium with the ionised species.

Distillable ionic liquids from the fascinating family of dialkylammonium carbamate salts have been described previously.[70–74] These are formed from the condensation of CO_2 with a dialkylamine to produce a carbamate anion and the dialkylammonium cation. These liquids usually show a "boiling point" at which the CO_2 begins to evaporate from the mixture and, on continued heating, the reformed dialkylamine can also be removed. However, the relative difficulty in handling the CO_2 component of these ionic liquids and the fact that they have a high vapour pressure of CO_2 at room temperature has meant that they are not as useful as a potentially distillable IL could be as an alternative solvent. It has also been noted that 1-methyl-3-ethylimidazolium chloride is distillable through partial decomposition then subsequent recombination to regenerate the ionic liquid.[75]

The liquids described here are based on the broader concept of a volatile acid and base forming a liquid salt *via* neutralization. For example, in the case of acetic acid and methyl pyrrolidine (mpy); $CH_3COOH + mpy \rightleftharpoons Hmpy + CH_3COO^-$ a fluid liquid salt, methylpyrrolidinium acetate (Hmpy acetate) is produced in an exothermic reaction. There are thus a vast number of potential cation–anion combinations of this type which can be produced by this simple neutralization reaction. Many examples of such protic ionic liquids are known.[26–32] However, many of these involve very strong acids and/or bases and hence the equilibrium lies heavily to the right.

Angell *et al.* have discussed the general properties of such protic ionic liquids in terms of their relative acidity and basicity.[76] They point out that such neutralization reactions will reach a point of equilibrium—which may not lie completely towards the ionised from unless the relative acidity of the acid and the protonated base (expressed as δpK_a) are such that there is a strong tendency towards the ionised forms. They show also that the aqueous solution-based pK_a values are useful, at least in a relative sense, in understanding the likely state of ionisation.

The additional distinguishing feature required of the ionic liquids described here is that to be ultimately distillable the individual starting materials must be volatile at some accessible temperature and pressure. To access these volatile states, the acidity of the progenitor organic acid and the conjugate acid of the base must be sufficiently different (as expressed by δpK_a) such that the degree of ionisation is sufficient to render the liquid substantially the pure salt, but not be so extremely different such that the equilibrium lies too heavily to the right and the vapour pressures of the neutral species therefore un-usefully low. These requirements significantly narrow the possible acid/base combinations from the broad field of protic ionic liquids. The field is narrowed still further by the possibility of amide formation during the heating/volatilization of primary or secondary amines. For example, Bicak has recently reported the synthesis of 2-hydroxyethylammonium formate,[36] but this decomposes on heating to form a formamide.

The preparation and properties of a number of possible distillable ionic liquids is described here. Full experimental details are given in the supplementary information. The properties of a number of examples are listed in Table 4. As can be seen, some very simple anions such as acetate and formate are extremely useful in this respect. The volatility of these ionic liquids is clearly illustrated in the thermogravimetric analysis (TGA) traces of Fig. 9. In some cases the ionic liquids lose mass almost continuously from around 50 °C and are completely removed by ~150 °C. The complete volatilisation temperature, T_v, can be used to compare the volatility of different ionic liquids (nonetheless the IL is clearly volatile well below this temperature).

By way of an example of a bulk distillation of these ionic liquids, distillation of Hmpy formate was carried out at 70 °C and 120 Pa using a liquid nitrogen trap to condense the distillate. Close to 100% distillation was achieved. NMR and mass spectroscopy data of the distillate was unchanged from

Table 4 Properties of distillable ionic liquids

Comound	Acronym	Mp/ °C	T_g/ °C	T_v/ °C	Conductivity/ S cm^{-1}	Viscosity/ mPa s	Distillation conditions	Water content (%)	ΔpK_a^{aq}
N-methylpyrrolidinium trifluoroacetate	Hmpy trifluoroacetate	38		260	1×10^{-3}	Solid	4 Pa, 110 °C	—	10.3
N-methylimidazolium trifluoroacetate	Hmim trifluoroacetate	51		255	1×10^{-3}	Solid	4 Pa, 110 °C	—	7.0
N-methylpyrrolidinium formate	Hmpy formate	−32	−116	155	20×10^{-3}	7.5	120 Pa, 70 °C	0.07	6.5
N-methylpyrrolidinium acetate	Hmpy acetate	—	−108	140	2×10^{-3}	3.2	120 Pa, 45 °C	0.05	5.5
N-methylimidazolium formate	Hmim formate	—	−99	220	20×10^{-3}	6.7	4 Pa, 60 °C	0.08	3.1
N-methylimidazolium acetate	Hmim acetate	−23	−98	160	4×10^{-3}	5.6	120 Pa, 70 °C	0.03	2.1
N-methylpiperidinium formate	Hmpi formate	Two phase liquid mixture							

