Preparation of protic ionic liquids with minimal water content and ^{15}N NMR study of proton transfer†

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Low-molecular-weight Brønsted acids and amine bases were used to reproducibly prepare very dry, high-purity room-temperature protic ionic liquids (PILs). A series of eight amine bases and six Brønsted acids were combined to produce 48 mixtures, of which 18 were liquid at room temperature. The phase transitions and thermal decomposition temperatures were determined for each mixture; whereas viscosity, density and conductivity were determined for the room-temperature liquids. By utilising ^{15}N NMR it was possible to distinguish between neutral and ionised amine bases (ammonia *vs.* ammonium-type ion), which indicated that the protic ionic liquids were completely ionised when made as a stoichiometric mixture. However, a Walden plot comparison of fluidity and molar conductivity indicated the majority of PILs had much lower conductivity than predicted by viscosity unless the base contained excess proton-donating groups. This disparity is indicative of protic ionic molecules forming neutral aggregates or non-Newtonian fluid hydrogen-bonded networks with a secondary Grotthuss proton-hopping mechanism arising from polyprotic bases.
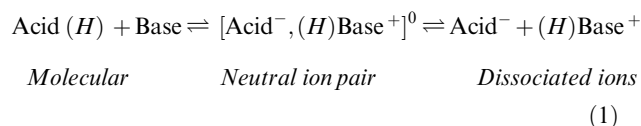
1. Introduction

The field of ionic liquids (ILs) has been rapidly expanding, in concurrence with the number of applications in which ILs have been used.[1] However, for some of the more frequently encountered ILs there are several aspects which are seen as undesirable for certain applications. Such negative aspects include trace halogen impurities from metathesis, the potential requirements of a toxicological profile for new materials, and the cost of ILs relative to molecular solvents.[2]

One method to bypass these potential problems is to use protic ionic liquids (PILs), which are formed by a neutralisation reaction of Brønsted acids and bases.[3] As has been often stated, in 1914 Walden reported the synthesis of ethylammonium nitrate by transferring a proton from a Brønsted acid to a Brønsted base without the use of a solvent.[4] The acid and base typically used are commercially available Brønsted acids and bases with a long history of use in industry, where the neutralisation reactions are able to produce a final mixture free of contaminant species.[5]

Much effort has been made to exploit these PILs in applications such as reaction media,[6] catalysis,[7] and fuel cells.[8] Although a large number of PILs have been prepared and characterised to date, there is still debate on the ionic nature of the PILs once the neutralisation is complete.[9]

As PILs are formed by neutralisation of a molecular acid and base species, a possible equilibrium may exist which can return the components to the un-ionised state [eqn (1)]. The reported low ionic conductivities of many PILs have suggested that either proton transfer is incomplete and significant neutral molecular species remain in the PILs or that neutral ion-pairs are formed, possibly even as larger multi-ion aggregates [eqn (1)].[10] Different techniques have been used to provide qualitative information about the overall ionic nature of bulk PILs from the transport properties, including NMR,[11] IR spectroscopy,[12] and ionic conductivity *via* a Walden plot.[13] However, there has been no method to clearly distinguish between the ionic states of a PIL. Hence, a method of confirming proton transfer is necessary to identify the ionisation states of species in solution rather than the overall ionisation of the PIL.

$$\text{Acid}\,(H) + \text{Base} \rightleftharpoons [\text{Acid}^-,(H)\text{Base}^+]^0 \rightleftharpoons \text{Acid}^- + (H)\text{Base}^+$$

| *Molecular* | *Neutral ion pair* | *Dissociated ions* |

(1)

Finally, it is often assumed that PILs (and to a lesser extent, aprotic ILs) are produced as an equal binary pair. In our experience, when reagents were diluted in sufficient solvent to facilitate removal of the exothermic energy from the neutralisation reaction, removal of solvent *in vacuo* also removed more of one of the PIL component than the other.[14] Regardless of the preparative method and the Brønsted acid and base used, if less than 100% yield were obtained, it is naive to assume that the product is an equimolar mixture. Therefore, a method to produce PILs of known and predictable stoichiometry was developed so as to accurately examine ionisation and proton transfer, with an emphasis on the use of low-molecular-weight volatile reagents.

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We have investigated 48 unique mixtures using eight common substituted amine bases and six Brønsted acids to better understand proton transfer behaviour and the extent of ionisation in PILs.

