Protic Ionic Liquids: Properties and Applications

Tamar L. Greaves[†] and Calum J. Drummond*,[†,‡]

CSIRO Molecular and Health Technologies (CMHT), Bag 10, Clayton, Vic 3169, Australia, and CSIRO Materials Science and Engineering (CMSE), Private Bag 33, Clayton MDC, Vic 3169, Australia

Contents

* To whom correspondence should be addressed. E-mail: calum.drummond@csiro.au.
[†] CSIRO Molecular and Health Technologies (CMHT).
[‡] CSIRO Materials Science and Engineering (CMSE).

Tamar Greaves obtained her B.Sc. (1999) and Ph.D. (2004) degrees in Physics from Monash University, where her research supervisor was Assoc. Prof. John Cashion. Since then she has been a postdoctoral fellow with CSIRO at the Molecular Health and Technologies division, within Prof. Calum Drummond's group.

Calum Drummond received a Ph.D. in Physical Chemistry from The University of Melbourne in 1987. He is currently Chief of CSIRO Materials Science and Engineering and is the recipient of an Australian Research Council Federation Fellowship hosted by CSIRO Molecular and Health Technologies. He is also classified as a CSIRO Chief Research Scientist. Immediately prior to these current appointments, he was seconded from CSIRO to be the inaugural Vice President Research at CAP-XX. CAP-XX manufactures electrical double-layer capacitors for consumer electronic products. The World Economic Forum designated CAP-XX as a 2005 global Technology Pioneer. In April 2006 CAP-XX listed on the London AIM. Calum's research interests are in the area of physical chemistry, particularly colloid and surface science, including application to energy storage and amphiphile self-assembly materials.

1. Introduction

The field of ionic liquids (ILs) is growing at a very fast rate, as the many beneficial properties of these liquids are identified and utilized. A subset of ILs are protic ionic liquids (PILs), which are easily produced through the combination of a Brønsted acid and Brønsted base. To our knowledge, there has been no review that focuses exclusively on PILs, despite the increasing number and attractive features of these complexes. In contrast, there have been reviews of nearly all aspects of aprotic ILs (AILs), including their role in electrochemistry,[1-3] synthesis of nanostructured materials,[4] and reaction media and catalysis,[5-10] with a general history of ILs up to 1994 having been given by Wilkes.[11] There is a comprehensive review written by Poole in 2004 that covers the use of both PILs and AILs in chromatography.[12] In the present work, the literature is reviewed up to early 2007, containing the physicochemical and solvent properties of PILs, a description of the variety of applications that have been investigated, and the significant potential for other applications. The collation of the physicochemical data allows structure−property trends to be discussed, and these can be used as a foundation for the development of new PILs to achieve specific properties.

The key properties that distinguish PILs from other ILs is the proton transfer from the acid to the base, leading to the presence of proton-donor and -acceptor sites, which can be used to build up a hydrogen-bonded network. PILs have a number of unique properties compared to other ILs, with the exception of some Brønsted acidic ILs.

Generally, ILs are defined as those fused salts with a melting point less than 100 °C, with salts with higher melting points referred to as molten salts. As far as we can ascertain, the first IL discovered was ethanolammonium nitrate, reported in 1888 by Gabriel,[13] which has a melting point of 52−55 °C[13,14] and is also a PIL. Ethylammonium nitrate (EAN), reported in 1914 by Walden[15] with a melting point of 12.5 °C,[12] was the first truly room-temperature ionic liquid discovered and has been the focus of most of the PIL investigations, whereas ethanolammonium nitrate has received little attention. EAN stands out from other ILs, and many other solvents, because of its waterlike properties,[16] in that it can form a three-dimensional hydrogen-bonded network and has an equal number of hydrogen donor and acceptor sites.[17]

Closely related to the PILs are Brønsted acidic ILs, which are either PILs or AILs depending on whether the available proton is on the cation or the anion, respectively. The Brønsted acidic AILs have been incorporated within the organic synthesis section, since that is the principal application of those compounds.

A second related series of compounds are the alkylammonium alkylcarbamates,[18] such as DIMCARB, which is made from the combination of dimethylamine and carbon dioxide in a 1.8:1 ratio.[19-21] These have not been included within this review, since they usually consist of nonstoichiometric ratios of ions and contain a number of neutral and ionic species in equilibrium. These are probably better categorized as ionic media than as ionic liquids.

In this review, we have taken the liberal view to include all PILs and protic molten salts with melting points up to 200 °C. The inclusion of fused salts with higher melting points was to allow structure−property correlations to be made across a wider range of complexes. Primarily PILs with stoichiometric ratios of Brønsted acid to base have been covered, though some mention and comparison has been made to nonstoichiometric mixtures.

The ionicity, physicochemical and thermal properties of the PILs are covered first in this review, followed by a description of the applications where they have been used, including organic synthesis, chromatography, biological applications, fuel cells, explosives, and, very recently, industrial lubricants.

2. PIL Formation through Proton Transfer

As previously mentioned, PILs are formed through the transfer of a proton from a Brønsted acid to a Brønsted base, according to Scheme 1. This leads to distinguishing features between PILs and AILs, in that all PILs have a proton available for hydrogen bonding and usually non-negligible

Scheme 1. PIL Formation through Proton Transfer from a Brønsted Acid (A) to a Brønsted Base (B) (e.g., EAN Formation, CH$_3$CH$_2$NH$_2$ + HNO$_3$ → CH$_3$CH$_2$NH$_3$$^+$ $^-$NO$_3$)

$$B + A \rightarrow HB^+ + A^-$$
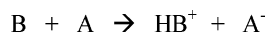
vapor pressure, and some are distillable media, where their boiling point occurs at a lower temperature than decomposition (see section 2.2).

The proton-transfer process can be improved through the use of stronger acids and/or stronger bases, hence leading to a greater driving force for the proton transfer. The pK_a values of acids and bases may be considered as an indication of how strongly a proton will be transferred from the acid to a base, though it must be noted that the pK_a's that are usually considered are for aqueous solutions[22,23] and may not be appropriate for the nonaqueous PILs.

The cations most commonly used in PILs are represented in Figure 1, including primary, secondary, or tertiary
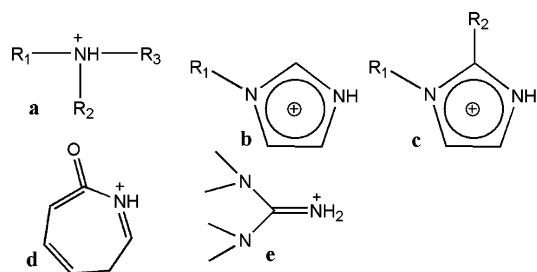
Figure 1. Representative cations used in PILs, including (a) primary, secondary, or tertiary ammonium cations (where R$_1$, R$_2$, and/or R$_3$ can be hydrogen atoms), (b) 1-alkylimidazolium cations, (c) 1-alkyl-2-alkylimidazolium cations, (d) caprolactam, and (e) 1,1,3,3-tetramethylguanidinine.

ammonium ions, mono- or di- imidazolium ions, caprolactam, and guanidinium ions. The wide range of heterocyclic ions that contain nitrogen within the ring have not been represented. The imidazolium and other heterocyclic rings can contain substituents on any of the carbons in the ring, so long as the nitrogen containing the positive charge retains a proton. A large variety of anions have been coupled with these cations, with commonly used ones shown in Figure 2,

Figure 2. Representative anions, including (a) carboxylates, (b) trifluoroacetate (TFA), (c) bis(perfluoroethylsulfonyl)imide (BETI), (d) bis(trifluoromethanesulfonyl)imide (TFSI), (e) nitrate, and (f) hydrogen sulfate.
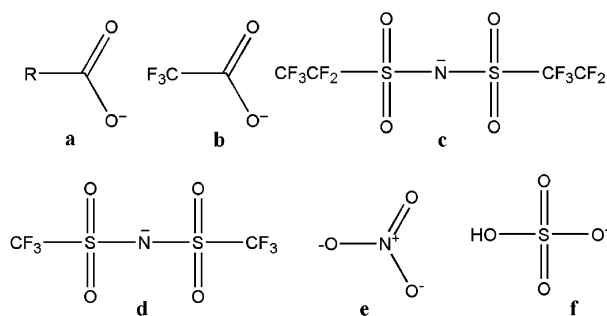
including organic (such as carboxylates), inorganic (such as nitrate or hydrogen sulfate), or fluorinated (such as bis-(trifluoromethanesulfonyl)imide (TFSI), trifluoroacetic acid (TFA), and bis(perfluoroethylsulfonyl)imide (BETI), tetrafluoroborate, or hexafluorophosphate).

2.1. Ionicity

Ideally in PILs, the proton transfer is complete from the acid to the base, such that the only individual species present

are the resulting cation and anion. In reality, this is unlikely since the proton transfer may be less than complete, resulting in the neutral acid and base species being present, and aggregation and association of either ions or neutral species can occur. Consequently, it is important to have techniques that enable a measure of the ionicity and structure of ionic liquids. Relevant investigations into the molecular interactions of carboxylic acids and amines were conducted a few decades ago by Kohler et al.[24−26] However, few investigations have been conducted into the ionicity of ILs, with PILs receiving more attention[22,23,27−30] than AILs.[31] There is currently no "standard" method for determining the ionicity of PILs nor a standard method for classifying which should be considered pure ionic liquids.

The Walden plot of the log(equivalent conductivity) versus log(fluidity) can be used to show how good an ionic liquid is (see section 3.2). Using this method, PILs have generally been shown as poor ionic liquids,[22,32] though it is not possible to differentiate whether this is due to incomplete proton transfer, aggregation, or the formation of ion complexes.

MacFarlane et al. have suggested that some concentration of neutral species present in PILs should still lead to the mixture being defined as an ionic liquid, where the properties of the mixture are clearly of the ionic liquid rather than of the neutral species.[23] Continuing on from this, MacFarlane and Seddon have recently proposed the question "How far toward the right does the equilibrium have to lie, or how high does the degree of proton transfer have to be, in order for the substance to be properly termed an ionic liquid?".[33] Their suggested answer is to set a limit of 1% neutral species in an IL for it to be classed as a "pure ionic liquid", with those with higher levels of neutral species perhaps better thought of as mixtures of ionic liquids and neutral species.[33]

A number of different techniques have been used to provide information about the ionicity of PILs, including NMR,[23,27,30] changes in thermal properties as a function of stoichiometry,[27,29,30] IR spectroscopy,[27] and ionic conductivity in the form of a Walden plot.[22] These techniques generally give a qualitative measure of the ionic nature of PILs. Similarly, the aqueous pK_a values for the precursor acids and bases have been employed to provide an estimate of how complete the proton transfer is,[22,23] where a large ΔpK_a (pK_a(base) − pK_a(acid)) is suggestive of good proton transfer. Investigations by Angell et al. indicate that PILs with ΔpK_a > 8 have nearly ideal Walden behavior.[22,34]

The early investigations by Kohler and co-workers into 1:1 mixtures of carboxylic acids with primary, secondary, or tertiary alkylamines suggested that there were aggregates present. The triethylammonium cation appears to have a strong preference for the formation of A$_3$B$_1$ aggregates (A = acid, B = base), with free amine present at the 1:1 composition.[24−26] The primary and secondary amines investigated showed a preference toward the 1:1 complexes.[24,25]

An empirical method was developed by Kohler et al. for determining the size of aggregates in these salts through the ratio of the relative molecular weight, M_{visc}, (based on the viscosity of the salts) compared to the calculated molecular weight, M, of the 1:1 complex.[24] Surprisingly, we do not believe that anyone has applied this method to estimate the aggregate size in ILs before.

The aggregation numbers for PILs calculated from M_{visc}/M have been determined using Kohler's method, and a summary is reported in Table 1. For comparison, the aggregation was calculated for commonly used AILs, and these are included

Table 1. Calculated Aggregation Numbers for PILs and Commonly Used AILs

PILs	aggregation number
alkylammonium carboxylates[32]	4.6−7.0
alkylammonium nitrates[12,32]	4.9−5.2
alkylammonium thiocyanates[12]	4.6−4.8
dialkylammonium thiocyanates[12]	3.8
trialkylammonium thiocyanates[12]	3.3
long-chain alkylammonium TFSA or BETI[227]	1.4−1.6
long-chain trialkylammonium TFSA or BETI[227]	1.1−1.4
primary heterocyclic cation with fluorinated anions[22,57,132]	1.7−3.8
primary heterocyclic cation with carboxylate anions[22,57,132]	3.3−3.5
1-alkyl-3-alkylimidazolium with fluorinated anions (AIL)[3,47,228]	2.2−3.0
quaternary ammonium with fluorinated anions (AIL)[46]	1.5−3.2

in Table 1. Only PILs where the viscosity and density were known could be included, which unfortunately did not include any imidazolium PILs.

Interestingly, there appears to be a trend for aggregation to follow the series primary > secondary > tertiary. The long-chain alkylammonium PILs with the very strong acids of TFSI and BETI led to very little aggregation. The quaternary ammonium AILs with fluorinated anions had surprisingly comparable aggregation numbers to the alkylammonium PILs with fluorinated anions.

An investigation into the hydration of sulfuric acid has shown that this system does not undergo direct proton transfer to form $H_3O^+ \, HSO_4^-$ but instead forms larger clusters, with at least three water molecules required to deprotonate each sulfuric acid molecule.[41−43] The importance of this study is that it highlights the complicated nature of these systems, with, in this case, significantly different energy barriers for the formation of single ionic species compared to clusters.[43] With respect to the PIL systems, it strongly suggests that there will be some aggregation and association occurring.

Angell et al. have shown that there appears to be a correlation between the excess boiling point, ΔT_b, which is how much higher the boiling point of the PIL is than the average of the acid and base boiling points, and ΔpK_a, as shown in Figure 3.[22] This technique is limited to PILs where the boiling points can be determined and assumes that the aqueous pK_a values are representative of the values in the ionic liquids. However, it can be seen in Figure 3 that a
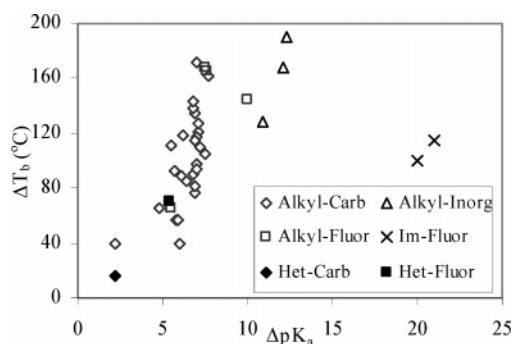

Figure 3. Excess boiling point (ΔT_b) versus ΔpK_a. The PILs contain alkylammonium cations (alkyl) with either carboxylate (Carb), fluorinated (Fluor), or inorganic (Inorg) anions.

reasonable correlation does generally exist for the PILs shown. Since the excess boiling point can be considered to be related to the degree of proton transfer, then the existence of a relationship between ΔT_b and ΔpK_a suggests that the aqueous pK_a values are relevant for the PILs, with ΔpK_a being useful for predicting the degree of proton transfer in PILs.

The thermal properties of a large collection of PILs and protic molten salts containing primary ammonium cations with organic and inorganic anions have been reported by Angell et al. in early 2007.[34] The properties of these salts were consistent with their earlier findings.[22]

A recent comprehensive investigation by Tokuda et al. on the ionicity of AILs used the ratio of molar conductivities $\Lambda_{imp}/\Lambda_{NMR}$ determined by electrochemical impedance spectroscopy, Λ_{imp}, and pulse-field-gradient spin-echo NMR, Λ_{NMR}.[31] This ratio gives the proportion of the charged species that migrate under an electric field compared to the total number that should be free to migrate. For AILs, the ratio gave a good estimate of the degree of aggregation in AILs (and it is assumed that it will be applicable to proton transfer for PILs).