the original ionic liquid, while small traces of coloration in the original IL were no longer visible in the distillate.

The distillation process taking place in this experiment is, of course, complex. The stoichiometric 1 : 1 compound formed from the acid and base is simply one composition in a series of binary mixtures of acid and base. The equilibrium producing the salt will produce a deep minimum in the vapour pressure *vs.* composition diagram. Distillation will take place *via* fractional distillation of the most volatile component first, followed by a gradual enrichening with respect to the less volatile neutral component.

All of the examples in Table 4 are distillable. However, the extent of neutralization in the ionic liquid is not necessarily 100% in all cases and this remains a key question for this family of materials. To the extent that the liquid is not fully ionised, it is then best described as a *liquid mixture* containing the ionic liquid and the neutral species. For example, when one compares Hmpy formate with Hmpy acetate one observes that the former has much higher conductivity, yet is more viscous and distills at higher temperature (despite the lower boiling point of the component acid and base). All of this evidence would suggest that the latter liquid is less completely ionised. However, measurement of the absolute extent of ionisation to provide some concrete data in this respect is fraught with difficulty and one is forced to resort to prediction and circumstantial evidence, as discussed in more detail below.

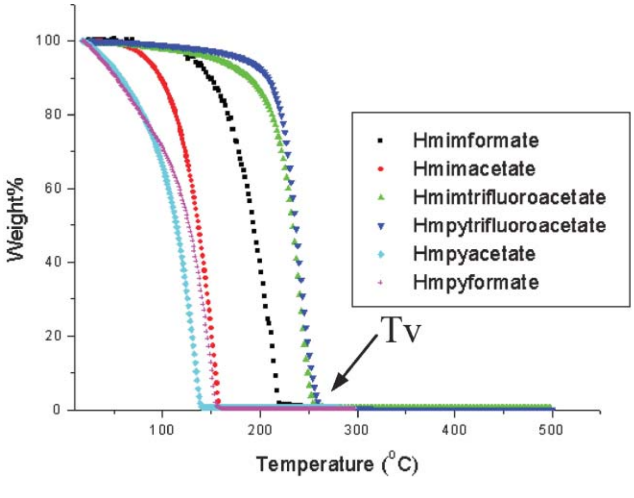

Fig. 9 Thermogravimetric analysis traces of several weak-base, protic ionic liquids showing *complete* volatilization at relatively low temperatures.

As outlined above, there are two key requirements that the acid–base pair must satisfy in order for their salt to display the phenomena observed here. Firstly, the equilibrium:

$$HA + B \rightleftharpoons A^- + HB^+ \qquad (4)$$

must produce substantial ionisation such that the material can justifiably be described as an ionic liquid, but not lie so far to the right such that the equilibrium concentrations of the volatile species HA and B are too low. The latter requirement means that the basicities of B and A^- in the ionic liquid must not be too extremely different, or alternatively the difference in acidities of HA and HB^+ in the ionic liquid not too large, as measured by δpK_a(IL). Generally speaking this means that the anion A^- must be one of the weak base anions such as acetate, as opposed to the extremely weak base anions, such as triflate and TFSA *etc.*, since in the latter case a correspondingly weak base B would be required. In principle, however, volatile weaker base anions may be found which, if matched with a cation formed from an equally weak base, could produce a less basic, but nonetheless volatile, medium. In other words, an ionic liquid based on the triflate anion might be volatile if it involves a cation formed by protonation of a sufficiently weak ammonium or phosphonium base. On the other hand, the mere existence of a facile equilibrium of this sort challenges the description of these materials as ionic liquids. The widely accepted definition of an ionic liquid is: "an ionic compound which exists in the liquid state at ambient temperatures (*i.e.* < 100 °C)". The issue in the context of the present salts is the existence in their liquid state of small amounts of the neutral acid and base in equilibrium with the ions. Certainly in the situation where the neutral acid and base represent some tens of mol% of the ionic liquid, then it would correctly be described as a mixture, thereby to properly recognize the complexity of behaviour introduced by the existence of the additional components. In the circumstance where the concentrations of the neutral forms are below an arbitrary amount, say 1 mol%, the situation becomes more straightforward. The properties of the liquid will be substantially those of the imagined "pure" material, the transport and thermodynamic properties not strongly affected by the neutral species present—other than the volatility that they induce. Thus our attention has been devoted to those materials where the extent of ionisation is potentially >99%. The challenge is to provide an unambiguous measurement of the degree of ionisation in such cases.