2. Experimental

2.1 Materials and chemicals

Formic (HO_2CH) and glacial acetic (AcOH) acids were obtained from Ajax Chemicals (Auckland, New Zealand). Di-n-Butylamine (Bu_2NH), tri-n-butylamine (Bu_3N), diethylamine (Et_2NH), triethylamine (Et_3N), di-n-propylamine (Pr_2NH), diethanolamine (($HOEt)_2NH$), triethanolamine (($HOEt)_3N$), pyrrolidine (Pyrr), ethylenediamine (EDA), di-n-butyl-phosphate (($BuO)_2PO_2H$), methylsulfonic acid (MsOH), saccharin (Sacc), and sulfamic acid (OSA) were obtained from Sigma-Aldrich (St Louis, MO). EDA was shaken over freshly baked alumina before fractional distillation. ($HOEt)_2NH$ and ($HOEt)_3N$ were fractionally distilled twice and the middle two thirds retained in each step. Other bases were purified by fractional distillation twice from CaH_2 under an inert atmosphere and the middle two thirds retained. HO_2CH was refluxed with boric anhydride and fractionally distilled. AcOH was heated at reflux with $KMnO_4$ with 4% acetic anhydride and distilled twice. OSA was recrystallized twice from deionised (mQ) water and Sacc was recrystallized twice from ethanol—both were then dried by heating up to 100 °C in vacuo. MsOH was diluted with water, treated with 2.5% w/w $Ba(OH)_2$, then filtered and concentrated in vacuo. The resulting solution was stirred over 4% w/v P_2O_5 before distillation under vacuum. All reagents were degassed by nitrogen bubbling and stored away from light under an inert atmosphere.

The water content of PILs was determined by Karl–Fischer titration using an 831 Metrohm (Herisau, Switzerland) Karl–Fischer Coulometer. For room-temperature PILs a neat sample of the PIL was injected for analysis and measurements were averaged over 5 values (data not shown)—standard deviations were less than 5%. Room-temperature solid PILs were examined as per previous reports.[14] Water content for the majority of PILs was in the approximate range of 50–125 ppm, with the exception of OSA-containing compounds which were in the approximate range of 225–275 ppm.

2.2 Physiochemical characterisation procedures

^1H, ^{13}C and ^{15}N NMR measurements of neat liquid samples were acquired with a Varian (Palo Alto, CA) INOVA 500 MHz NMR spectrometer. The neat liquids were transferred under an inert atmosphere to a standard 5 mm NMR tube and equipped with a Wilmad (Buena, NJ) NMR coaxial capillary insert of volume 60 μl containing 1% (w/w) sodium 3-(trimethylsilyl)propionic acid-d_4 acid (TSP) in D_2O solution as a reference/lock solution. ^1H and ^{13}C spectra were externally referenced to TSP as 0 ppm. ^{15}N NMR neat PIL samples were externally referenced to saturated aq. NH_4Cl. Standard ^{15}N measurements were performed with a 45° pulse, inverse-gated decoupling, repetition time 3 s, 1000–2000 transients, and 3 Hz line broadening.

Differential scanning calorimetry (DSC) was performed using a PerkinElmer (Waltham, MA) PYRIS Sapphire system in a sealed aluminium pan under a nitrogen atmosphere. Samples of mass 10–20 mg were run using three temperature cycles and examined from −100 °C at a heating rate of 10 °C $min.^{-1}$

Density was determined using an Anton Paar (Ostfildern, Germany) DMA 4100 M density meter. Dynamic viscosity was conducted using a TA Instruments (New Castle, DE) AR-G2 controlled stress cone and plate rheometer.

The ionic conductivity of the liquid samples was obtained at 25 °C by measuring the complex impedance between 0.1 Hz and 1 MHz with a Solartron (Farnborough, UK) 1260 immediate response analyzer. A locally designed conductivity cell made from two platinum wires was used for the measurements. The cell constant was determined by calibration using an aqueous 0.01 M KCl solution.

3. Results and discussion

3.1 Preparation of high-purity PILs

Previous work has demonstrated the negative effect of vacuum on component ratios of a protic ionic liquid, particularly those containing volatile starting reagents.[14] Attempts to remove solvent and trace water under moderately low pressures (0.3–0.4 mbar) removed volatile PIL species, leaving an excess of the relatively non-volatile component and a non-stoichiometric mixture. Despite the common use of an in vacuo step to dry ILs, significant amounts of water (∼1% w/w) can still remain.[15] It is possible that as water concentrations minimise, the remaining water becomes strongly hydrogen bonded or ionised in the ILs and, thus, is less likely to be removed compared to some other species.