2.2. Distillation of Ionic Liquids

A very beneficial property of many PILs is that they are easily distillable, so long as they do not undergo decomposition before boiling. The mechanism involves the simple proton transfer from the cation back to the anion to reform the original acid and base neutral species. On condensing, the PIL is reformed.[44] Designing PILs that are suitable for distillation requires a compromise with ionicity. Strong proton transfer is essential for good ionicity, while, in contrast, distillation requires a weakly basic anion; otherwise, the PIL will undergo decomposition before boiling.[23]

A couple of classes of PILs are not generally suitable for distillation, which are those containing the carboxyl anion, since they are susceptible to amide formation, and those containing the nitrate anion, which undergo exothermic decomposition (explode).

The ability of DIMCARB, which is closely related to PILs, to be distilled has been known for many years;[19−21] similarly, the boiling points of PILs before decomposition were reported by Angell et al. in 2003.[22] In contrast, it was only very recently that certain AILs were shown to be distillable.[44] There are a number of key differences between the distillation of PILs and AILs. Usually the PILs just require heating to moderate temperatures, whereas AILs require heating to higher temperatures at low pressures to prevent decomposition. The mechanism for volatilization of AILs has been proposed to involve clusters of ionic species rather than the formation of neutral species, which occurs for PILs through proton transfer.[44,45] The AILS containing the strongly basic anion TFSI were found to distill well,[44] whereas PILs require weakly basic anions.[23]

3. Physicochemical Properties

The thermal properties of the PILs including glass transition, T_g, melting point T_m, boiling point T_b, and chemical transformation or decomposition point, T_d, are given in Table 2. The physicochemical properties of density, ρ; surface tension (for liquid−air interfaces), γ; viscosity, η; refractive index, n_D; and ionic conductivity, κ, for the PILs are given in Table 3. In Tables 2 and 3, the PILs are grouped based

Table 2. Thermal Phase Behavior of PILs, Including the Glass Transition (T_g), Melting Point (T_m), boiling point (T_b), and Temperature where the Sample Undergoes Chemical Change or Decomposition (T_d) (All Temperatures in °C)[a]

protic ionic liquid	water (wt %)	T_g	T_m	T_b	T_d
hydronium TfO	<1[34]		27.4[34]	212.7[34]	
hydronium H$_2$PO$_4$	<1[34]		21[34]	158[34]	
ammonium formate	<1[34]		120[34]		
ammonium HF$_2$	<1[34]		125.6[34]		240[34]
ammonium nitrate	<1[34]		163.5[34]	223.8[34]	
ammonium HSO$_4$	<1[34]	−65.6[34]	116.3[34]		
ammonium H$_2$PO$_4$	<1[34]	−23.3[34]	193.3[34]		
ammonium TfO	<1[34]				225[34]
Alkylammonium					
methylammonium formate	0.42[32]	−114[32]	13[32]	182[32]	
	<1[34]	−108.2[34]	−21.7[34]	162.1[34]	
methylammonium BF$_4$	<1[34]		77.1[34]		
methylammonium HF$_2$	<1[34]	−104.1[34]	−11.8[34]	174.5[34]	
methylammonium PO$_3$F	<1[34]	47.8[34]			
methylammonium nitrate	<1[34]		108−112[216]	206.8[34]	260[215]
			110.5−11.5[14]		
			109[215]		
			104.7[34]		
methylammonium HSO$_4$	<1[34]		73.2[34]		302.3[34]
methylammonium H$_2$PO$_4$	<1[34]	−28.8[34]	96.8[34]		254.2[34]
methylammonium CH$_3$SO$_3$	<1[34]		91[34]		260.2[34]
ethylammonium formate	0.38[32]	−106[32]	−15[32]	180[32]	
	<1[34]	−127.5[34]	−72.9[34]	176.1[34]	
ethylammonium acetate	0.12[32]		87[32]	156[32]	
ethylammonium propionate	0.42[32]	−94[32]		121[32]	
ethylammonium butyrate	0.26[32]	−88[32]		130[32]	
ethylammonium glycolate	0.50[32]	−67[32]		130[32]	
ethylammonium lactate	0.85[32]	−57[32]		142[32]	
ethylammonium BF$_4$	<1[34]		152.4[34]		
ethylammonium TfO	<1[34]		172.1[34]		
ethylammonium HF$_2$	<1[34]	−100.3[34]	3.5[34]	176.4[34]	
ethylammonium nitrate	0.22[32]	−91.5[34]	9[32]	240[34]	242[32]
	<1[34]		13[34]		170[167]
	520 ppm[16]		14−16[16]		
	>0.005v/v%[68]		11−13[68]		
	800 ppm[229]		12[229]		
			12.5[167]		
			14[89]		
			8[230]		
ethylammonium HSO$_4$	0.31[32]	−84[32]	40[32]		323[32]
	<1[34]	−96.4[34]	31.9[34]		
ethylammonium H$_2$PO$_4$	0.38[32]	−31.3[34]	134[32]		
	<1[34]		109.5[34]		
ethylammonium perchlorate	<1[34]		151.9[34]		
ethylammonium CH$_3$SO$_3$	<1[34]		112.5[34]		288.6[34]
propylammonium formate	0.61[32]	−124.7[34]	50[32]	185[32]	
	<1[34]	42[22]	−55.4[34]	213.1[34]	
				165[22]	
propylammonium TFA				205[22]	
propylammonium nitrate			4.0[12,167]		120[12,167]
propylamminium HSO$_4$	<1[34]		33.9[34]		304.5[34]
propylammonium H$_2$PO$_4$	<1[34]		145.6[34]		315.3[34]
butylammonium formate	0.32[32]	−95[32]	2[32]	179[32]	
	<1[34]	−120.1[34]	−46.8[34]	224.5[34]	
butylammonium thiocyanate			20.5[12,167]		190[12]
					130[167]
butylammonium TFSA	<1[56]		16.2[56]		352[56]
butylammonium BF$_4$	<1[34]		198.2[34]		310.5[34]
butylammonium PO$_3$F	<1[34]	−50.1[34]			
butylammonium HSO$_4$	<1[34]	−63.4[34]	33.5[34]		307.9[34]
butylammonium H$_2$PO$_4$	<1[34]	−33.3[34]	113.3[34]		275.7[34]
butylammonium CH$_3$SO$_3$	<1[34]	−89.6[34]	131.8[34]		292.2[34]
tert-butylammonium BF$_4$	<1[34]		118.3[34]		243.6[34]
tert-butylammonium TfO	<1[34]		11.6[34]		243.4[34]
tert-butylammonium HSO$_4$	<1[34]		130.6[34]		243.9[34]
pentylammonium formate	0.26[32]	−93[32]	12[32]	179[32]	
benzylammonium nitrate			137.5−138.5[14]		
2-methylpropylammonium formate	0.71[32]	−92[32]	26[32]	173[32]	
2-methylbutylammonium formate	0.64[32]	−95[32]	−1[32]	173[32]	
3-methylbutylammonium formate	0.41[32]	−90[32]	47[32]	180[32]	
ethanolammonium formate	0.55[32]	−85[32]	−82[58]	192[32]	150[58]
	<1[34]	−88.3[34]			
ethanolammonium acetate	0.47[32]	−67[32]		210[32]	

Table 2 (Continued)

protic ionic liquid	water (wt %)	T_g	T_m	T_b	T_d
Alkylammonium (Continued)					
ethanolammonium glycolate	0.17[32]	−52[32]	106[32]	216[32]	
ethanolammonium lactate	0.51[32]	−53[32]		132[32]	
ethanolammoniun BF$_4$	<1[34]		0.5[34]		
ethanolammonium TfO	<1[34]	−66[34]	74.8[34]		
ethanolammonium nitrate	0.72[32]	−82[32]	51[32]	255.4[34]	280[32]
	<1[34]	−87.4[34]	52−53[14]		
			−25.2[34]		
ethanolammonium CH$_3$SO$_3$	0.48[32]	−44[32]	99[32]		
2-propanolammonium formate	0.45[32]	−64[32]		185[32]	
[C$_8$H$_{17}$]NH$_3$ TFSA					350[b 227]
[C$_8$H$_{17}$]NH$_3$ BETI					354[b 227]
glycine BF$_4$			116[51]		220[51]
glycine PF$_6$			101[51]		157[51]
glycine nitrate			111[51]		192[51]
					145−147[14]
glycine chloride			186[51]		195[51]
alanine TFA			82[51]		119[51]
alanine BF$_4$			78[51]		241[51]
alanine PF$_6$					176[51]
alanine nitrate			159[51]		168[51]
(alanine)$_2$ SO$_4$			141[51]		193[51]
valine nitrate			134[51]		169[51]
isoleucine nitrate			105[51]		167[51]
threonine nitrate					147[51]
proline TFA			78[51]		192[51]
proline BF$_4$			76[51]		236[51]
proline PF$_6$					168[51]
proline nitrate					138[51]
(proline)$_2$ SO$_2$			92[51]		206[51]
glycine methyl ester nitrate		−26[51]	44[51]		178[51]
glycine ethyl ester nitrate		−10[51]	49[51]		182[51]
alanine methyl ester acetate		−23[51]			172[51]
alanine methyl ester lactate		−24[51]	38[51]		77[51]
alanine methyl ester thiocyanate		−38[51]	62[51]		139[51]
alanine methyl ester TFSA		−61[51]	−17[51]		150[51]
alanine methyl ester BF$_4$		−48[51]	−18[51]		230[51]
alanine methyl ester PF$_6$		−35[51]			209[51]
alanine methyl ester nitrate		−34[51]	61[51]		186[51]
alanine ethyl ester lactate		−29[51]	75[51]		82[51]
alanine ethyl ester nitrate		−45[51]	−17[51]		187[51]
valine methyl ester nitrate		−33[51]	74[51]		195[51]
leucine methyl ester nitrate		−31[51]	75[51]		210[51]
isoleucine methyl ester nitrate		−36[51]	−14[51]		172[51]
phenylalanine methyl ester nitrate		−32[51]	92[51]		224[51]
threonine methyl ester nitrate		−32[51]	−12[51]		156[51]
serine methyl ester nitrate		−30[51]	105[51]		179[51]
proline methyl ester lactate		−20[51]			140[51]
proline methyl ester BF$_4$		−20[51]			234[51]
proline methyl ester PF$_6$		−22[51]			221[51]
proline methyl ester nitrate		−67[51]	−16[51]		159[51]
(proline ethyl ester)$_2$ nitrate		−50[51]	−17[51]		183[51]
1,1,3,3-tetramethylguanidinium formate			67.0[132]		151.04[132]
1,1,3,3-tetramethylguanidinium lactate			<−50[132]		190.98[132]
1,1,3,3-tetramethylguanidinium TFA			42.0[132]		312.58[132]
1,1,3,3-tetramethylguanidinium TfO			41.0[132]		353.87[132]
1,1,3,3-tetramethylguanidinium perchlorate			33.2[132]		189.37[132]
1,2,3-triaminoguanidinium nitrate					>180[217]
di(ethylammonium) sulfate	0.31[32]	−64[32]	∼200[32]		
di(ethylammonium) HPO$_4$	0.42[32]		120[32]		
dimethylammonium formate	<1[34]			152[34]	
dimethylammonium HF$_2$	<1[34]	−111[34]	−22.9[34]	178.4[34]	
dimethylammonium PO$_3$F	<1[34]	−51.5[34]			
dimethylammonium nitrate	<1[34]		75.5−76.5[14]		222[215]
			76[215]		
			75[34]		
dimethylammonium HSO$_4$	<1[34]		40.1[34]		310.9[34]
dimethylammonium H$_2$PO$_4$	<1[34]	−36.8[34]	117.3[34]		
dimethylammonium CH$_3$SO$_3$	<1[34]	−95[34]	122.1[34]		278[34]
diethylammonium nitrate			104−105[14]		
diethylammonium HSO$_4$	<1[34]		77.3[34]		301.5[34]
dipropylammonium thiocyanate			5.5[12]		180[12]
dipropylammonium PO$_3$F	<1[34]	−31.5[34]			
dipropylammonium nitrate			5.5[167]		140[167]

Table 2 (Continued)

protic ionic liquid	water (wt %)	T_g	T_m	T_b	T_d
Alkylammonium (Continued)					
dibutylammonium formate	<1[34]	−116.4[34]		234.7[34]	
		−120[231]			
dibutylammonium TFSA	<1[56]		42.6[56]		325[56]
dibutylammonium BF$_4$	<1[34]		212.8[34]		330.1[34]
dibutylammonium PO$_3$F	<1[34]	−39.5[34]	75.7[34]		
dibutylammonium HSO$_4$	<1[34]		130.9[34]		283.5[34]
dibutylammonium H$_2$PO$_4$	<1[34]	−15.6[34]	98[34]		
dibutylammonium CH$_3$SO$_3$	<1[34]	−49[34]	42.7[34]		331.9[34]
diphenylammonium TFSA	<1[56]		51.5[56]		193[56]
1-methylpropylammonium thiocyanate			22[12,167]		200[12,167]
methylbutylammonium BF$_4$	<1[34]		77.1[34]		350.3[34]
methylbutylammonium HSO$_4$	<1[34]	−79.6[34]	42.2[34]		285.8[34]
ethylbutylammonium formate	<1[34]	−119.6[34]		207.3[34]	
ethylbutylammonium HSO$_4$	<1[34]		54.4[34]		295.1[34]
monomethylhydrazinium nitrate			74−78[216]		>60[216]
monomethylhydrazinium dinitrate			37[216]		>60[216]
trimethylammonium PO$_3$F	<1[34]	−44.5[34]			
trimethylammonium nitrate			155−156[14]		202[215]
			157[215]		
trimethylammonium HSO$_4$	<1[34]		72.9[34]		308.9[34]
triethylammonium TFSA	<1[56]		3.5[56]		350[56]
triethylammonium BF$_4$	<1[34]		104.3[34]		286.7[34]
triethylammonium TfO	<1[34]				312.5[34]
triethylammonium PO$_3$F	<1[34]	−59.7[34]			
triethylammonium nitrate			113−114[14]		
triethylammonium HSO$_4$	<1[34]	−100.1[34]	84.2[34]		262.8[34]
triethylammonium H$_2$PO$_4$	<1[34]	−34.4[34]			
triethylammonium CH$_3$SO$_3$	<1[34]	−96.5[34]	21.6[34]		269.7[34]
tripropylammonium PO$_3$F	<1[34]	−56.60[34]	30[34]		
tributylammonium PO$_3$F	<1[34]	−59.1[34]			
tributylammonium nitrate			21.5[12,167]		119[167]
					120[12]
tributylammonium HSO$_4$	<1[34]	−57.1[34]	86.6[34]		250.3[34]
[C$_8$H$_{17}$]$_3$NH TFSA					357[b 227]
dimethylethylammonium formate	<1[34]	−121.1[34]		187.4[34]	
dimethylethylammonium HSO$_4$	<1[34]	−91.4[34]	3.3[34]		302.6[34]
dimethylethylammonium CH$_3$SO$_3$	<1[34]		94.7[34]		295.8[34]
diisopropylethylammonium TFA			92−93[159]		
methoxyethylammonium formate	<1[34]	−103[34]	−22.4[34]	209.1[34]	
methoxyethylammonium BF$_4$	<1[34]				206.9[34]
methoxyethylammonium TfO	<1[34]				283.5[34]
methoxyethylammonium H$_2$PO$_4$	<1[34]	−20.3[34]	90.5[34]		278.6[34]
methoxyethylammonium CH$_3$SO$_3$	<1[34]		62.6[34]		282.4[34]
methoxypropylammonium formate	<1[34]	−116.4[34]			
methoxypropylammonium nitrate	<1[34]	−82.7[34]			
trinitropropylammonium nitrate					>150[232]
N,N′-dimethylcyclohexylammonium BF$_4$			89.0[41]		
N,N′-dimethylcyclohexanmethylammonium BF$_4$		−18.4[41]	143.8[41]		
Imidazolium					
imidazolium TFSA	<1[30,56]		73.0[30,56]		379[30,56]
imidazolium BF$_4$	<1[34]		131.2[34]		363.2[34]
imidazolium TfO	<1[34]		122.9[34]	308.4[34]	
imidazolium CF$_3$SO$_3$	<1[34]		122.9[34]		
1-methylimidazolium formate	0.08[23]	−99[23]			
1-methylimidazolium acetate	0.03[23]	−98[23]	−23[23]		
1-methylimidazolium lactate					245[c 155]
1-methylimidazolium TFA			51[23]		
1-methylimidazolium TFSA	<0.5[53]	−84[53]	9[53]		
1-methylimidazolium BETI	<0.5[53]	−73[53]	11[53]		
1-methylimidazolium BF$_4$	<1[34]		35.8[34]		387[34]
	<0.5[53]		36.9[41]		
			37[53]		
1-methylimidazolium PF$_6$	<0.5[53]	−4[53]	116[53]		
1-methylimidazolium TfO	<1[34]	45.8[34]	92[34]		323.5[34]
	<0.5[53]		84[53]		
1-methylimidazolium nitrate	<0.5[53]		70[53]		
1-methylimidazolium HSO$_4$		−99[199]			320[199]
1-methylimidazolium H$_2$PO$_3$		−70[199]	47[199]		122[199]
1-methylimidazolium H$_2$PO$_4$		57[199]	137[199]		164[199]
1-methylimidazolium H$_3$PO$_7$		−40[199]			197[199]
1-methylimidazolium perchlorate	<0.5[53]		157[53]		
1-methylimidazolium chloride	<0.5[53]		72[53]		
1-methylimidazolium bromide	<0.5[53]	−60[53]	41[53]		