As proposed by Angell *et al.*,[76] an estimate of the extent of ionisation can usefully be deduced from a relatively simple analysis of the equilibrium involved in eqn (4) and its equilibrium constant K. Unfortunately, values for equilibrium constants for reactions such as eqn (4) are not known under these (non-aqueous) conditions and are not easily measured. An approximation to the value of K can be obtained by observing that an appropriate combination of the aqueous acid dissociations reactions $HA + H_2O \rightleftharpoons A^- + H_3O^+$ $HB^+ + H_2O \rightleftharpoons B + H_3O^+$ produces eqn (4) with:

$$K = K_a^{aq}(HA)/K_a^{aq}(HB^+) \quad (5)$$

or $pK = \Delta pK_a^{aq}$ where the superscript aq serves to remind us that these are values corresponding to solution in water. In this context the K_a^{aq} values and their combination in K represent a measure of relative proton donating ability and thus represent a useful approximate method of assessing the extent of ionization.

Before proceeding, however, we must assess the validity of this approach. K_a data are typically relevant to conditions where the activity of the water is close to unity and the dissolved species are typically 1 mol% or less of the total. The properties of the solvent are thus not strongly altered by the reaction taking place in water, whereas they certainly are in this IL case. The effect of hydration/hydrogen bonding on the extent of each reaction in particular must also be considered. Both of these differences are of significance; however, to a degree there is a cancellation of such differences in the ratio which makes up K in eqn (5) and hence such effects would need to be much stronger in one of the acid/base pairs than the other in order to create a substantial error.

Calculating the degree of ionization as a function of ΔpK_a^{aq} produces a curve as shown in Fig. 10, which indicates that the desired 99% ionization can be achieved, in principle, at $\Delta pK_a^{aq} = 4$. As ΔpK_a^{aq} drops below this value the presence of the neutral species becomes increasingly significant. In Table 4, it can be seen that ΔpK_a^{aq} exceeds 4 for all of the Hmpy compounds. However, comparison of the properties of the acetate and formate suggest that the former is influenced by the presence of the neutral species and hence that the $\Delta pK_a^{aq} > 4$ criterion may not be adequate in this case, presumably due to the influence of the approximations discussed above.

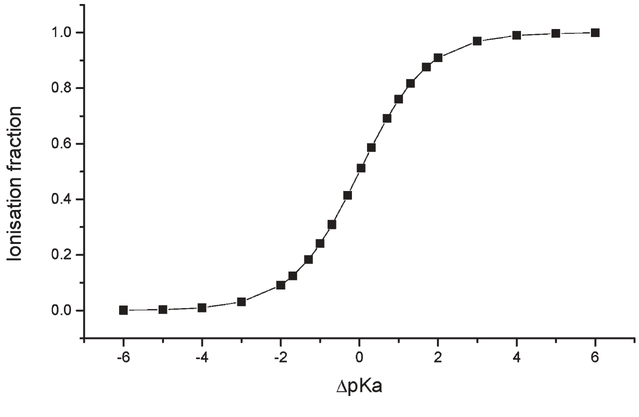

Fig. 10 Calculated ionisation fraction for an ionic liquid consisting of an acid base mixture, as a function of $pK = \Delta pK_a^{aq}$ where K is the equilibrium constant for the proton transfer reaction in the IL.