Hence, in order to produce high-purity PILs of known stoichiometry a simple method was selected to remove the need for solvent and introduction of incidental water. Thus, similar to reports of others, the Brønsted acid and base reagents were mixed as neat liquids.[16] However, neutralisation is well known to be an exothermic reaction. In extreme cases, the localised heating from adding a neat base to acid volatilised some PIL components (i.e., loss of formic acid), again leading to non-stoichiometric ratios. The exothermic reaction was also observed to initiate the formation of other by-products, e.g. the condensation reaction between formic acid and secondary amines, which produces ionically neutral amides and water. ^1H NMR spectra revealed a relatively large proportion of amide compared to amine/ammonium a short time after addition of Pyrr to AcOH commenced (data not shown).

It was noted that the reaction exotherms decreased as the mixture approached neutrality. Therefore, an optimal method was found when the mixture remained consistently near neutral (stoichiometric rather than pH neutral) by simultaneously adding both neat reagents to the reactor. Indeed, by simultaneously adding equivalent amounts of both acid and base in a steady stream of drops with vigorous stirring, the exothermic reaction heat was readily dissipated and no amide was detected in the final mixture by ^1H NMR. Localised

heating was avoided and the addition rate was only limited by the removal of overall uniform reaction heat. The addition rate scaled with respect to the reaction volume and ranged between 0.2–10 ml min^{-1}. The rate followed an approximate rule-of-thumb of $n/5$ ml min^{-1}, where n was the total volume of reagents added to the reactor and $1 \leq n \leq 200$. It has been estimated that several litres of PIL could be obtained by this method in less than an hour by simply cooling using circulating water.

When the starting reagents were purified, dried and handled under inert atmosphere, minimal water was introduced into the final mixture. In all reactions observed, significantly less water was detected when compared to the same PILs made *via* solvent dilution/removal *in vacuo* according to a previous method (Table 2).[14] Water content was in the range of ~100 ppm for the majority of PILs, almost an order of magnitude lower than produced by solvent removal *in vacuo*. An exception was OSA-containing PILs where the higher water content was attributed to the acid purification involving recrystallisation from water. Degassing liquid reagents by bubbling nitrogen and storing PILs away from light prevented formation of colour as a result of amine browning. Hence, two of the most significant contaminants that can alter the properties of PILs were minimised. All PILs made by this method together with their thermal properties are detailed in Table 1.

PILs with solid reagents were made by controlled addition of the neat liquid reagent to the dried and purified solid reagent. To reduce the amount of any contaminating water, the reagent and pre-weighed vessel were dried in a 100 °C oven overnight and the loaded vessel cooled under inert gas. The slow uptake of the solid reagent into the liquid phase sufficiently reduced the rate of reaction such that the strong exothermic reaction observed when two liquids were mixed, was not observed with the solid reagents.

A significant drawback to using neat reagents occurred when the product was not a liquid at room temperature. The lack of a significant fluid phase resulted in poor mixing and typically produced an inhomogeneous amorphous solid. Nevertheless, heating the product above the melting point allowed for the melt to mix homogeneously and gave products with ratios consistent with that of the added components as confirmed by ^{1}H and ^{13}C NMR.

Some liquid phase acid/amine products remained inhomogeneous when made as a stoichiometric mixture (Table 1). On the other hand, biphasic mixtures were not observed when mixing occurred in a solvent medium. For instance, the trialkylamines, triethylamine (Et$_3$N) and tributylamine (Bu$_3$N), when mixed stoichiometrically with AcOH formed discrete liquid layers, whereas the dialkylamines, diethylamine (Et$_2$NH) and dibutylamine (Bu$_2$NH), formed homogeneous mixtures. However, compounds with hydroxyl groups formed homogeneous liquids regardless of the degree of nitrogen substitution. The biphasic mixtures were characterised by NMR to have a bottom acid layer with an excess of acid (typically 2:1 or 3:1 acid:base). The top layer consisted almost entirely of un-reacted base, indicating that a mobile proton may be required for neutralisation and that the neat reagent was not sufficiently reactive.

By using the mass of reagents, PIL ratios of acid and base (mol%) were able to be estimated to an accuracy of 0.1%. Although ^{1}H NMR indicated both the purity and approximate stoichiometry, the required precision was inadequate for high-purity results. Often some reagent loss was observed from the mass difference between the product PILs and the starting reagents, but no mixture gained mass during the reaction. The difference error was applied as though both the reagents had lost that equivalent amount of mass, and when converted to a molar scale, typical relative errors in the ratio were 0.1–0.2%.