Table 2 (Continued)

protic ionic liquid	water (wt %)	T_g	T_m	T_b	T_d
	Imidazolium (Continued)				
3-methylimidazolium Br−HBr		17−20[156]		100[156]	
1-ethylimidazolium TFSA	<0.5[53]	−89[53]			
1-ethylimidazolium BETI	<0.5[53]	−86[53]			
1-ethylimidazolium BF$_4$	<0.5[53]	−87[53]			
1-ethylimidazolium PF$_6$	<0.5[53]	−62[53]			
1-ethylimidazolium TfO	<0.5[53]		8[53]		
1-ethylimidazolium nitrate	<0.5[53]		31[53]		
1-ethylimidazolium HSO$_4$		−75[199]			200[199]
1-ethylimidazolium H$_2$PO$_3$		−76[199]	53[199]		129[199]
1-ethylimidazolium H$_2$PO$_4$		−49[199]	80[199]		168[199]
1-ethylimidazolium H$_3$PO$_7$		−42[199]			212[199]
1-ethylimidazolium perchlorate	<0.5[53]	−81[53]	21[53]		
1-ethylimidazolium chloride	<0.5[53]	−57[53]	58[53]		
1-ethylimidazolium bromide	<0.5[53]		60[53]		
1-ethylimidazolium acrylate		−61[52]			
1-ethylimidazolium vinyl sulfonate		−77[52]			
1-ethylimidazolium styrene sulfonate		−95[52]			
1-ethylimidazolium vinyl phosphonate		−78[52]			
1-butylimidazolium lactate					265[b, 155]
1-hexylimidazolium lactate					260[b, 155]
1-decylimidazolium lactate					245[b, 155]
benzimidazolium TFSA	<1[56]		101.9[56]		368[56]
N-vinylimidazolium BF$_4$			55.4[209]		
1-vinylimidazolium vinylsulfonate		−83[208]			
1-vinylimidazolium sulfopropyl acrylate		−73[208]			
1,2-dimethylimidazolium nitrate	<0.5[53]		84[53]		
1,2-dimethylimidazolium chloride	<0.5[53]	−86[53]	181[53]		
1,2-dimethylimidazolium bromide	<0.5[53]		176[53]		
1-ethyl-2-methylimidazolium TFSA	<0.5[53]	−84[53]			
1-ethyl-2-methylimidazolium BETI	<0.5[53]		−19[53]		
1-ethyl-2-methylimidazolium BF$_4$	<0.5[53] <1[34]	−88[34,53]			
1-ethyl-2-methylimidazolium PF$_6$	<0.5[53]	−42[53]			
1-ethyl-2-methylimidazolium TfO	<0.5[53]		33[53]		
1-ethyl-2-methylimidazolium nitrate	<0.5[53]		75[53]		
1-ethyl-2-methylimidazolium perchlorate	<0.5[53]	−76[53]	7[53]		
1-ethyl-2-methylimidazolium chloride	<0.5[53]		178[53]		
1-ethyl-2-methylimidazolium bromide	<0.5[53]		144[53]		
1-benzyl-2-ethylimidazolium TFSA	<0.5[53]	−57[53]			
1-benzyl-2-ethylimidazolium BETI	<0.5[53]	−54[53]			
1-benzyl-2-ethylimidazolium BF$_4$	<0.5[53]	−43[53]			
1-benzyl-2-ethylimidazolium PF$_6$	<0.5[53]	−24[53]			
1-benzyl-2-ethylimidazolium TfO	<0.5[53]	−48[53]			
1-benzyl-2-ethylimidazolium nitrate	<0.5[53]	−31[53]	52[53]		
1-benzyl-2-ethylimidazolium perchlorate	<0.5[53]	−31[53]			
1-benzyl-2-ethylimidazolium chloride	<0.5[53]	−86[53]	171[53]		
1-benzyl-2-ethylimidazolium bromide	<0.5[53]	−30[53]	123[53]		
1,2-dimethylimidazolium TFSA	<0.5[53]	−79[53]	22[53]		
1,2-dimethylimidazolium BETI	<0.5[53]		15[53]		
1,2-dimethylimidazolium BF$_4$	<1[34] <0.5[53]	−74.7[34] −97[53]	31.3[34]		365.2[34]
1,2-dimethylimidazolium PF$_6$	<0.5[53]		115[53]		
1,2-dimethylimidazolium TfO	<0.5[53] <1[34]		119[53] 115.3[34]	298.9[34]	
1,2-dimethylimidazolium perchlorate	<0.5[53]	−3[53]	64[53]		
1-methylbenzimidazolium BF$_4$			99.9[41]		
1-C$_6$H$_{13}$OCH$_2$-imidazolium lactate					230[a, 155]
1-C$_6$H$_{13}$OCH$_2$-imidazolium salicylate					220[a, 155]
4,4′-trimethylenedipyridine TFSA		160[28]			301[28]
1-alkylimidazolium DL-lactate (alkyl from H to C$_{12}$)			<20[177]		194.0−244.5[177]
1-alkyloxymethylimidazolium DL-lactate (alkyl from C$_4$ to C$_{12}$)			<20[177]		188.0−245.5[177]
1-alkylimidazolium L-lactate (alkyl from H to C12)			<20[177]		191.3−238.5[177]
1-alkyloxymethylimidazolium L-lactate (alkyl from C$_4$ to C$_{12}$)			<20[177]		186.6−238.9[177]
1-alkylimidazolium L-lactate (alkyl from C$_6$ to C$_{12}$)					191.3−222.5[182]
1-alkyloxymethylimidazolium L-lactate (alkyl from C$_6$ to C$_{12}$)					201.8−238.9[182]
1-alkylimidazolium DL-lactate (alkyl from C$_6$ to C$_{12}$)					194.0−226.0[182]
1-alkyloxymethylimidazolium DL-lactate (alkyl from C$_6$ to C$_{12}$)					207.5−245.5[182]
1-alkyloxymethylimidazolium salicylate (alkyl from C$_6$ to C$_{12}$)					199.5−240.0[182]
	Heterocyclic				
pyridinium TFSA	<1[56]		60.3[56]		314[56]
2-methylpyridinium TFA		−74[c, 22] −80[114]	25[c, 22]	170[c, 22]	
2-methylpyridinium TfO		−87[c, 22]	72[114]		

Table 2 (Continued)

protic ionic liquid	water (wt %)	T_g	T_m	T_b	T_d
			Heterocyclic (Continued)		
2-methylpyridinium formate		-77^{c} [22]		130^{c} [22]	
2-methylpyridinium CH$_3$SO$_3$			99[114]		
4,4′-trimethylenedipyridinium TFSA	<1[56]		62.0[56]		386[56]
2-fluoropyridinium TfO	<1[34]		58.3[34]	286[34]	
pyrrolidinium TFSA	<1[56]		35.0[56]		373[56]
2-pyrrolidonium chloroacetate			32[57]		
2-pyrrolidonium TFA		-90[57]			125[57]
2-pyrrolidonium BF$_4$		-73[57]			233[57]
2-pyrrolidonium nitrate		-76[57]	8[57]		168[57]
2-pyrrolidonium H$_2$PO$_4$		-46[57]			249[57]
2-pyrrolidonium phenolcarboxylate		-63[57]	7[57]		163[57]
1-methylpyrrolidinium BF$_4$			-31.9[41]		
N-methylpyrrolidinium formate	0.07[23]	-116[23]	-32[23]		
N-methylpyrrolidinium acetate	0.05[23]	-108[23]			
N-methylpyrrolidinium TFA		38[23]			
pyrrolium BF$_4$		0.1[41]			
1-methylpyrrolium BF$_4$		-15.9[41]			
2-methyl-1-pyrrolinium BF$_4$		-94.3[41]	17.1[41]		
1-ethyl-2-phenylindolium BF$_4$		-73.9[41]	29.8[41]		
1,2-dimethylindolium BF$_4$		-74.8[41]	24.5[41]		
2-methylindolium BF$_4$			131.0[41]		
carbazolium BF$_4$		59.9[41]			
1-ethylcarbazolium BF$_4$		-68.0[41]			
2,4-lutidinium BF$_4$		-44.8[41]	34.1[41]		
2,3-lutidinium BF$_4$			59.4[41]		
3,4-lutidinium BF$_4$		-33.3[41]	45.9[41]		
2,6-lutidinium BF$_4$		-10.9[41]	104.6[41]		
pyrazolium TFSA	<1[56]		58.9[56]		265[56]
1-methylpyrazolium BF$_4$		-109.3[41]	-5.9[41]		
piperidinium TFSA	<1[56]		37.9[56]		363[56]
1-ethylpiperidinium BF$_4$		-77.2[41]	-27.9[41]		
4,4′-trimethylenedipiperidinium TFSA	<1[56]		167.3[56]		403[56]
1,2,4-triazolium TFSA	<1[56]		22.8[56]		287[56]
1,2,3-benzotriazolium TFSA	<1[56]		136.6[56]		230[56]
1,5-diamino-1H-tetrazolium nitrate			138[224]		168[224]
1,5-diamino-1H-tetrazolium perchlorate			97[224]		192[224]
			125–130[225]		
caprolactam chloroacetate		-67[57]	29[57]		117[57]
caprolactam TFA		-73[57]			135[57]
caprolactam BF$_4$		-74[57]			239[57]
caprolactam nitrate			45[57]		188[57]
caprolactam H$_2$PO$_4$		-34[57]			
caprolactam phenolcarboxylate		-55[57]	31[57]		118[57]
2,5-diphenyl-1,3,4-oxadiazolium TFSA			80^{c} [29]		200^{c} [29]
acridinium TFSA	<1[56]		116.1[56]		353[56]
pyrazinium TFSA	<1[56]		53.6[56]		229[56]
piperazinium TFSA	<1[56]		172.7[56]		358[56]
morpholinium TFSA	<1[56]		58.5[56]		349[56]
quinoxalinium TFSA	<1[56]		74.1[56]		244[56]
anilinium nitrate					182–184[14]
anilinium TfO	<1[34]				250[34]

[a] PILs are described by their cation then their anion. Abbreviations used are bis(trifluoromethanesulfonyl)imide (TFSI), trifluoroacetic acid (TFA), bis(perfluoroethylsulfonyl)imide (BETI), tetrafluoroborate (BF$_4$), and hexafluorophosphate (PF$_6$). [b] Onset of decomposition. [c] Estimated from a figure contained in the reference.

on their precursor amines into alkylamine, imidazolium, and heterococyclic amines.

Tables 2 and 3 do not contain all known PILs, since a large number have been reported in the literature without stating any of these properties. While the data in Tables 2 and 3 are not comprehensive for many of the PILs, because of limited reporting in the literature, it is sufficient for the identification of many trends. The thermal properties are discussed below, followed by their physicochemical properties. The plots have been prepared using the available data.

The amount of water present in the samples has a significant effect on their physicochemical properties. This has recently been shown by Widegren et al., who measured the viscosity as a function of water concentration for three hydrophobic imidazolium based AILs.[80] It is expected that there will be discrepancies between values reported in the literature by different groups, because of varying water concentrations, many of which do not state the water concentration of their samples.

The physicochemical properties of the ILs, like all other materials, depend upon the intermolecular and intramolecular forces and, hence, upon the structure of the cation and the anion. A significant number of investigations have been conducted for AILs on the relationship between their physicochemical properties and the structure of their cation and anion.[38,40,60,79,81–84] In comparison, we believe there are few investigations that similarly observe trends for series of PILs.[32,60]