A more direct measure of degree of protonation is potentially available from the NMR spectra of the pyrrolidinium ring.[77] The protons on the ring carbons α to the nitrogen are strongly influenced by the protonation of the neighbouring nitrogen, much more strongly so than the β protons. Thus in Fig. 11 we have used the $\delta\alpha$–$\delta\beta$ chemical shift difference measured in neat samples of a series of ionic liquids to assess the degree of protonation of the methylpyrrolidine base. As can be seen, $\delta\alpha$–$\delta\beta$ tends towards a limit as ΔpK_a^{aq} becomes larger, the limit being expressed by the extremely weak base anions such as methanesulfonate. On the basis of these trends it would appear that the trifluoracetate ionic liquids are highly ionized, but that the formate and acetates are less so. It would thus appear that the ΔpK_a^{aq} estimations are incorrect by at least 2–3 pK_a units. The thermodynamic origins of this remain unclear but may lie, for example, in the special properties of the hydronium ion in aqueous acid base chemistry. Nonetheless, Fig. 11 provides an approximate basis and methodology for assessing both the extent of ionization and also a means by which true ionic liquids which are volatile can be found.

The second criterion for volatility relates to the volatility of the neutral species over the ionic liquid. Under ideal conditions the equilibrium mole fractions, x, of HA and B from eqn (4) will produce vapour pressures, p, over the ionic liquid according to Raoult's Law (*e.g.* $p_B = x_B p^0_B$ where p^0_B is the vapour pressure of pure B). If $x \sim 1$ mol% then these will be accessible pressures and distillation possible. On the other hand if there are strong interactions between the neutral species and the ionised forms (as compared to the pure neutral

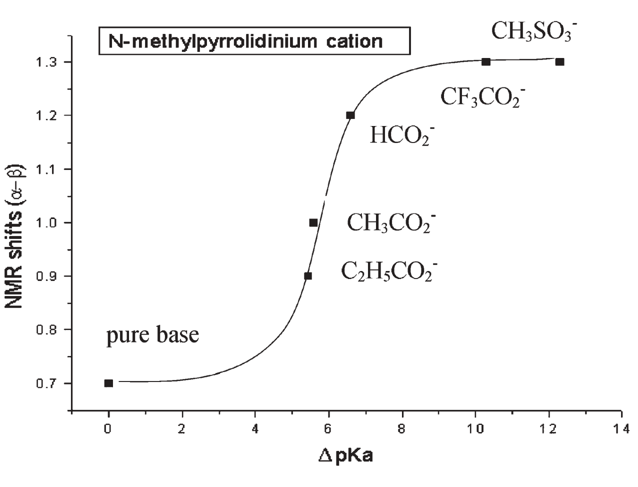

Fig. 11 Chemical shift difference between ring protons in the methyl pyrrolidinium cation as a function of ΔpK_a^{aq}. The point at $\Delta pK_a^{aq} = 0$ corresponds to the pure base.

liquids) then negative deviations from Raoult's law can be expected and the more difficult the distillation becomes. The unknowns in this discussion serve to highlight the huge data gap that exists in the physical properties of ionic liquids.

Finally, it is worth noting that one of the key features of the salts described here is that they typically involve weakly basic anions rather than the exceedingly weakly basic anions such as TFSA that are more typically present in ionic liquids. A related consequence of this is that the ionic liquids display a number of properties characteristic of this basicity, as discussed above. Thus the requirement of a weak base anion A^- and the presence of an active proton means that the ionic liquid itself represents a not unreactive medium. Certainly any chemical process which is sensitive to protons or basicitiy will be influenced by such a medium.

6. Conclusions

The ever-expanding family of ionic liquids express not a single solvent behaviour, but a wide spectrum of behaviours. Using acid/base properties as an indicator we find that we can classify ionic liquids into at least 3 classes. The majority of those described to date belong to the neutral class, but a growing number are now appearing which belong to the class of bases. The Lewis/Brønsted acid class will no doubt receive more attention in the future also.

This work represents a first step towards a full understanding of the state of acids and bases in ionic liquids of various types and classes. Quantitative measures of pK_a values in various ionic liquids are clearly required and it is our hope that this discussion will stimulate work in that direction.

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