In total, of the 48 possible component mixtures examined, 18 formed homogeneous liquids at room temperature and 12 remained as biphasic mixtures.

3.2 Determination of ionisation by ^{15}N NMR

Empirical studies to distinguish between H-bonding and proton transfer of a protonated nitrogen have been attempted using UV/VIS and ^{1}H NMR spectroscopy, but the required solvation and concentration changes are not possible for PILs.[17] It is known that the NMR chemical shift is dependent on both concentration and the solvent dielectric constant.[18] Concentration is also an important factor in ion-pairing.[19] Hence, PILs were examined as neat liquids in order to observe the properties of the ionic liquid, rather than the dynamics of a dilute acid–amine solution.

Another benefit of using neat liquid samples is that ^{15}N NMR data could be acquired in a reasonable time. ^{15}N is a spin-$\frac{1}{2}$ nucleus, which simplifies magnetic relaxation compared to ^{14}N, a quadrupolar spin-1 nucleus, but ^{15}N is only present at 0.37% natural abundance, which tends to limit applications unless enrichment or site-specific ^{15}N labelling is included. In the case of neat PILs, the large sample concentration in the rf coil made possible determination of the nitrogen substitution at the exchange site and to distinguish between a protonated and non-protonated nitrogen (*i.e.*, a substituted ammonia *vs.* ammonium ion).

^{15}N NMR spectroscopy has several desirable, but not always practical, characteristics when compared to other nuclei (*e.g.* ^{1}H, ^{13}C).[20] Intermolecular effects on ^{15}N are very important due to the presence of a lone pair on nitrogen. Nitrogen-containing bonds often exhibit a high polarity, which gives a chemical shift range in organic molecules that spans up to 400 ppm. This makes changes in electronic density on the nitrogen atom much more sensitive than either ^{13}C (~200 ppm) or ^{1}H (~12 ppm) and has been used to estimate the empirical order of ion pairing in amine–polyfluorinated acid mixtures.[21]

Due to fast intermolecular proton exchange, a single isotropic ^{15}N signal was obtained which was an average of protonated and molecular bases [Fig. 1(a)]. The neat base δ ^{15}N measurement was used as a reference for subsequent measurements, $\frac{R_2NH_2^+}{R_2NH} = K_0$. The maximum chemical shift was taken from a dilute solution of the base in excess neat acid, $\frac{R_2NH_2^+}{R_2NH} \approx K_\infty$. Despite the excess acid, it is possible that not all of the base may have been ionised, consequently, this value was taken to be the upper limit of proton transfer. Hence, the concentration of acid required for ionisation of a neat base