Table 3. Physicochemical Properties of PILs, Including the Density (ρ), Air–Liquid Surface Tension (γ_{LV}), Viscosity (η), Refractive Index (n_D), and Ionic Conductivity (κ); Abbreviations of Anions Same as in Table 2

protic ionic liquid	ρ (g/cm³)	γ_{LV} (mN/m)	η (cP)	n_D	κ (mS/cm)
Alkylammonium					
methylammonium formate	1.087[c 32]	43.1[c 32]	17[c 32]	1.4336[c 32]	43.8[c 32]
ethylammonium formate	1.039[c 32]	38.5[c 32]	32[c 32]	1.4344[c 32]	12.16[c 32]
ethylammonium propionate	1.018[c 32]	31.5[c 32]	75[c 32]	1.4358[c b32]	0.872[c 32]
ethylammonium butyrate	0.980[c 32]	29.6[c 32]	208[c 32]	1.4398[c 32]	1.03[c 32]
ethylammonium glycolate	1.189[c 32]	49.3[c 32]	1200[c 32]	1.4692[c b32]	0.864[c 32]
ethylammonium lactate	1.110[c 32]	39.3[c 32]	803[c 32]	1.4581[c 32]	0.26[c 32]
ethylammonium nitrate	1.216[c 32]	47.3[c 32]	32[c 32]	1.4524[c 32]	26.9[c 32]
	1.201[e 230]	49.1[c 233]	23.1[e 16]	1.4534[c 165]	39.6282[g 91]
	1.1219[c 165]	47.6[e 230]	11.5[h 16]		44.9600[h 91]
		46.6[h 16]	32.1[c 165]		
ethylammonium HSO$_4$	1.438[c 32]	56.3[c 32]	128[c 32]	1.4489[c 32]	4.4[c 32]
propylammonium nitrate	1.157[c 12]	41.4[c 69]	66.6[c 12]	1.4561[c 12]	
	1.1568[c 165]		66.6[c 165]	1.4561[c 165]	
butylammonium formate	0.968[c 32]	33.3[c 32]	70[c 32]	1.4422[c 32]	3.1[c 32]
butylammonium TFSA					10.4[l 56]
butylammonium thiocyanate	0.949[c 12,165]		97.1[c 12,165]	1.5264[c 12,165]	
pentylammonium formate	0.95[c 32]	31.9[c 32]	78[c 32]	1.4434[c 32]	1.53[c 32]
[C$_8$H$_{17}$]NH$_3$ TFSA	1.37[b 227]		331[b 227]		
			25[f 227]		
			14.2[k 227]		
[C$_8$H$_{17}$]NH$_3$ BETI	1.45[b 227]		763[b 227]		
			265[f 227]		
ethanolammonium formate	1.184[c 32]	65.0[c 32]	220[c 32]	1.4705[c 32]	3.4[c 32]
	1.204[m 58]		105[c 58]	1.4772[c 58]	3.3[c 58]
ethanolammonium acetate	1.176[c 32]	51.5[c 32]	701[c 32]	1.469[c 32]	0.3[c 32]
ethanolammonium lactate	1.228[c 32]	57.2[c 32]	1324[c 32]	1.4702[c 32]	0.048[c 32]
ethanolammonium nitrate	1.265[c 32]	50.6[c 32]	113[c 32]	1.4400[c 32]	9.35[c 32]
2-propanolammonium formate	1.144[c 32]	46.2[c 32]	854[c 32]	1.4642[c 32]	0.49[c 32]
glycine methyl ester nitrate			92[i 51]		
alanine methyl ester thiocyanate			103[j 51]		
alanine methyl ester BF$_4$			96[e 51]		
alanine ethyl ester nitrate			2030[e 51]		
leucine methyl ester nitrate			1550[j 51]		
proline methyl ester nitrate			186[e 51]		
1,1,3,3-tetramethylguanidinium lactate	1.07[g 132]		388.2[g 132]		0.101[c 132]
1,1,3,3-tetramethylguanidinium TFA	1.27[g 132]		143.7[g 132]		1.886[g 132]
1,1,3,3-tetramethylguanidinium TfO	1.29[g 132]		167.4[g 132]		2.680[g 132]
1,1,3,3-tetramethylguanidinium perchlorate	1.18[g 132]		80.6[g 132]		1.958[c 132]
dipropylammonium thiocyanate	0.9641[c 165]		85.9[c 12,165]	1.5062[c 12,165]	
	0.964[c 12]				
dibutylammonium TFSA					12.6[l 56]
diphenylammonium TFSA					8.5[l 56]
2-methylpropylammonium formate	0.978[c 32]	31.2[c 32]	225[c 32]	1.4434[c 32]	0.699[c 32]
2-methylbutylammonium formate	0.965[c 32]	30.8[c 32]	229[c 32]	1.4462[c 32]	0.858[c 32]
1-methylpropylammonium thiocyanate	1.0132[c 12,165]		196.3[c 12,165]	1.5262[c 12,165]	
triethylammonium TFSA					32.3[l 56]
triethylammonium BETI	1.48[b 227]		163[b 227]		
			67[f 227]		
			9.3[k 227]		
tributylammonium nitrate	0.9176[c 12,165]		636.9[c 12,165]	1.4627[c 12,165]	
[C$_6$H$_{13}$]$_3$NH TFSA	1.12[b 227]		170[b 227]		
			72[f 227]		
			9.7[k 227]		
[C$_8$H$_{17}$]$_3$NH TFSA	1.06[b 227]		219[b 227]		
			89[f 227]		
			11.7[k 227]		
N,N′-dimethylcyclohexylammonium BF$_4$					7.3×10^{-6}[c 41]
					9.8×10^{-5}[h 41]
N,N′-dimethylcyclohexanmethylammonium BF$_4$					1.3×10^{-5}[h 41]
Imidazolium					
imidazolium TFSA					27.1[l 56]
1-methylimidazolium formate			6.7[m 23]		20[c 23]
1-methylimidazolium acetate			5.6[m 23]		4[c 23]
1-methylimidazolium lactate	1.123[m 155]				
1-methylimidazolium TFA					1[c 23]
1-methylimidazolium TFSA	1.3672[e 234]		81[c 53]		7.23[c,p 53]
1-methylimidazolium BETI			218[c 53]		
1-methylimidazolium BF$_4$			>1000[c 53]		0.3[c 41]
					2.8[h 41]
1-methylimidazolium PF$_6$			>1000[c 53]		
1-methylimidazolium TfO			>1000[c 53]		
1-methylimidazolium HSO$_4$					6.5[e 199]

Table 3 (Continued)

protic ionic liquid	ρ (g/cm^3)	γ_{LV} (mN/m)	η (cP)	n_D	κ (mS/cm)
Imidazolium (Continued)					
1-methylimidazolium H$_2$PO$_3$					0.22^e [53]
1-methylimidazolium H$_2$PO$_4$					5.5×10^{-5} ^{e} [199]
1-methylimidazolium H$_3$PO$_7$					7.4×10^{-3} ^{e} [199]
1-methylimidazolium perchlorate			>1000^c [53]		
1-methylimidazolium Br-HBr	1.75^c [156]		17.0^c [156]		40.6^c [156]
1-ethylimidazolium TFSA			54^c [53]		4^{c,p} [53]
1-ethylimidazolium BETI			133^c [53]		1^{c,p} [53]
1-ethylimidazolium BF$_4$			41^c [53]		6^{c,p} [53]
1-ethylimidazolium PF$_6$			550^c [53]		0.8^{c,p} [53]
1-ethylimidazolium TfO			58^c [53]		
1-ethylimidazolium nitrate					5^{c,p} [53]
1-ethylimidazolium HSO$_4$					0.24^e [199]
1-ethylimidazolium H$_2$PO$_3$					0.33^e [199]
1-ethylimidazolium H$_2$PO$_4$					1.1×10^{-2} ^{e} [199]
1-ethylimidazolium H$_3$PO$_7$					2.7×10^{-2} ^{e} [199]
1-ethylimidazolium perchlorate			112^c [53]		5^{c,p} [53]
1-ethylimidazolium chloride					0.03^{c,p} [53]
1-ethylimidazolium bromide					0.01^{c,p} [53]
1-ethylimidazolium acrylate					0.14^e [52]
1-ethylimidazolium vinyl sulfonate					0.087^e [52]
1-ethylimidazolium styrene sulfonate					9.0^e [52]
1-ethylimidazolium vinyl phosphonate					0.15^e [52]
1-butylimidazolium lactate	1.060^m [155]				
1-hexylimidazolium lactate	1.037^m [155]				
1-decylimidazolium lactate	0.991^m [155]				
1-C$_6$H$_{13}$OCH$_2$-imidazolium lactate	1.025^m [155]				
1-C$_6$H$_{13}$OCH$_2$-imidazolium salicylate	1.096^m [155]				
1-vinylimidazolium vinylsulfonate					3.5^e [208]
1-vinylimidazolium sulfopropyl acrylate					0.65^e [208]
N-vinylimidazolium BF$_4$					0.10^e [209]
1-methylbenzimidazolium BF$_4$					1.3×10^{-5} ^{h} [41]
1-methyl-2-methylimidazolium TFSA			100^c [53]		3^{c,p} [53]
1-methyl-2-methylimidazolium BETI			>1000^c [53]		
1-methyl-2-methylimidazolium BF$_4$			100^c [53]		
1-methyl-2-methylimidazolium PF$_6$			>1000^c [53]		
1-methyl-2-methylimidazolium TfO			>1000^c [53]		
1-methyl-2-methylimidazolium perchlorate			>1000^c [53]		
1-ethyl-2-methylimidazolium TFSA			69^c [53]		2^{c,p} [53]
1-ethyl-2-methylimidazolium BETI			186^c [53]		
1-ethyl-2-methylimidazolium BF$_4$			67^c [53]		
1-ethyl-2-methylimidazolium PF$_6$			>1000^c [53]		
1-ethyl-2-methylimidazolium TfO			>1000^c [53]		4^{c,n} [53]
1-ethyl-2-methylimidazolium perchlorate			>1000^c [53]		
1-benzyl-2-ethylimidazolium TFSA			252^c [53]		0.08^{c,p} [53]
1-benzyl-2-ethylimidazolium BETI			552^c [53]		
1-benzyl-2-ethylimidazolium BF$_4$			>1000^c [53]		
1-benzyl-2-ethylimidazolium PF$_6$			>1000^c [53]		
1-benzyl-2-ethylimidazolium TfO			>1000^c [53]		
1-benzyl-2-ethylimidazolium perchlorate			>1000^c [53]		
1-alkylmethylimidazolium DL-lactate (alkyl from H to C$_{12}$)	0.9591–1.1231^a [177]				0.089–0.995^a [177]
1-alkyloxymethylimidazolium DL-lactate (alkyl from C$_4$ to C$_{12}$)	0.9804–1.0640^a [177]				0.091–0.281^a [177]
1-alkylmethylimidazole L-lactate (alkyl from H to C$_{12}$)	0.9626–1.1281^a [177]				0.066–0.978^a [177]
1-alkyloxymethylimidazolium L-lactate (alkyl from C$_4$ to C$_{12}$)	0.9826–1.0695^a [177]				0.088–0.260^a [177]
1-alkylimidazolium L-lactate (alkyl from C$_6$ to C$_{12}$)	0.9626–1.0383^a [182]				
1-alkyloxymethylimidazolium L-lactate (alkyl from C$_6$ to C$_{12}$)	0.9826–1.0350^a [182]				
1-alkylimidazolium DL-lactate (alkyl from C$_6$ to C$_{12}$)	0.9591–1.0374^a [182]				
1-alkyloxymethylimidazolium DL-lactate (alkyl from C$_6$ to C$_{12}$)	0.9804–1.0252^a [182]				
1-alkyloxymethylimidazolium salicylate (alkyl from C$_6$ to C$_{12}$)	1.0522–1.1396^a [182]				
Heterocyclic					
2-methylpyridinium formate	1.2969^{c,n} [22]				10^{c,p} [22]
2-methylpyridinium TFA	1.039^{c,n} [22]				3^{c,p} [22]
2-methylpyridinium TfO	1.3421^{c,n} [22]				0.1^{c,p} [22]
2-pyrrolidonium TFA	1.32^c [57]		11^c [57]		14.4^{c,q} [57]
2-pyrrolidonium BF$_4$	1.46^c [57]		350^c [57]		8.39^{c,q} [57]
pyrrolidinium TFSA					39.6^l [56]
N-methylpyrrolidinium TFA					1^c [23]
N-methylpyrrolidinium formate			7.5^m [23]		20^c [23]
N-methylpyrrolidinium acetate			3.2^m [23]		2^c [23]
1-methylpyrrolidinium BF$_4$					16^{41}, 25^h [41]
pyrrolium BF$_4$					1.4×10^{-6} ^{c} [41]
					3.4×10^{-6} ^{h} [41]
2-methyl-1-pyrrolinium BF$_4$					16^c [41]
					27^h [41]

Table 3 (Continued)

protic ionic liquid	ρ (g/cm^3)	γ_{LV} (mN/m)	η (cP)	n_D	κ (mS/cm)
Heterocyclic (Continued)					
1-ethyl-2-phenylindolium BF$_4$					8.9[c 41]
					16[h 41]
2,3-dimethylindolium BF$_4$					2.0×10^{-6}[h 41]
2-methylindolium BF$_4$					1.6×10^{-6}[h 41]
1-methylindolium BF$_4$					2.0×10^{-6}[h 41]
1,2-dimethylindolium BF$_4$					4.3[c 41]
					11[h 41]
1-ethylcarbazoliun BF$_4$					2.2[c 41]
					5.1[h 41]
2,4-lutidinium BF$_4$					0.23[c 41]
					0.59[h 41]
2,3-lutidinium BF$_4$					0.0059[c 41]
					0.080[h 41]
3,4-lutidinium BF$_4$					0.0036[c 41]
					0.053[h 41]
2,6-lutidinium BF$_4$					1.6×10^{-5}[c 41]
					1.8×10^{-4}[h 41]
1-methylpyrrolium BF$_4$					1.3×10^{-6}[c 41]
					1.7×10^{-6}[h 41]
1-methylpyrazolium BF$_4$					19[c 41]
					35[h 41]
carbazolium BF$_4$					1.3×10^{-6}[h 41]
1-ethylpiperidinium BF$_4$					0.094[c 41]
					0.59[h 41]
pyridinium TFSA					30.4[l 56]
piperidinium TFSA					23.5[l 56]
pyrazolium TFSA					26.5[l 56]
pyrazinium TFSA					33.8[l 56]
benzimidazolium TFSA					13.1[l 56]
1,2,4-triazolium TFSA					22.0[l 56]
4,4′-trimethylenedipyridinium TFSA					10.5[l 56]
caprolactam TFA	1.24[c 57]		28[c 57]		3.83[c,q 57]
					0.383[c 154]
caprolactam BF$_4$	1.33[c 57]		503[c 57]		7.31[c,q 57]
					0.731[c 154]
caprolactam nitrate					0.840[c 154]
morpholinium TFSA					10.8[l 56]
quinoxalinium TFSA					16.5[l 56]

[a] 23 °C. [b] 25 °C. [c] 27 °C. [d] 30 °C. [e] 45 °C. [f] 50 °C. [g] 130 °C. [h] Calculated from equation contained in reference. [i] Estimated from a figure contained in the reference. [j] The values given in the reference were a factor of 10 larger, which was unrealistic. Also, the comparison values in the paper for ILs from Bonhote et al.[48] were misquoted as being a factor of 10 too large. In a later paper by this group,[154] these values are another factor of 10 smaller. [k] Temperature unreported. [l] 70 °C. [m] 80 °C. [n] 40 °C. [p] 100 °C. [q] 20 °C.

3.1. Thermal Phase Behavior

The thermal phase behavior of the PILs, as with other ILs, provides a very good indication about the physicochemical properties of the salts. In general, low glass transitions and low melting points are highly desirable, while maintaining high decomposition temperatures is ideal, but usually less of a requirement. The effects of changes to the cation and anion structures are discussed below for the glass transition, the melting point, and the thermal stability of the PILs. The crystallization temperature has not been included, since only a few values have been reported.[22,32] The thermal properties reported for PILs are given in Table 2.

3.2. Glass Transition

For most applications where PILs are used, or considered for use, it is desirable to have low viscosities. In addition, some applications require high ionic conductivities. The viscosity and conductivity are often reflected in the glass transition, T_g, with low values leading to favorable properties.

The glass transition is indicative of the cohesive energy within the salt, which is decreased by repulsive Pauli forces from the overlap of closed electron shells and increased through the attractive Coulomb and van der Waals interactions.[85] Hence, T_g can be decreased through minimizing the cohesive energy within the salt, which is usually achievable through modification of the cationic or anionic component of the salt.