Table 1 Phase transitions of PILs upon heating from -100 °C at 10 °C min^{-1}

Protic ionic liquid	Base:acid (%)		T_g/°C	T_m/°C	Phase transition/°C
(HOEt)$_2$NH·(BuO)$_2$PO$_2$H	50.7	49.3	-71.4	28.8	-39.0
(HOEt)$_2$NH·OSA	50.1	49.9	-56.9	—	—
(HOEt)$_2$NH·Sacc	67.9	32.1	—	a	—
(HOEt)$_2$NH·AcOH	50.0	50.0	-58.5	—	—
(HOEt)$_2$NH·HO$_2$CH	49.6	50.4	-71.9	—	—
(HOEt)$_2$NH·MsOH	49.1	50.9	-62.2	29.0	—
(HOEt)$_3$N·(BuO)$_2$PO$_2$H	49.9	50.1	-59.7	43.2	-11.1, 24.3
(HOEt)$_3$N·AcOH	50.1	49.9	-58.6	48.4	-14.2
(HOEt)$_3$N·HO$_2$CH	50.6	49.4	-52.4	63.3	—
(HOEt)$_3$N·Sacc	48.7	51.3	—	a	—
(HOEt)$_3$N·MsOH	50.0	50.0	-78.6	69.9	—
(HOEt)$_3$N·OSA	49.6	50.4	—	a	—
Bu$_2$NH·(BuO)$_2$PO$_2$H	50.5	50.0	—	63.4	-65.1, -10.3, 31.4
Bu$_2$NH·AcOH	52.5	47.5	—	45.0	-31.1, -12.3
Bu$_2$NH·HO$_2$CH	56.2	43.8	-76.6	27.8	—
Bu$_2$NH·MsOH	50.3	49.7	-46.9	72.4	26.2, 59.1, 68.8
Bu$_2$NH·OSA	66.5	33.5	-38.9	87	26.5
Bu$_2$NH·Sacc	52.0	48.0	-24.7	88.3	16.0, 67.8
Bu$_3$N·(BuO)$_2$PO$_2$H	50.0	50.0	-82.9	—	—
Bu$_3$N·AcOH	50.7	49.3	—	a	—
Bu$_3$N·HO$_2$CH	52.6	47.4	—	a	—
Bu$_3$N·MsOH	39.0	61.0	-25.5	70.8	29.1
Bu$_3$N·OSA	50.5	49.5	—	a	—
Bu$_3$N·Sacc	49.1	50.9	—	a	—
EDA·(BuO)$_2$PO$_2$H	49.9	50.1	-70.4	-18.3	24.9
EDA·AcOH	50.3	49.7	-71.1	—	—
EDA·HO$_2$CH	49.9	50.1	-85.7	—	—
EDA·MsOH	51.2	48.8	-82.4	54.9	—
EDA·OSA	50.3	49.7	—	a	—
EDA·Sacc	51.7	48.3	-64.6	—	—
Et$_3$N·(BuO)$_2$PO$_2$H	49.6	50.4	-91.0	—	—
Et$_3$N·AcOH	50.6	49.4	—	a	—
Et$_3$N·HO$_2$CH	54.7	45.3	—	a	—
Et$_3$N·MsOH	50.0	50.0	-78.9	24.3	-31.6
Et$_3$N·OSA	50.3	49.7	—	a	—
Et$_3$N·Sacc	49.6	50.4	-27.4	72.0	36, 59.4
Et$_2$NH·(BuO)$_2$PO$_2$H	48.7	51.3	-89.9	-6.8	-18.4
Et$_2$NH·AcOH	49.4	50.6	-62.1	47.5	-14.5, 21.7
Et$_2$NH·HO$_2$CH	49.4	50.6	—	35.8	—
Et$_2$NH·MsOH	49.6	50.4	—	45.1	—
Et$_2$NH·OSA	50.4	49.6	—	a	—
Et$_2$NH·Sacc	51.7	48.3	-22.2	77.9	66.4
Pyrr·(BuO)$_2$PO$_2$H	49.1	50.9	-93.9	-3.7	-43.7
Pyrr·AcOH	49.5	50.5	—	30.7	—
Pyrr·HO$_2$CH	50.9	49.1	—	10.6	—
Pyrr·MsOH	49.4	50.6	-15.1	122.1	—
Pyrr·OSA	50.1	49.9	—	a	—
Pyrr·Sacc	50.1	49.9	-62.1	33.4	-42.2

a Inhomogeneous.

Table 2 Water content from Karl–Fischer titration produced by two different PIL mixing methods

	Water content ($\pm 5\%$)/ppm	
PIL	Vacuum^a	Neat addition
(HOEt)$_2$NH·OSA	9408	227
(HOEt)$_2$NH·AcOH	2033	67
(HOEt)$_2$NH·HO$_2$CH	5371	119
(HOEt)$_2$NH·MsOH	1200	102
Bu$_2$NH·HO$_2$CH	5539	94
Et$_3$N·HO$_2$CH	12102	124
Et$_3$N·MsOH	1205	106

a Data from Zhao et al.[14]

was able to be determined by examination of a range of concentrations between K_0 and K_∞ [Fig. 1(b)].

The sample with a base composition of 75% required only 128 pulses to obtain satisfactory signal-to-noise (S/N) ratio. However, the 20% base sample required greater than 2000 pulses (~ 2 h) and had a comparatively poor S/N ratio [Fig. 1(a)]. While this was partially due to a change in concentration of ^{15}N active nuclei in the sample, the altered dynamics of the ionised nitrogen also contributed. The increased linewidth near equimolar concentrations also suggested that the molecular relaxation times had altered significantly, possibly due to broadening from increased proton-exchange rate or interaction with a strong dipole from a close-contact ion, such as would be found in a short-lived aggregation of ionised species.

In the case of (HOEt)$_2$NH·AcOH, K_∞ had a chemical shift of ~ 10 ppm. A shift of similar magnitude was also present at

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(a) ^{15}N NMR spectra

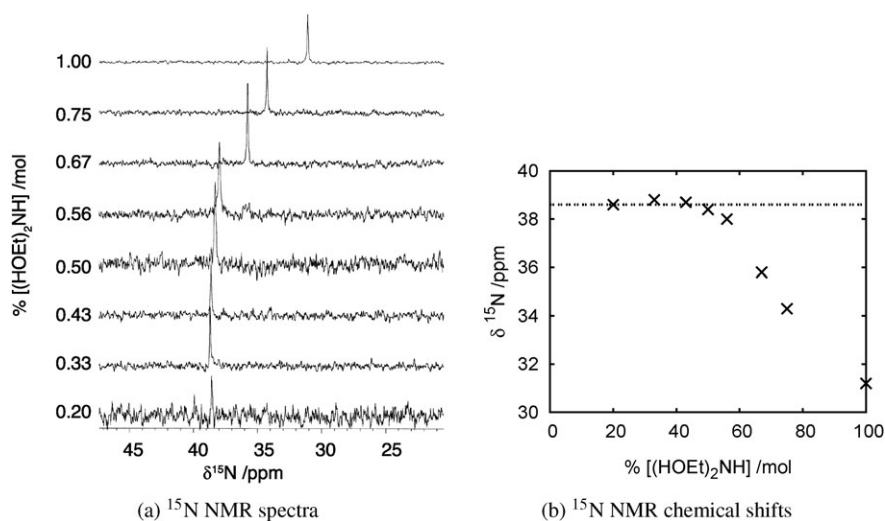(b) ^{15}N NMR chemical shifts

Fig. 1 ^{15}N NMR spectra of diethanolamine samples with different acetic acid concentrations.

the neutralisation point [Fig. 1(b)], indicating the nitrogen species in equimolar solution were mostly in the ionised state. Concomitantly, at stoichiometric concentrations all of the acid species had formed anions, which was confirmed by ^{13}C NMR (see the ESI†), albeit with a lesser change as the carbon nuclei were not directly involved in the ion exchange. Comparison of both strong and weak acids showed that proton transfer was complete for stoichiometric PILs.

3.3 Transport properties

As ILs are proposed to be composed entirely of ions, they are considered to be among the most concentrated electrolytic fluids with large numbers of charge carriers per unit volume. In particular, ion transport properties can be crucial in electrochemical devices and for reaction kinetics in a synthetic process.[22] Very high conductivities are possible when charge carriers are mobile and, hence, conductivity provides important insight into the molecular transport properties of PILs. Therefore, the density, viscosity and ionic conductivity of the 18 room-temperature liquid mixtures were examined to characterise the PIL transport properties (Table 3).

The density of the PILs was relatively constant and close to unity with only a few exceptions. Bases with an excess of hydrogen bond (H-bond) donors (diethanolamine ($(HOEt)_2NH$), ethanediamine (EDA)) were more dense than the N-substituted alkyl bases. The two sulfur-containing acids (methanesulfonic acid (MsOH), sulfamic acid (OSA)) also gave an increased density over the carboxylic acids (AcOH, HO_2CH). Thus, predictably the least dense compounds had a combination of N-substituted alkyl amines and formic acid (*i.e.*, $Bu_2NH \cdot HO_2CH$), whereas PILs with the highest density had multiple possible H-bond exchange sites and a sulfur-containing acid ($(HOEt)_2NH \cdot OSA$).

Viscosity was correlated with density results—PILs with excess H-bond donors had higher viscosity than PILs that only had exchangeable hydrogens at the presumed ionic exchange site. Dibutylphosphate ($(BuO)_2PO_2H$) was the acid that produced the largest number of room-temperature liquid PILs, increasing in viscosity approximately 30-fold as the number of protons attached to base heteroatoms increased from zero (Et_3N, Bu_3N) or one (Pyrr, Et_2NH) to multiple (EDA, $(HOEt)_2NH$). Also, HO_2CH gave a viscosity 3–8 times