There are two useful plots based on T_g, which are the Arrhenius and Walden plots. The Arrhenius plot of the PILs is shown in Figure 4, where the fragility increases toward the bottom right of the plot and Arrhenius behavior is represented by the solid line. Arrhenius plots typically contain multiple data plots for each sample, showing their behavior as a function of temperature. However, since there is only one measurement for many of these PILs, typically at ambient temperature, single data points have been used. All the PILs where viscosity and T_g are known are included in Figure 4. Through comparison to the plots presented by Angell et al., it was evident that these PILs are all displaying fragile behavior, where fragility indicates that, as the temperature increases, the viscosities will decrease at a faster rate than predicted by the Arrhenius relationship.[86] The large series of PILs characterized by Angell et al. recently found PILs to have fragilities from intermediate to high fragility, with most having intermediate fragilities.[34]
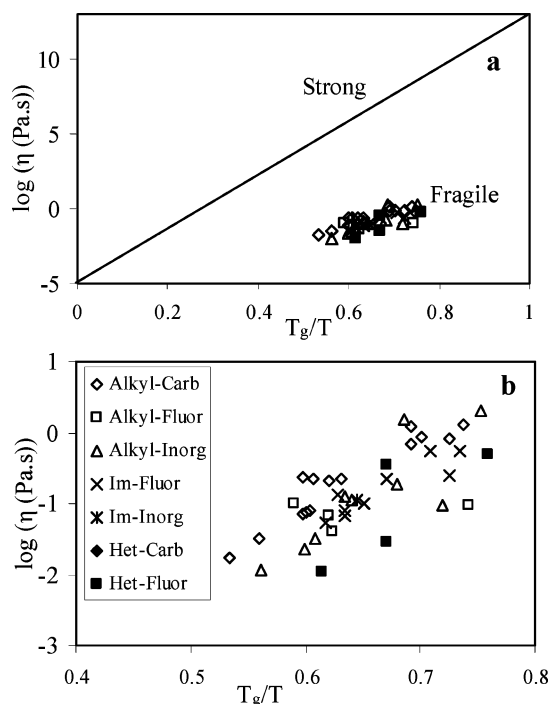
Figure 4. Arrhenius plot of log(viscosity) against T_g/T, where (a) shows the strong and fragile regions and (b) shows a close-up of the region occupied by the PILs. The PILs are categorized by their cation as either alkylammonium (Alkyl), imidazolium (Im), or heterocyclic (Het) and by their anion as either carboxylate (Carb), fluorinated (Fluor), or inorganic (Inorg). The legend in (b) is for both plots.
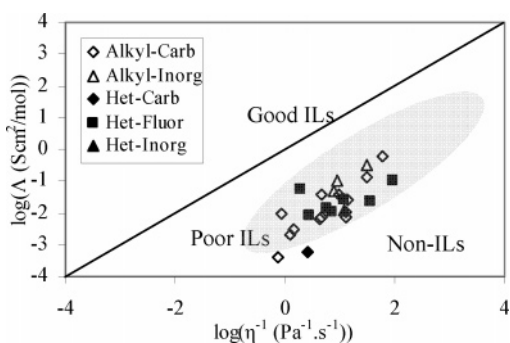

Figure 5. Walden plot of log(equivalent conductivity) against log-(fluidity). This plot uses the same designation of symbols as in Figure 4. The PILs are classified using the scheme of Angell and co-workers,[85] with the solid line indicating good ionic liquid behavior, while below the line indicates poor ionic liquid behavior.

The Walden plot is of the equivalent conductivity against the log of the fluidity (inverse viscosity) and is shown in Figure 5. The Walden plot is a way to represent the ionicity of the ILs, with those having good ionicity likely to have other related good properties, such as high ionic conductivity.

The Walden plot requires that the density, viscosity, and ionic conductivity are known, and the PILs that have these values reported are included in Figure 5. The PILs are generally located in a similar region and are classified as "poor" ionic liquids according to the classification scheme devised by Angell et al.[85] The salts with the tetrafluoroborate anion, BF_4, are an exception, having particularly good ionicity, while the salt with the triflate anion has poor ionicity. It would be interesting to know the location of PILs containing the very strong acid TFSI on the Walden plot; however, insufficient information has been reported for those

compounds. It is envisaged that they would show better ionicity.

A number of investigations have identified certain trends that lead to lower T_g values in ILs.[32,60] Decreasing the cation size, or increasing the asymmetry of the cation, has been shown to lower T_g values through decreasing the packing and cohesive energy of the salts.[60] For primary alkylammonium based PILs, it was found that T_g increases slowly with increasing alkyl chain lengths for anion or cation, and T_g increases significantly with the substitution of a hydroxyl group onto either the anion or cation.[32]

For fluorinated anions, it appears that larger anions weaken the electrostatic interactions between the cation and the anion, hence decreasing T_g.[40] Decreasing the electrostatic interaction dominates over the increase of van der Waals interactions because of the low polarizability of the fluorine atoms. For example, the ion interactions in BF_4 have the electrostatic interactions dominating over the van der Waals forces, while the larger fluorocarbon$-BF_3$ salts have the van der Waals forces slightly dominating, since T_g increases slightly with size.[40]

3.3. Melting Point

The salts listed in Table 2 have a broad range of melting points, from below room temperature (RT-PILs) to above 100 °C (protic molten salts). In general, the melting point can be lowered through decreasing the packing efficiency of the ions. Numerous factors that influence the melting points of the PILs and AILs have been discussed in the literature.[22,55,62,65,87,88] The key factors involve having sufficient steric hindrance to disrupt the packing efficiency and minimize the hydrogen bonding.

The alkylammonium nitrate salts and salts containing the 1-alkyl-2-alkylimidazolium cation with chloride or bromide anions were mostly molten salts, in that their melting points were >100 °C. In contrast, the PILs that contained alkylammonium cations with small carboxylic acids and most of the salts with an imidazolium cation were predominately RT-PILs, or had low melting points.

The PILs containing imidazolium based cations with TFSI or BETI generally led to salts with low melting points. This has been attributed to the relatively large radius of these fluorinated anions weakening the electrostatic interaction with the cation.[62] However, the low melting points for imidazolium based salts with the BF_4 anion were not consistent with this trend.[22] It was recognized that the strength of the acid was likely to be more important than the radius, with acids with low pK_a values leading to salts with higher ionicity. This was seen for the very strong acid HTFSI in comparison to nitric acid. When these anions were combined with the triethylammonium cation, the salts produced had melting points of 3.5 and 113 °C for HTFSI and nitric acid, respectively.

A series of amino based PILs were directly derived from natural α-amino acids.[55] The cations used were $^+H_3N-$(RCH)$-$COOH and $^+H_3N-$(RCH)$-$COOR', where the $-$COOR' group instead of $-$COOH reduced the extent of hydrogen bonding and, hence, decreased the melting point.[55]

3.4. Thermal Stability

The PILs either undergo a boiling point, T_b, or decompose, T_d, upon heating, as mentioned in section 2.2. PILs with a large proton-transfer energy will decompose before reaching

their boiling point.[34] The decomposition temperatures of the PILs given in Table 2 lie mostly between 120 and 360 °C. These values were generally defined as where there was 10% mass loss using thermogravimetric analysis (TGA).[37,53] The thermal stability of the PILs has been reported to be improved by anions with little interactions with other ions or by inorganic anions.[84]

The most thermally stable PILs reported were those with the TFSI anion, as shown in Table 2 with alkylammonium cations,[53] the imidazolium cation,[53] and a variety of heterocyclic cations.[62] These PILs all had decomposition temperatures stated as >200 °C, with most >300 °C. In contrast, PILs containing a carboxylate anion, particularly formate, may have lower thermal stability due to undergoing a condensation reaction to form amides.[32,54]

3.5. Density and Molar Volume

The density values that have been reported are given in Table 3. The density of a material depends on how closely the ions can pack together and, hence, on the size and shape of the ions and ion−ion interactions. Plots of glass transition versus density showed no significant correlation.

It is apparent that the density decreases slowly as the alkyl chain length increases for alkylammonium cations, alkylimidazolium cations, or alkylcarboxylate anions, which is consistent with what has been seen for AILs.[40,89] Tributylammonium nitrate had the lowest density, due to having the bulkiest cation. It is expected that primary amines are likely to have higher densities than secondary or tertiary amines. The densities with heterocyclic amine cations were generally higher than those of the alkylammonium cations.

For lactam based PILs with fluorinated anions, it was seen that increasing the ring number of the cation decreased the density and increased the viscosity. This has been attributed to the modification of the cation−anion interaction because of the increase in the cation size.[37]

The ion−ion spacing in ideal ILs can be represented using the molar volume, V_m.[85] It was previously shown on the Walden plot in Figure 5 that PILs are not ideal and instead may have some association of the ions and/or incomplete proton transfer from the acid to the base. Hence, V_m only gives an indication of the ion−ion spacing for PILs. These PILs had generally lower molar volumes than had been seen for the AILs reported by Angell et al.[85]

The substitution of a hydroxyl group onto the alkyl chain of either the cation or the anion increased the density significantly, probably because of increased hydrogen bonding decreasing the ion−ion separations.[32] The alkyl- and alkoxylimidazolium complexes showed a similar trend for small alkyl chains, with the alkyoxyl chains leading to a higher density. For longer chains, there was negligible difference in their densities, indicating that the increased bulkiness of the hydrocarbon chains is dominating in keeping the ions separated compared to the attractive interaction due to hydrogen bonding.

3.6. Refractive Index and Molar Refractivity

The refractive index, n_D, of a material can give a measure of its polarity, and the molar refractivity, M_R, is directly related to the polarizability of the material. Values have only been reported for PILs with alkylammonium cations,[32] and the n_D values are given in Table 3. The n_D values indicate that these PILs can be considered to be moderately polar
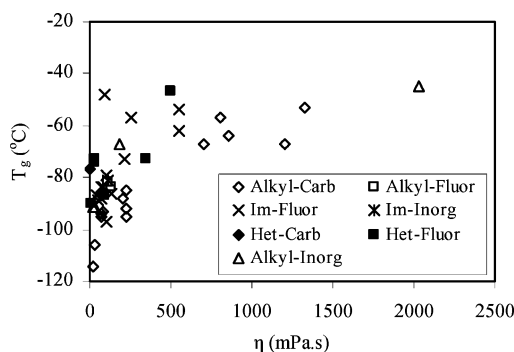

Figure 6. T_g versus viscosity. All viscosities were measured at 25 °C. This plot uses the same designation of symbols as in Figure 4.

media. We have previously shown that n_D increased slowly with increasing alkyl length, while the substitution of a hydroxyl group caused a more significant increase.[32]

The molar refractivity of PILs with alkylammonium cations and carboxyl anions was shown to behave similarly to organic molecules, with methylene groups on the cation contributing 6.1 ± 0.3 cm^3/mol and those on the anion contributing 7.8 cm^3/mol. These values compared well to literature values for the contribution of methylene groups to the molar refractivity of related organic molecules such as amines, carboxylic acids, and alcohols.[32] It is anticipated that PILs will behave similarly to other organic molecules, enabling molar refractivities to be tailorable based on the components of the cation and the anion.

3.7. Surface Tension

The surface tension has only been reported for PILs with alkylammonium cations, and the values are given in Table 3. Changes to either the cation or anion structures had a similar effect on the surface tension,[32] indicating that both ions are present at the surface and influence the surface tension. Similar behavior has previously been noted by Bagno et al. to occur for AILs.[88]

A model has been proposed for alkylammonium based PILs using the assumption that the hydrocarbon chains are exposed to air while the charged groups are positioned toward the bulk of the PIL. For these PILs, it was observed that increasing the alkyl chain length decreased the surface tension, substituting a hydroxyl group onto either the cation or the anion significantly increased the surface tension, and branching in the alkyl chain decreased the surface tension.[32] Hence, in general, the surface tension will be decreased when the ions have a higher packing efficiency or increased when the cohesiveness of the PIL increases (such as through an increase in the amount of hydrogen bonding).

3.8. Viscosity

The viscosity is dependent on the ion−ion interactions, such as van der Waals interactions and hydrogen bonding, with greater interactions leading to higher viscosities. Previously for AILs, it has been shown that increasing the length of alkyl chains increases the viscosity through stronger van der Waals interactions,[79] while delocalization of the charge on the anion, such as through fluorination, decreases the viscosity by weakening hydrogen bonding.[88] The reported viscosity values for PILs are given in Table 3.

A plot of T_g against viscosity is shown in Figure 6. It can be seen from the plot that, as T_g increased, the viscosity generally increased. The anion structure has a far greater

effect on the viscosity than similar changes to the cation. It is unknown why the viscosity is more dependent on the anion structure, but it is consistent with what has been seen for AILs.[40] It was mentioned by Ohno et al. that, for their series of imidazolium based PILs, the size of the ions had little effect on the viscosity.[62]

For the PILs with alkylammonium cations, it was observed that the viscosity increased with increasing alkyl chain length and significantly increased with hydroxyl or methyl substitution onto the alkyl chain. Tributylammonium nitrate had a particularly high viscosity, which has been attributed to an increase in the van der Waals interaction from the three hydrocarbon chains.

Similar trends were seen for the PILs with imidazolium cations, with the viscosity affected more by changes to the anion than to the cation. The high viscosity for a benzene substituted imidazolium PIL was attributed to stacking of benzene rings leading to more ion−ion interactions. Disubstituted imidazolium rings had much higher viscosities than monosubstituted rings, which is consistent with the increase in the van der Waals interaction. Surprisingly, the substitution of a methyl group onto the imidazolium ring led to a higher viscosity than with an ethyl group.

For lactam based PILs, the fluorinated anion BF_4^-, when compared to CF_3COO^-, led to higher viscosities and densities.[37] Also, for the lactam based PILs, it was found that increasing the ring number of the cations increased the viscosity and decreased the density, which has been attributed to the increase in the cation size modifying the interaction between the cation and the anion.[37]

3.9. Ionic Conductivity

The ionic conductivity is governed by the mobility of the ions, which depends on the viscosity and the number of charge carriers, which in turn depend on the molecular weight, density, and ion sizes.[60,79,88,89] Any ion association will cause a decrease in the ionic conductivity through decreasing the number of available diffusible ions[83] (see section 2.1 for the aggregation numbers of PILs). Consequently, PILs with more delocalized charges and fewer ion−ion interactions will have higher conductivities.

It is important to take into account the viscosities when comparing the conductivity, such as through the Walden plot, since some high conductivities are related to very low viscosities.[34] The ionic conductivities were well-reported for the PILs, and the values are given in Table 3. A few of the alkylammonium based PILs had high ionic conductivities of over 10 mS/cm at 25 °C, including MAF (methylammonium formate), EAN, EAA (ethylammonium acetate), and EAF (ethylammonium formate). The conductivity for PILs with alkylammonium and alkylimidazolium cations decreased as the alkyl chain length increased, with the greatest change for short chains (C_1-C_4) and little change for longer chains (C_4-C_{12}). PILs and protic molten salts have been reported by Angell et al.[86] with ionic conductivities comparable to those of aqueous systems.

The ionic conductivities of the heterocyclic PILs increased as the molecular mass decreased or as the cation became less symmetrical. The cyclic lactam based PILs of Du et al. had very high ionic conductivities reported at room temperature,[37] though this is almost certainly a mistake with the values given being a factor of 10 times too large, as ascertained by comparing cited values to the original papers.

The values given in Table 3 for the ionic conductivity of these lactam based PILs have been altered by a factor of 10.

3.10. Polarity

The polarities of PILs have been determined using solvent probes with chromatography and comparing to conventional organic solvents,[90] as well as using solvatochromic pyridinium *N*-phenolate betaine dyes and the $E_T(30)$ polarity scale.[91] Schrödle et al. recently used the dielectric response of AILs to more accurately and reliably obtain information about polarity,[92] which may be extended to PILs in the future. The dielectric spectra of EAN has been reported by Halder et al., and it has been suggested that there is little contribution from the translational motion of ions (DC contribution).[93]

Table 4 contains a summary of the reported polarity solvent parameters for PILs, along with comparison values of water and representative values for molecular solvents and AILs. The solvent paramters within the table consist of the $E_T(30)$ scale, determined from Reichardt's dye, E_T^N, where that scale has been normalized so that water has a value of 1, and the Kamlett−Taft parameters for dipolarity/polarizability, π^*, the hydrogen bond donating ability, α, and the hydrogen bond accepting ability, β.

In general, PILs have been shown to be highly polar solvents. On the basis of the $E_T(30)$ polarity scale, and compared to common organic solvents, Reichardt et al. showed that primary and secondary ammonium based PILs were the most polar class of all ILs, with polarities comparable to water,[91] while the tertiary ammonium based PILs had slightly lower polarities.[91] The polarity of PILs formed from the *N*-alkylimidazolium cation with a variety of different acids showed that stronger acids (based on their pK_a values) led to higher polarities, as did larger anions.[100] The alkylammonium formates, EAF, PAF, and BAF, were shown chromatographically to have polarities similar to those of methanol and acetonitrile.[98] We note, however, that care must be taken when interpreting the results of solvatochromic probes, as they may be selectively solvated in the PILs.