Table 3 Physical properties of room-temperature PILs

Protic ionic liquid	Density/g ml^{-1}	Viscosity/cP	Conductivity/mS cm^{-1}
$(HOEt)_2NH \cdot (BuO)_2PO_2H$	1.110	2409	0.06
$(HOEt)_2NH \cdot OSA$	1.430	449	0.14
$(HOEt)_2NH \cdot AcOH$	1.181	5647	0.11
$(HOEt)_2NH \cdot HO_2CH$	1.220	762	0.93
$(HOEt)_2NH \cdot MsOH$	1.344	1590	0.32
$Bu_2NH \cdot HO_2CH$	0.920	113	1.05
$Bu_3N \cdot (BuO)_2PO_2H$	0.941	105	0.07
$EDA \cdot (BuO)_2PO_2H$	1.068	2945	0.08
$EDA \cdot AcOH$	1.103	958	0.59
$EDA \cdot HO_2CH$	1.107	112	9.83
$Et_2NH \cdot (BuO)_2PO_2H$	1.009	201	0.08
$Et_3N \cdot (BuO)_2PO_2H$	1.007	94.4	0.23
$Et_3N \cdot HO_2CH$	0.992	17.7	8.85
$Et_3N \cdot MsOH$	1.135	100	1.91
$Pyrr \cdot (BuO)_2PO_2H$	1.056	105	0.28
$Pyrr \cdot AcOH$	1.067	36.3	3.02
$Pyrr \cdot HO_2CH$	1.050	15.4	20.05
$Pyrr \cdot Sacc$	1.101	499	0.91

lower than that of AcOH with the same base; PILs with MsOH were also close to an order of magnitude more viscous. Most surprising was the high viscosity of $(HOEt)_2NH \cdot AcOH$, which may be explained by the formation of acetic acid dimers and trimers that could lead to large species more resistant to flow.[23]

The high viscosity had a major impact on the measured conductivity of the PILs. This was foremost with the relative fluid formic acid mixtures, which had conductivity values an order of magnitude higher than any other ion combination. Although in general there is a correlation between viscosity and conductivity, the viscosity alone cannot account for the conductivity behaviour. For instance, pyrrolidine (Pyrr) PILs, Pyrr·Sacc and Pyrr·AcOH had similar conductivity values but the measured viscosity differed by almost two orders of magnitude. Furthermore, $EDA \cdot HO_2CH$ and $Bu_2NH \cdot HO_2CH$ had a similar viscosity but a large difference in conductivity. The diverse results suggest the possibility that multiple modes of proton transport may be a significant process in PIL conductance, i.e., Grotthus proton-hopping and ion transport.[24] Many other factors, which can contribute to the conductivity (i.e., ion size, density and ion aggregation), however, were not examined.

One way to understand the correlation between ionic conductivity and viscosity is to use the qualitative approach of Angell et al. based on the classical Walden rule:[13,25]

$$\Lambda \eta = k \qquad (2)$$

where Λ is the molar conductivity, η is the viscosity, and k is a temperature-dependent constant. Dilute aqueous solutions, molten salts and ionic liquids have been observed to approximately follow the Walden rule with conductivity inversely related to viscosity.[26] A log–log plot of Λ vs. η predicts a straight line that passes through the origin; 0.01 M KCl, which exists as dissociated ions, provides a reference 'ideal' line for the plot. Compounds that lie close to the ideal line are said to be ionic, except for one or two notable exceptions, most ILs fall below, suggesting neutral species in the liquid.[27] Improved fits to the Walden plot are possible by compensating for the size of the conductive species although the Walden plot remains a qualitative analysis.[28]

Of the 18 binary liquid mixtures examined via Walden plots, two main types of behaviour were observed (Fig. 2). Firstly, eight PILs lie close to the ideal line; secondly, the majority of the room-temperature PILs were significantly below the ideal line, suggesting between 10–20% ionic species by the Walden definition. PILs close to the ideal line typically were relatively high viscosity—conversely, highly fluid and conductive PILs were typically much below the ideal line. The only compound slightly above the ideal line, Pyrr·Sacc, had a large freezing/melting point hysteresis and remained liquid at room temperature below its T_m, suggesting some thermal phase property may influence the mechanism of conduction.