4. Ethylammonium Nitrate (EAN)

The most extensively studied PIL is definitely ethylammonium nitrate (EAN). The interest in this salt has been largely driven by its many similarities in properties and behavior to water. These are discussed below, along with the behavior of surfactants in EAN−water solutions and the critical behavior of binary EAN and *n*-octanol solutions. The use of a greater range of PILs as self-assembly media is discussed in section 5.

4.1. Comparison of EAN and Water

Early work from the 1980s by Evans and co-workers showed many similarities between EAN and water, based strongly on the ability of EAN to promote aggregation of surfactants.[16,101,102] However, later work by Mirejovsky et al. showed that there are key differences between EAN and water, based on their heat capacities.[48]

The main waterlike properties of EAN are that it can promote the formation of micelles,[16] has a high cohesive energy density,[48,76] is highly polar with solvophobic behavior,[16,99] and has waterlike properties in its enthalpy and entropy changes for the transfer of nonpolar gases to EAN.[102]

Water and EAN both have hydrogen bonding acceptor and donor sites and, hence, can form a hydrogen-bonded network

Table 4. Solvent Parameters for PILs, Water, and Representative AILs and Molecular Solvents

PIL	$E_{T(30)}$ (kcal/mol)	E_T^N	π^*	α	β
water	63.1	1.0			
molecular solvents		0.099–0.460[235]	0.49–1.01[235]	0.00–0.76[235]	0.00–0.19[235]
1,3-alkylimidazolium AILs	66.49–76.34[112] 50.9–52.4[31]	0.645–0.685[235]	0.971–1.015[235] 0.948–1.04[31]	0.233–0.248[235] 0.561–0.675[31]	0.635–0.705[235]
quaternary ammonium AILS	43.3–48.6[236] 45.5–50.9[237]	0.46–0.62[237]	0.99–1.08[237]	0.03–0.35[237]	0.80–1.00[237]
quaternary phosphate AILs	42.3–44.5[236]				
ammonium TFA	43.6 (130°C)[236]				
ethylammonium formate	56.2[65]	0.79[65]	0.80[65]	0.85[65]	0.73[65]
ethylammonium nitrate	61.6[237] 59.8–60.3[70]	0.95[237]	1.24[237]	0.85[237]	0.46[237]
ethylammonium chloride	62.3 (50–120°C)[236]				
n-propylammonium formate	55.4[65]	0.76[65]	0.73[65]	0.87[65]	0.75[65]
propylammonium nitrate	60.6[237]	0.92[237]	1.17[237]	0.88[237]	0.52[237]
n-butylammonium formate	54.8[65]	0.74[65]	0.68[65]	0.89[65]	0.78[65]
butylammonium thiocyanate	61.4[237]	0.95[237]	1.23[165,237]	0.92[237]	
sec-butylammonium thiocyanate	61.6[237]	0.95[237]	1.28[165,237]	0.91[237]	
dimethylammonium chloride	60.3 (130°C)[236]				
diethylammonium nitrate	65.5 (110°C)[236]				
dipropylammonium thiocyanate	63.3[237]	1.01[237]	1.16[237]	0.97[237]	0.39[237]
tributylammonium nitrate	56.7[237]	0.80[237]	0.97[237]	0.84[237]	
HMIm TFSA		0.653[235]	0.971[235]	0.259[235]	0.650[235]
HBIm BF$_4$	74.35[112]				
HBIm ClO$_4$	63.82[112]				
HBIm Cl	73.59[112]				
HBIm Br	73.68[112]				
bpy TFSA		0.613[235]	1.009[235]	0.214[235]	0.539[235]

structure.[16] However, the nature of the structure is different, which was determined by Mirejovsky et al. based on EAN having a negligible heat capacity for dissolving nonpolar gases compared to that of water.[48]

4.2. Amphiphile Self-Assembly and Micelle Formation in EAN

4.2.1. Cationic Amphiphiles

The first experiments that showed the micelle formation of surfactants in EAN were conducted by Evans and co-workers using cationic surfactants.[16,101] The critical micelle concentrations (CMCs) of the surfactants were observed to be 5–10 times larger in EAN than in water,[16] and the micelles formed were smaller in EAN than in water and were described as small hard spheres.[101] The size difference was attributed to hydrocarbons being slightly more soluble in EAN than in water and, hence, enabling micelles to form where some of the hydrocarbon tail was in contact with the EAN.[101]

Later work using the cationic surfactants, N-alkylpyridinium chlorides and N-alkylpyridinium bromides, showed that these surfactants did not form cubic mesophases in EAN, though they did in other nonaqueous polar solvents.[103] It is not reported whether other phases were observed in EAN for these surfactants.

Recently, the micelle formation in neat EAN using pentyl-, octyl-, decyl-, and dodecyl ammonium nitrates was investigated.[104] The CMC decreased with increasing alkyl chain length on the amphiphiles,[104] and the formation of micelles caused no significant augmentation of the partial molar volume, unlike in aqueous systems, and hence, the carbon chains do not perturb the spatial arrangement of EAN as a solvent.[104]

4.2.2. Nonionic Amphiphiles

Recent investigations have been conducted into the behavior of nonionic surfactants in EAN,[105–107] where the self-assembly is purely solvophobic, with no counterion effects. Generally, the surfactant alkyl chains were required to be longer by a $(CH_2)_2$ linkage in EAN to produce similar liquid crystal phases to those seen in water, though otherwise very similar behavior was seen in EAN compared to aqueous systems. It was proposed that, based on the similarity to water, other self-assembly phases should easily and predictably be able to be formed in EAN.[106] The solvophobic effect of polyoxyethylene based surfactants in EAN showed that the hydrogen-bonding capability of EAN was important in the formation of lyotropic liquid crystals.

A specific polyoxyethylene surfactant, with hexaethylene glycol monohexadecyl ether ($C_{16}E_6$), was self-assembled in EAN at an EAN–graphite interface to make regularly spaced hemimicelle aggregates.[107] The behavior was generally similar to aqueous systems, with again some differences, such as requiring a longer-chained surfactant than in water. There was a much higher surface aggregation concentration of the polyoxyethylene surfactant in EAN of ∼9 wt %, compared to ∼8 × 10^{-5} wt % in water, which was consistent with higher CMCs in EAN. It was proposed that the amount of hydrogen bonding is less in EAN than in water, based on the smaller separation of the hemimicelles, the lower solvophobic interactions, and the ability of the surfactant layers to be desorbed from EAN, whereas they are permanently attached in water. The self-assembly required a strong solvophobic attraction between the surfactant tail and the surface, with graphite working well as the surface, whereas silica did not, because of EAN having a stronger affinity for the surface than the surfactant did.[107]

4.2.3. Phospholipid Amphiphiles

Extensive work has been conducted into the self-assembly behavior of a variety of phospholipids in EAN.[108–112] Throughout the investigations, a number of liquid crystal phases have been observed, including smectic A, lamellar, and inverse hexagonal. In comparison to water, generally fewer liquid crystal phases were seen, such as intermediate

phases,[108,109] and the phases had higher enthalpies, probably because of the closer packing of the phospholipids through modification of the repulsive forces between head groups.[109,111]

4.2.4. Drug Delivery Applications

EAN has been claimed to have potential use as a structured liquid for assembling inverse cubic or inverse hexagonal phases that can be used to solubilize some pharmaceuticals.[113-115] In one such system, the self-assembling media, which could be EAN, contained a surfactant and a nonparaffinic liquid in which the pharmaceutical was more soluble. Paraffinic liquids were chosen that contained polar groups that could help solubilize polar pharmaceuticals that are otherwise hard to solubilize.[113,114] In another system, a dry amphiphile was used that could form a cubic phase in a protic self-assembly media, such as EAN or water, in which a pharmaceutical could be contained.[115] In both these systems, an encapsulating compound could be included to allow the slow release of the pharmaceutical for a longer therapeutic half-life.[113,115]

4.3. Binary Solutions

The miscibility of EAN in water, acetonitrile, and methanol has enabled a number of investigations to be conducted on the electrolyte behavior for all concentrations of salts in solutions, especially intermediate and high concentrations. A unique benefit of using EAN compared to AILs was that it provided an opportunity to observe a hydrogen bonding solvent other than water and, hence, could be used to determine which properties of water are due to hydrogen bonding and which are not.

At low concentrations, the PILs are fully dissociated and behave as most other salts, while at high concentrations, they behave as molten salts. There does not appear to be a clear definition for what concentration ranges constitute "low" and "high" concentrations for water−EAN solutions.[116-119]

In addition to the EAN studies, in 1956 Kraus investigated ion-pair formation using various electrolytes in solvents, including the PILs butylammonium picrate and triisoamylammonium picrate in benzene.[116] Investigations of binary systems have also been conducted on AILs, such as tetra-n-butylammonium picrate, which is miscible in a number of different solvents.[120]

In the investigation by Kraus, intermediate concentrations of butylammonium picrate and triisoamylammonium picrate, and other non-PIL electrolytes in benzene, were used to observe ion-pair formation. The PILs showed different behavior to other electrolytes because of their ability to form hydrogen bonds, which stabilized ion pairs[116] and led to far lower dissociation constants compared to similar AILs. The effect of the hydrogen bonding was seen for (butyl)$_n$ammonium picrates (where $n = 1, 2, 3$, and 4), with the dissociation constant decreasing rapidly from quarternary to tertiary and more slowly from tertiary to primary, corresponding to the increasing amount of hydrogen bonding.[116]

The properties of anionic, cationic, and nonionic surfactants in EAN−water solutions were investigated by Letellier and co-workers,[51,121] with low EAN concentrations behaving as dilute electrolytes and those with high EAN concentrations behaving as ionic liquids.[105] Solutions of acetonitrile (AN) and EAN were used by Perron et al. to investigate electrolyte solutions with intermediate concentrations where EAN behaved neither as a dilute electrolyte nor a molten salt.[117]

4.3.1. EAN–n-Octanol Binary Solutions (Critical Behavior)

The binary system of EAN and n-octanol forms a critical fluid when the mole fraction of EAN is between 0.766[75] and 0.77,[122] where the exact value depends on the amount of water present,[123] and has a critical point between 44.06[75] and 42.2 °C.[122] This unusual EAN based binary system has been the focus of many studies over the past decade.[75,122-126]

The behavior of a critical liquid can be described by mean-field or Ising-type models, which are used to describe ionic or uncharged fluids, respectively. Normally in ILs, the mean-field model is used, since the long-range Coulomb forces dominate; however, the hydrogen bonding present in EAN causes Debye shielding of the long-range forces.[126] Schröer et al. proposed that the best description of the critical behavior of EAN and n-octanol involves a change from mean-field to Ising-like behavior near the critical point,[126] with the critical point having Ising-like behavior.[75,126] A more recent study by Heimburg et al. described the binary mixture as nonionic above the critical temperature and having intermediate states below it.[123]

4.4. Force of Interaction Between Surfaces in EAN Compared to Other Solvents

Water−EAN solutions between two mica surfaces were used to investigate the forces present as the surfaces were brought together closer than 5 nm.[127] The force versus surface separation behavior observed was comparable at low concentrations to that seen for other electrolytes, in particular the alkali-metal chlorides, and at high concentrations to that seen for many polar and nonpolar solvents.

As the mole fraction, x, of EAN increased from 1.8×10^{-6} to 0.0018, the surface potential of the surfaces decreased, then increased, then decreased again. At very low concentrations, $x = 1.8 \times 10^{-6}$, and small surface separations, the van der Waals force dominated, while for low concentrations, $x < 0.0018$, the EAN solutions formed electrical double layers.[127] The proposed explanation by Horn et al. was based on the surface adsorption of hydrogen and EAN ions, where the decreasing potential with increasing EAN concentration was due to the replacement of hydrogen with EAN, and the small region of increasing potential was due to the adsorbed EAN cations preventing cations from being adsorbed at neighboring sites.[127]

For highly concentrated solutions, with $x > 0.17$, and surface separations less than 5 nm, oscillations were observed in the force versus surface separation curves.[127] These oscillations are due to EAN forming a Stern layer of adsorbed ions on the mica surfaces, followed by more layers that contain anions and cations, with the number of layers increasing with the concentration of EAN. Some differences were observed between the oscillations seen with aqueous electrolytes and with EAN that have been attributed to the difference in the ion sizes and, hence, differences in how they pack to make up the layers. While this oscillatory behavior has been observed for solvents other than water, water has an additional background repulsive force present as well as the oscillations. This background force was not observed for the EAN solutions, which indicates that it is not due to a hydrogen-bonded network, which was previously thought possible.

The force of interaction between a Teflon AF1600 coated micron-sized colloidal sphere and a Teflon AF1600 coated flat plate was measured using atomic force microscopy

(AFM) in the solvents EAN, water, glycerol, formamide, ethylene glycol, formic acid, ethanol, methanol, diiodomethane, 1-bromonaphthalene, hexadecane, and hexane.[128] A long-range interaction was seen for water, EAN, and many of the organic solvents.[128] This long-range interaction was caused by a "solvophobic force", not due to orientational ordering from hydrogen bonds, electrostatic, or condensates of loosely attached surface material, which have been said in other studies to contribute to the "hydrophobic force".

5. Self-Assembly in PILs other than EAN

Depending on their structure, some PILs can be used as cationic surfactants in a solvent, can be used as self-assembly media for amphiphiles (lyotropic phase behavior), or can undergo phase transitions with changes in temperature (thermotropic phase behavior). These three behaviors are described below.

5.1. PILs as Amphiphiles

PILs containing long alkyl chains have been used as surfactants in a solvent, such as a series of 1-alkylimidazolium nitrates or chlorides (with alkyl chains of $n = 14$, 16, or 18),[129] which formed liquid crystals in water, acidic water, or tetrahydrofuran (THF). The CMCs of hexyl-, heptyl-, and octylammonium nitrates in water were found to decrease with increasing alkyl chain length and were larger than the CMCs of the anionic surfactant sodium dodecyl sulfate (SDS) or the cationic surfactant dodecyltrimethylammonium bromide (DTAB).[130]

5.2. Lyotropic Phase Behavior

The ability of many PILs to promote the self-assembly of a broad range of surfactants is probably one of their most unique features and is not shared by any other large group of solvents. The inclusion of many PILs as self-assembly media has the potential to vastly increase what is currently a limited number of generally recognized protic solvents with this ability. The ability to promote self-assembly has been reported for many different PILs, including EAN,[16,101,106−109,111,112] a wide range of alkylammonium based PILs,[130−132] alkylimidazolium based PILs,[129,133,134] and other heterocyclic cation based PILs.[103] Recent experiments have also shown conclusively that some AILs share the ability to promote self-assembly, such as [BMIm]PF$_6$, which has been used to self-assemble a block copolymer.[135]

The most comprehensive investigation into the use of PILs as self-assembly media was previously reported for a series of primary alkylammonium based PILs in conjunction with the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) and the nonionic surfactants myverol 18-99K and phytantriol.[32,131,132] Representative liquid crystal phase textures are given in Figure 7 for some CTAB−PIL, myverol−PIL, and phytantriol−PIL systems. All the main lyotropic liquid crystalline phases have been observed in these PILs, including normal hexagonal, bicontinuous cubic, lamellar, inverse bicontinuous cubic, and inverse hexagonal.

Most of the PILs displayed fewer lyotropic liquid crystalline phases than were observed in aqueous systems. There were some differences in the thermal stability ranges of the liquid crystalline phases, particularly the inverse hexagonal phase for myverol and phytantriol, whose onset temperature is 84 or 44 °C in water, respectively, and was seen from below room temperature in many of the PILs.[131]
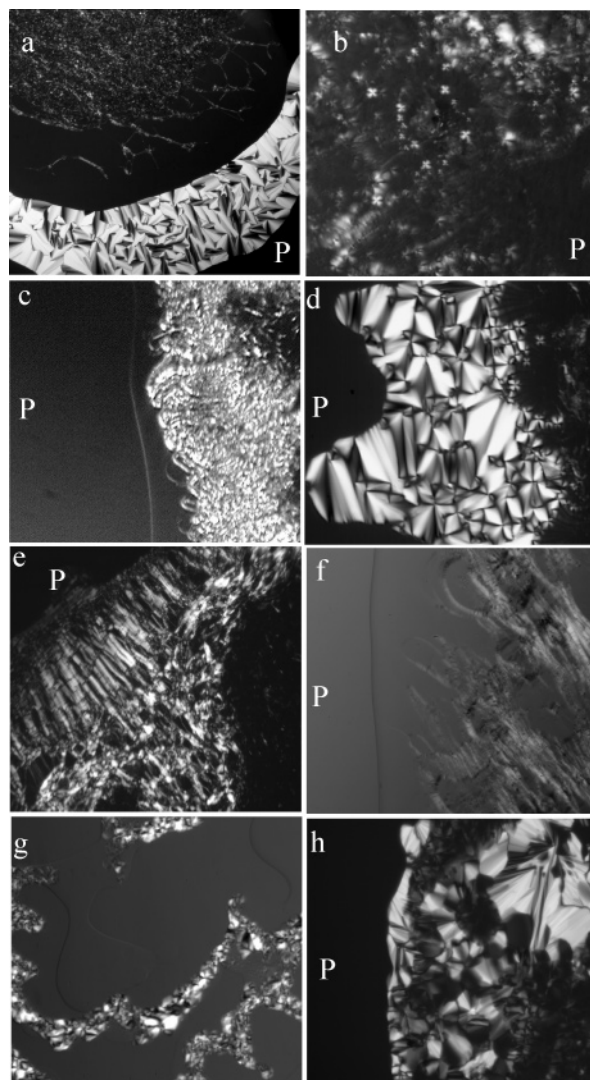

Figure 7. Penetration scans showing the LCP for different amphiphiles with PILs. The direction the neat PIL is penetrating from is denoted by a P, except for (g) where the interface is too complex: (a) CTAB-2−propylammonium formate at 97 °C with anisotropic hexagonal, isotropic cubic, and anisotropic lamellar phases; (b) CTAB−butylammonium formate at 90 °C with anisotropic lamellar phase (maltese crosses are evident); (c) Myverol−methylammonium formate at 24 °C showing neat MAF, isotropic (cubic), and lamellar; (d) Myverol−ethylammonium propionate at 31 °C, neat EAP inverse hexagonal, isotropic (inverse micellar), and myverol crystals; (e) Myverol−EAN at 37 °C, neat EAN, lamellar, and myverol crystals; (f) phytantriol−ethylammonium hydrogen sulfate at 22 °C, neat EAHS, isotropic (cubic), lamellar; (g) phytantriol−ethylammonium glycolate at 24 °C, the LCP phase is inverse hexagonal, with isotropic (cubic) next to it, followed by neat EAG. (h) phytantriol−EOAN at 29 °C, neat EOAN, inverse hexagonal. Reproduced from Greaves et al. *J. Phys Chem. B* **2007**, *111*, 4082 and Greaves et al. *Langmuir* **2007**, *23*, 402. Copyright 2007 American Chemical Society.

The Gordon parameter, G, gives a measure of the cohesiveness of a solvent[136] and, hence, a measure of the ability of the PIL to be amphiphile self-assembly media. The Gordon value is described by eq 1, where γ is the surface tension and V_m is the molar volume,[136] and can be considered to indicate the driving force of the PILs toward self-assembly.

$$G = \gamma / V_m^{-1/3} \tag{1}$$

PILs with higher Gordon parameters are likely to have greater diversity and thermal stability of the liquid crystalline

phases. The alkylammonium PILs represent the group of protic solvents with the lowest known Gordon parameters that still can self-assemble amphiphiles, with the current minimum of 0.552 J/m^3.[32,131,132] The Gordon parameter can be increased through the substitution of hydroxyl groups onto the cation or the anion or decreased through increasing the branching of the alkyl component of the cation.[132]

The Gordon parameter is potentially useful in the design of new PILs, in that structural features can be chosen with the aim of producing PILs that are good self-assembly media, such as those which are likely to increase the surface tension or to a lesser extent decrease the molar volume (i.e., increase the density or decrease the molecular weight). With the large focus on the design of new PILs, it is essential to have known parameters that quantify desired properties, such as the Gordon parameter giving a measure of self-assembly aptitude.

The critical packing parameter, CPP, is described by eq 2, where v is the average volume of the amphiphile, a is the effective head group area, and l is the effective chain length of the surfactant in the molten state.[136] The CPP can be used to predict the aggregate structures and to correlate structural changes of the surfactant (or PIL) with changes to the self-assembly phases.

$$CPP = v/al \qquad (2)$$

Using the CPP, two structural differences have been proposed to account for the differences between the lyotropic phase behavior in PILs compared to water. These are that (1) PILs have a lower solvation of polar groups and a higher affinity for hydrocarbon regions than water and (2) PILs partition into the amphiphile–solvent interface region, especially PILs with long alkyl chains.[131]

5.3. Thermotropic Phase Behavior

The formation of liquid crystals from ionic liquids, including many PILs, has been comprehensively reviewed by Binnemans up to August 2005.[137] These ionic liquids typically have long alkyl chains and undergo thermotropic behavior between the solid and isotropic liquid states.

Since that review, Chen et al. have reported on the supramolecular interaction of polyethyleneimines with carboxylic acids, which form through proton transfer from the acid to the imine groups. Thermotropic liquids crystal nematic phases were observed for those PILs at temperatures between 58 and 138 °C.

6. Organic Synthesis

A wide range of ILs usually containing imidazolium cations have been used as the solvents and catalysts for a number of different organic reactions. In addition to PILs, Brønsted acidic ILs have been used, where an available proton is present on the anion or on a functionalized group on the cation. Brønsted acidic AILs have been included in this section for completeness. In most applications in organic synthesis, there appears to be little difference in the behavior of these two classes of ILs. The Brønsted acidic AILs were often functionalized to provide an available proton, either through tethering a sulfonic acid group or carboxylic acid group to the cation. The use of ILs in organic synthesis typically involved trialing many ILs to achieve the desired activity.

There are major potential benefits in using ILs as solvents and catalysts for organic reactions. The main driving force for their use is the environmental advantage of using the relatively benign ILs to replace organic solvents and what are usually highly acidic catalysts. The Brønsted acidic ILs have been found to give good yields and selectivity in a number of organic reactions, often comparable or better than currently used systems. The main application of these ILs is as catalysts in reactions that required a Lewis or Brønsted acidic catalyst or, more rarely, a basic catalyst. These ILs are mostly easy and cheap to produce, can be easily recycled and reused, usually involve simple reaction processes, and often only produce one byproduct, water. In comparison, most traditional methods for these organic reactions involve large amounts of acidic waste, waste molecular solvents, and either waste catalyst or expensive and time-consuming catalyst-recycling procedures.

There have been a number of good review papers covering different aspects of the use of ILs in organic synthesis and catalysis, which reflects the vast interest in this application. The driving force behind the use of ILs in this field has been to find "greener" alternatives; hence, high conversions, high selectivities, and the ability to reuse the IL are important. An early review by Welton in 1999 introduces the reactions that had been conducted in ILs as solvents. At that time, there had been a large focus on the use of chloroaluminate ILs, where, because of their acidic nature, they could frequently catalyze the reactions, with no additional catalyst required.[138] The use of ILs as solvents, or as cocatalysts for transition metal-mediated catalysis, for organic synthesis reactions have been well-covered by reviews.[9,138–140] The vast majority of work conducted on using PILs or Brønsted acidic AILs in organic synthesis has been since 2004. The review by Shi et al. in 2004[6] inadvertently highlights how recent the interest has been in the use of ILs as solvents and catalysts, with, at that time, only five reactions described where ILs are used as solvents and catalysts and only a brief discussion on SO$_3$H functionalized ILs. A more recent paper by Jain et al. from early 2005 focused on the use of ILs as solvents, with some reactions where they act as the catalyst, too.[140] A review paper by Sheldon in 2001 has an excellent section outlining general considerations on catalysis in ILs, including the general properties of ILs, which are beneficial to this application and possible scenarios where the ILs could be the solvent or solvent and catalyst.[141]

The acidity of the PILs is often important for their use in organic synthesis and is described in the following section. The specific organic reactions that have utilized PILs or Brønsted acidic ILs as solvents and/or catalysts are then described. The PIL and Brønsted acidic AILs were recyclable for all of the following reactions. Typically, the IL could be reused 3–5 times with little loss of activity.

6.1. Acidity

One of the key properties of PILs and Brønsted acidic ILs is their Brønsted acidity, and surprisingly little research has been conducted into this, though it has been clearly shown to have a strong correlation to the catalytic activity for many organic synthesis reactions.

Different techniques have been utilized to give a measure of the acidity of these ILs. When the same cation was used, the relative acidity of the ILs could be determined from the basicity of the anion (as described by its pK_a value).[95,142] Another method was to correlate the NH shift for the

available proton using ^{1}H NMR with the Brønsted acidity, where larger shifts indicated higher Brønsted acidity.[95,142] Alternatively, the Hammett acidity scale was used, where the absorbance of protonated and unprotonated indicators in a solution of the IL, indicator, and aprotic polar solvent was measured using UV−vis spectroscopy.[37,70,143] Last, the pK_a values for a number of different Brønsted acidic AILs were determined through titration against KOH.[144]

There was a strong correlation between acid strength and catalytic activity, regardless of which of the methods was used.[37,70,95,142,143,145,146] Reactions have been used that probe the acid catalytic strengths of certain PILs and Brønsted acidic ILs. For example, in the Friedel−Crafts alkylation of phenol with *tert*-butyl alcohol, the main products depend on the acidity of the acid catalyst, with 2-*tert*-butylphenol formed using a weak acid catalyst, 4-*tert*-butylphenol formed for a medium acid catalyst, and 2,4-di-*tert*-butylphenol formed for a strong acid catalyst.[70,146] A series of PILs containing pyridinium cations led to selectivities that compared very well to the Hammett acidities, showing 2-methylpyridinium TFSI was a strong acid, whereas 2-methylpyridinium methanesulfonate was a weak to moderate acid.[70] In comparison, a series of SO₃H functionalized imidazolium Brønsted acidic AILs with the HSO_4^- anion all had similar selectivities for this reaction, which indicated fairly moderate acidity.[146]

6.2. Carbon−Carbon Bond-Forming Reactions

6.2.1. Knoevenagel Condensation

In the Knoevenagel condensation reaction, a carbon−carbon bond is formed between carbonyl and active methylene compounds, and it is traditionally catalyzed using a base, though other catalysts have been used. The use of PILs as solvents and catalysts for this reaction has been shown to be very promising with significant advantages compared to conventional methods.

The first reported use of an IL for this reaction was in 2002 by Hangarge et al., who utilized EAN as the solvent and catalyst for the reaction of aromatic aldehydes with 3-methyl-1-phenylpyrazolin-5-(4H)-one, shown in Scheme 2a, and 4-oxo-(4H)-1-benzopyran-3-carbaldehydes with 3-methyl-1-phenylpyrazolin-5-(4H)-one, shown in Scheme 2b.[147] Later work showed very similar results for EAN as the solvent and catalyst for the reaction of 1,3-diphenyl-1H-pyrazole-3-carbaldehydes with 3-methyl-1-phenylpyrazolin-5-(4H)-one, shown in Scheme 2c.[148] The yields and reactions times are given in Table 5. Compared to standard methods, the use of EAN led to shorter reaction times, much higher yields (typical yields of 33−47% using conventional techniques[147]), and very mild reaction conditions.

A few different PILs and AILs were trialed for the Knoevenagel condensation reaction of Meldrum's acid with aromatic aldehydes, shown in Scheme 2d,[149,150] and active methylene compounds with aromatic aldehydes, shown in Scheme 2e.[151] The yields and reaction times in Table 5 illustrate the excellent ability of these PILs as solvents and catalysts for the Knoevenagel condensation reaction.

For comparison, imidazolium AILs with BF_4 or PF_6 anions led to yields of 54−77% in 24 h, for a reaction where the yield was 94% in 30 min for EAN.[150] In another reaction, only trace amounts were seen for the AILs after 6 h, where EAN led to 94% yields after 3 h.[151] The better performance of the PILs has been attributed to their Brønsted acidic
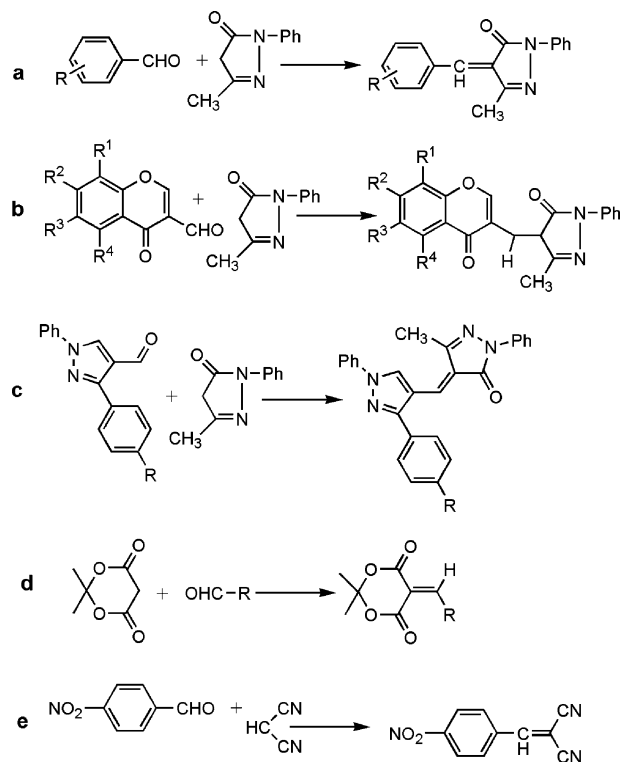
Scheme 2. Knoevenagel Condensation Reactions

Table 5. Summary of Knoevenagel Reactions; All Reactions Were Conducted at Room Temperature.

scheme	IL	yield (%)	reaction time (h)
2a[119]	EAN	70−75	0.3−0.5
2b[119]	EAN	78−92	0.3−0.5
2c[120]	EAN	78−85	0.4−0.5
2d[121]	EAN	80−97	0.5−2
2d[122]	[HMIm]TFA	50−95	0.5
2e[123]	EAN	83−97	0.2−12

nature.[150] The product isolation was very simple for all these Knoevenagel reactions. Addition of water precipitated the product, which could then be obtained through filtration, and the IL could be reused.

6.2.2. Other Condensation Reactions

A range of one-pot organic synthesis reactions have been conducted very successfully using imidazolium PILs as the solvent and catalyst. No additional catalysts were required, and compared to conventional methods, the yields were higher, the reaction times were shorter, less hazardous solvents were used, there were milder conditions, and the ILs could be reused.

The synthesis of 1,5-benzodiazepines from *o*-phenylenediamines and α,β-unsaturated carbonyl compounds using imidazolium or pyridinium PILs is shown in Scheme 3a.[143] Of the imidazolium PILs trialed, [HBIm]CF₃SO₃ was identified as having the best activity for this reaction, whereas [HBIm]CF₃CO₂ led to effectively no yield, highlighting the strong effect of the anion.