PILs close to the ideal line were $(HOEt)_2NH$- or EDA-type, bases with exchangeable protons away from the proposed ion-forming proton transfer position (i.e.,–NH_2, –OH). In a given series, $EDA \cdot HO_2CH$ was an order of magnitude less viscous than $EDA \cdot AcOH$ and ~ 2 orders less than
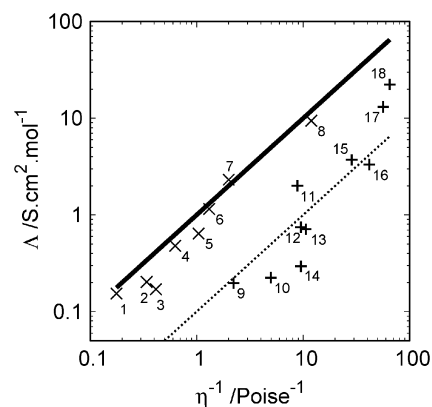
Fig. 2 Walden plot of PILs fluid at room temperature. PILs are numerically denoted as: (1) $(HOEt)_2NH \cdot AcOH$, (2) $EDA \cdot (BuO)_2PO_2H$, (3) $(HOEt)_2NH \cdot (BuO)_2PO_2H$, (4) $(HOEt)_2NH \cdot MsOH$, (5) $EDA \cdot AcOH$, (6) $(HOEt)_2NH \cdot HO_2CH$, (7) Pyrr·Sacc, (8) $EDA \cdot HO_2CH$, (9) $(HOEt)_2NH \cdot OSA$, (10) $Et_2NH \cdot (BuO)_2PO_2H$, (11) $Bu_2NH \cdot HO_2CH$, (12) $Pyrr \cdot (BuO)_2PO_2H$, (13) $Et_3N \cdot (BuO)_2PO_2H$, (14) $Bu_3N \cdot (BuO)_2PO_2H$, (15) Pyrr·AcOH, (16) $Et_3N \cdot MsOH$, (17) $Et_3N \cdot HO_2CH$, and (18) $Pyrr \cdot HO_2CH$.

$EDA \cdot (BuO)_2PO_2H$, all roughly the same distance from the ideal line. This suggests ion transport mechanisms and intermolecular interactions were constant for a given base, with the acid size determining transport properties. $(HOEt)_2NH$ follows a similar pattern (ηHO_2CH < MsOH < $(BuO)_2PO_2H$) with notable exceptions. $(HOEt)_2NH \cdot AcOH$ was the most viscous PIL examined, possibly due to AcOH forming larger multi-ion aggregates;[23] $(HOEt)_2NH \cdot OSA$ was similar to PILs without exchangeable hydrogens, possibly as OSA can form a zwitterion depending on the proton solvation and may not be involved in ionic conduction. There was an overall implication that a proton-hopping mechanism increased molar conductivity when a base had more than one proton capable of inter-molecular exchange.[29]

It has been suggested that the relative difference in aqueous pK_a between the acid and base of PILs can provide some measure of proton transfer. A large $\Delta pK_a(aq)$ PIL, i.e., $Et_3N \cdot MsOH$, would be predicted to be more 'ionic' than the small $\Delta pK_a(aq)$ $(HOEt)_2NH \cdot AcOH$—the opposite of observations.[26] However, it must be remembered that aqueous $\Delta pK_a(aq)$ values are not necessarily the same in non-aqueous solutions.[30] PILs have also been observed to alter the pK_a of acids depending on the paired base.[31] For this work, the $\Delta pK_a(aq)$ approach was too simple to account for all intermolecular phenomena related to 'good' or 'poor' PILs, particularly with regard to hydrogen bonding or a mobile proton.

Regardless, the majority of PILs appeared to be poorly ionised as predicted by conductivity and were clustered approximately an order of magnitude below the ideal line (Fig. 2). However, ^{15}N NMR indicated that proton transfer was complete and the molecules in PILs were ionic. Therefore, a significant amount of the ionic molecules must have ordered in such a way as to be electrically neutral, i.e., an ion-pair,[10,32] or the viscosity was greater than predicted for a Newtonian electrolyte fluid, i.e., a liquid crystalline order.[33] The large number of PILs in about the same region on the Walden plot suggests that all PILs may be mostly ion-paired or

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liquid-phase ordered—a Grotthuss proton-hopping mechanism then promotes conductivity if appropriate functional groups were included.

4. Conclusion

A series of protic ionic liquids has been prepared and their physical properties characterised. PILs produced by simultaneous addition of pre-dried reagents were at least an order of magnitude drier than comparative methods and component stoichiometry was known to better than 0.1 mol%. The physical characteristics of the PILs were strongly influenced by the functional groups of the base: those with protons capable of undergoing exchange led to higher viscosity PILs than similar bases without exchangeable hydrogens (protons). ^{15}N NMR of neat acid–amine PILs provided a straight-forward method to show that proton transfer from acid to amine had occurred in individual molecules of a PIL. However, for many PILs, conductivity did not match theoretical values based on viscosity and indicated that significant neutral species (ion aggregates) or liquid-phase order were present in PILs. Possible reasons for neutral species formed from ionised molecules may include neutral ion pairs or increased viscosity from hydrogen-bond networks.

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