The synthesis of 1-pyridylimidazol[1,5-*a*]pyridines from the condensation reaction of 1,2-dipyridylketone, 2-benzoyl and 2-acetyl pyridines, aromatic aldehydes, and ammonium acetate is shown in Scheme 3b.[95] A small selection of imidazolium PILs and AILs were trialed as solvents and catalysts, and for a specific reaction under the same conditions, the PILs led to yields of 69−93%, compared to those
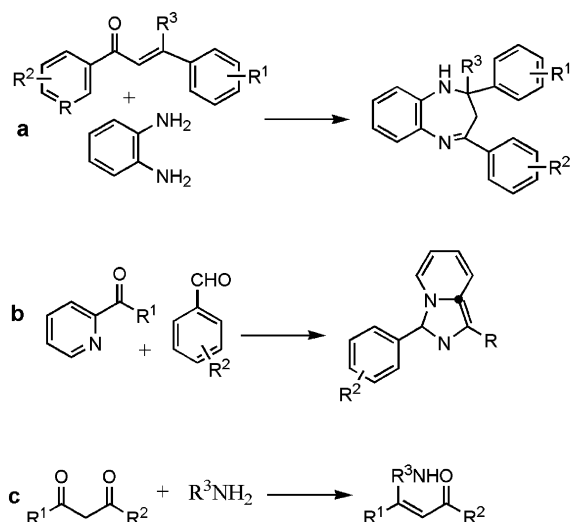
Scheme 3. Condensation Reactions

a

b

c

Table 6. Summary of Yields and Reactions Times for the Reactions Shown in Scheme 3

scheme	IL	yield (%)	reaction time (h)	reaction temperature (°C)
3a[115]	[HBIm]CF3SO3	80−93	2−3	80
3b[112]	[HBIm]BF4	85−94[a]	1−2.3	100
3c[124]	[HMIm]TFA	80−98	0.25−4[b]	r.t.

[a] One reaction had a yield of only 55%. [b] One reaction went for 24 h with a yield of only 65%.

Scheme 4. Diels−Alder Condensation Reaction
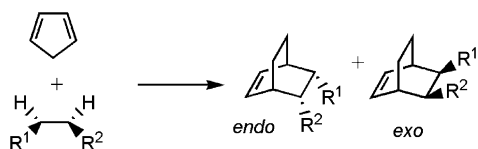
for the AILs of only 38−55%, and those for conventional molecular solvents of 17−28% (acetone was an exception with a yield of 70%). The ability of the IL to promote the reaction had a strong correlation to the basicity of the anion of the IL and the polarity and Brønsted acidity of the IL.[95]

The condensation reaction in [HMIm]TFA of 1,3-dicarbonyl compounds with amines to form β-enamino esters and β-enaminones is shown in Scheme 3c,[152] and the yields and reaction times are given in Table 6.

6.2.3. Diels–Alder Reaction

The Diels−Alder reaction of cyclopentadiene with a dienophile, shown in Scheme 4, was trialed in a PIL in 1989 using EAN.[153] We believe this was the first reported use of a PIL as the reaction media and catalyst in an organic synthesis reaction. The selectivity toward the endo product compared to the exo product was lower in EAN, with endo/exo ratios of 6.4/7.4, compared to 7.4/9.3 in water, and the conversion rate was slower in EAN. However, the key feature was demonstrating that reactions of this type were feasible in PILs.

More recently, this reaction was trialed using protic imidazolium ILs with lactate, salicylate, BF4, or TFSI anions.[154] The selectivities of endo/exo were mostly in the range of 3.2−3.8, with excellent yields of 90−97%. The selectivity was significantly increased to 5.2−6.0 through using the TFSI anion in the IL.

Scheme 5. Henry Reaction
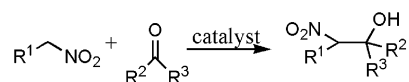
A novel application of PILs was the use of liquid crystals of N-alkylimidazolium PILs as a solvent for the Diels−Alder reaction. The alkyl group contained an even number of between 10 and 18 carbons, with these long alkyl chains leading to a bilayer solvent structure. The use of this partially ordered solvent gave a selectivity of the exo product of 54%, where normally the endo product is dominant.[129]

6.2.4. Alkylation

Non-chloroaluminate ILs for alkylation reactions were first investigated by Wassercheid et al., where imidazolium Brønsted acidic AILs containing the HSO4 anion were used as additives to sulfuric acid for benzene alkylation with 1-decene. The yields obtained were between 3.5 and 68%, with selectivities from 35 to 41%, and while fairly low, these showed the potential of this type of IL for alkylation reactions.[155]

A range of PILs was trialed in the Friedel−Craft alkylation of phenol with tert-butyl alcohol to produce tert-butyl alcohol as mentioned in section 6.1. These included a series of pyridinium PILs specifically designed for use as acid catalysts by Duan et al.[70] and SO3H functionalized Brønsted acidic AILs.[146] It was shown successfully from the pyridinium PILs that a range of PILs could be easily produced that modified the acidities, catalytic activities, and, hence, selectivities and conversions for this reaction type, with the best performance by 2-methylpyridinium, with a conversion of 95%, and a selectivity toward 2,4-di-tert-butylphenol of 82%.[70] In general, the SO3H functionalized AILs led to comparable selectivities and conversions for this reaction as the PILs.[146] Some nonstoichiometric salts containing pyridinium cations with HF anions have been used successfully as the catalyst and reaction media for the isobutane−olefin alkylation reactions.[156]

6.2.5. Henry Reaction

The Henry reaction forms carbon−carbon bonds between nitroalkanes and carbonyl derivatives to produce 2-nitroalcohols as shown in Scheme 5. This reaction requires a basic catalyst, with guanidine compounds having been successfully used in the past to achieve milder conditions and shorter times than the conventional catalysts used. Following on from this, a guanidine PIL, 1,1,3,3-tetramethyl guanidine lactate, was trialed for use as a catalyst and reaction media for the Henry reaction. Generally good yields of 14−73% were achieved with reaction times from 6 to 20 h. The yields were higher for aromatic aldehydes than for aliphatic aldehydes. The PIL was successfully reused 15 times while retaining catalytic activity.[157]

6.2.6. Direct-Aldol Reaction

The use of PILs for the direct−Aldol reaction is similar to the Henry reaction. This carbon−carbon bond forming reaction, shown in Scheme 6, also requires a basic catalyst, and again PILs containing the 1,1,3,3-tetramethyl guanidine cation have been used, though this time paired with the lactate and TFA anions.[158] Generally, the yields were good to high (70−97%) after 24 h of reaction, except when the

Scheme 6. Direct-Aldol Reaction
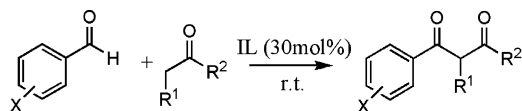
Scheme 7. Mannich Reaction
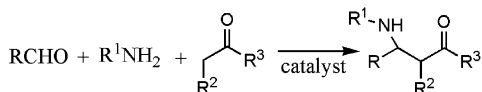
Scheme 8. Dimerization of α-Methylstyrene
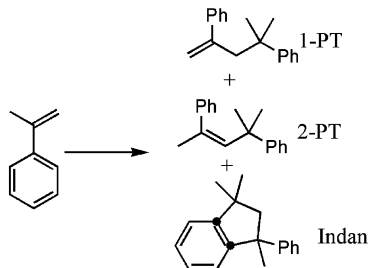
ketones 2-butanone or 2-pentanone were used, which led to low yields of 25−28%, even after much longer reaction times.

6.2.7. Mannich Reaction

The Mannich reaction involves the synthesis of β-aminocarbonyl compounds from an amine and two carbonyl compounds, as shown in Scheme 7. An acid catalyst is usually required, though a base catalyst can be used.[159] The Mannich reaction of benzaldehyde, aniline, and acetophenone was used by Han et al. to compare the suitability of the ILs and clearly showed that PILs displayed better performance than AILs as solvents for this reaction. Using CF_3COOH as the catalyst in 1,1,3,3-tetramethylguanidine containing PILs or the AILs [BMIm]BF_4 and [BMIm]PF_6 led to yields in the PILs of 68−75% compared to only 34−45% in the AILs. Also, the PILs were reusable, whereas the AILs were not.[36] The use of PILs and AILs as the reaction media and catalysts for this reaction again saw to better performance by the PILs, with [HMIm]TFA leading to a yield of 83% compared to the Brønsted acidic AILs [BMIm]H_2PO_4 with a yield of 67% and [BMIm]HSO_4, which did not promote the reaction at all.[159]

The use of ILs as the solvents and catalysts for the Mannich reaction for a range of reactants led to limited success. The ILs that were trialed included imidazolium containing Brønsted acidic AILs and PILs,[159] SO_3H functionalized imidazolium and triphenylphosphine AILs,[160] and SO_3H−quaternary ammonium AILs (which were used as acid catalysts in water).[161] There was a strong dependence on the starting compounds, with, for example, the aliphatic amines leading to many unwanted products.[159] The yields and reaction times also had a strong dependence on the reactants and varied from 0 to 98% and from 0.75 to 24 h, respectively.[159,160]

6.2.8. Dimerization

The dimerization of α-methylstyrene leads to the desired linear 2,4-diphenyl-4-methyl-1-pentene (1-PT) product as well as two other dimers, as shown in Scheme 8. Consequently, selectivity toward 1-PT is crucial for the catalyst. The use of HMIm BF_4 at 60 °C led to selectivities

Scheme 9. Fischer Esterification
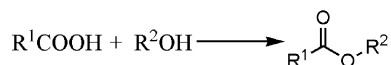
comparable to those of other catalytic systems, while beneficially being a far simpler process. The optimized reaction had 90% yields with 96% conversion.[145] Conducting this reaction at higher temperatures significantly affected the product distribution. The maximum selectivities for 1-PT were 93% at 60 °C and 100% for Indan at 170 °C.[162]

6.3. Carbon−Oxygen Bond-Forming Reactions

6.3.1. Fischer Esterification

The Fischer esterification reaction, shown in Scheme 9, has been investigated by a number of groups using different imidazolium and pyridinium PILs and SO_3H functionalized Brønsted acidic AILs as solvents and catalysts. The conversions, selectivities, and reaction conditions are summarized in Table 7. Generally, the conversions and selectivities were very good, though some of the ILs trialed did not promote the reaction.

The commonly used Brønsted acidic PIL of [HMIm]BF_4 was used as the catalyst and solvent in a large range of esterification reactions of alcohols and acids with excellent results, as shown in entry 1 in Table 7.[163] This PIL was successfully reused 8 times for an esterification reaction, maintaining 100% selectivity with the conversion decreasing from 97% to 94%.

The use of pyridinium PILs for the esterification of cyclic olefines with acetic acid is summarized in entries 2−4 in Table 7, where it is evident that the choice of anion was significant. The TFSI anion promoted excellent conversions and selectivities, while the TFA anion led to excellent selectivity but poor conversion, and the HSO_4 anion produced no reaction at all.[70]

Imidazolium PILs and AILs with BF_4, PF_6, and PTSA (*para*-toluenesulfonate) anions were trialed in the esterification of benzyl alcohol with acetic acid with all giving good-to-excellent conversions and selectivities in fairly short times.[164] The AIL [BMIm][PTSA] led to 100% conversion and 100% selectivity, indicating that the esterification reaction does not require a proton for the catalytic process.[164] However, a mechanism has been proposed by Arfan et al. that requires a proton for the esterification process.[165]

The first use of SO_3H functionalized Brønsted acidic AILs as catalysts and solvents in organic synthesis was by Forbes et al. in 2002, where ILs containing either an imidazolium or phosphonium cation were trialed in a number of reactions including Fischer esterification. The results are given in entries 5 and 6 in Table 7.[166] The results indicate that the phosphonium IL led to better yields in significantly shorter times, though it must be noted that the ILs contained different anions and were used to promote the reaction of different reactants. The SO_3H functionalized triphenylphosphonium IL was further used by Forbes et al. in the esterification of acetic acid with ethanol. The presence of some water within the IL was shown to have an ideal amount for maximizing the yield. The yield increase was attributed to the decrease in viscosity of the IL due to the presence of water.[169] In addition to the phosphonium and imidazolium AILs, the SO_3H functionalized quaternary ammonium AILs had good catalytic activity for the Fischer esterification reaction, entry

Table 7. Summary of Yields and Reactions Times for the Reaction Shown in Scheme 8; 2-MPyH is 2-Methylpyridinium and TMAPS is Trimethylammonium−Propane Sulfonate

	IL	conversion (%)	selectivity (%)	reaction time (h)	reaction temperature (°C)
1	[HMIm]BF$_4$[136]	80−99	100	2−10	110
2	[2-MPyH]TFSA[114]	98−100	99	3	90
3	[2-MPyH] [CH$_3$SO$_3$][114]	22−31	99	3	90
4	[2-MPyH]TFA[114]	0	0	6	120
5	SO$_3$H functionalized imidazolium AIL[139]	82^a	b	48	22
6	SO$_3$H functionalized phosphonium AIL[139]	96^a	b	0.75	22−175
7	[TMAPS][HSO$_4$]^c [141]	86−97	85−90	1.5−2.5	r.t.
8	SO$_3$H functionalized imidazolium AILs[143]	78−100	6−100	4	120

^{a} Yield, not conversion. ^{b} Not reported. ^{c} When solid acid reactants were used, the reaction required higher temperatures and longer times.

Scheme 10. Protection of Carbonyl Groups through Acetalization
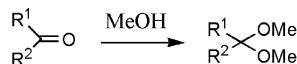
7 in Table 7.[167] However, these triphenylphosphonium ILs have high melting points, which limits their potential use.[170]

Other investigations using SO$_3$H functionalized imidazolium AILs are summarized by entry 8 in Table 7.[168] The extensive selectivity range was due to a strong dependence on the olefin reactant, with cycloolefins all leading to 100% selectivities, whereas the straight-chain olefins were far more susceptible to side reactions.[168]

A comparison of SO$_3$H functionalized imidazolium, pyridinium, and quaternary ammonium PILs with the HSO$_4$ anion demonstrated similar conversions for the esterification of ethanol with acetic acid and all led to 100% selectivity. These PILs were developed as alternatives to those containing BF$_4$ or other halogens.[171] In contrast, nonfunctionalized pyridinium AILs showed significantly better catalytic performance (43% conversion after 30 min) than imidazolium AILs (13% conversion after 30 min) for the reaction of propanoic acid with *neo*-pentanol.[165] A series of SO$_3$H functionalized pyridinium AILs with the HSO$_4$ anion had higher yields than those with the BF$_4$ or PTSA anions, which was attributed to those ILs being stronger Brønsted acids.[170]

6.3.2. Protection of Carbonyl Groups by Acetalization

A representative reaction for the protection of carbonyls through acetalization is shown in Scheme 10 for aldehydes and ketones. A variety of imidazolium PILs and AILs have been trialed as solvents and catalysts for these reactions. The use of [HMIm]BF$_4$ in a range of acetalization reactions led to good-to-excellent yields and selectivities[172−174] and was successfully reused 8 times.[173]

The HMIm cation with a variety of anions demonstrated the strong dependence of the reaction on the anion. The anions BF$_4$, CF$_3$SO$_3$, PhSO$_3$, and CF$_3$CO$_2$ led to conversions of 96, 89, 87, and 0%, respectively, for the desired acetal product.[172] The use of [HMIm]PF$_6$ and [HMIm]Br led to nearly 100% selectivity toward the nondesirable aldol product,[174] and imidazolium and pyridinium AILs had poor-to-moderate selectivities toward the diol of 8−60%.

6.3.3. Protection of Alcohol Groups as Ethers

The reaction for the protection of alcohols as tetrahydro-pyranyl ethers is shown in Scheme 11. A series of imidazolium PILs and AILs were trialed as the solvent and catalyst for this reaction, with the Brønsted acidic AILs [BMIm]-[HSO$_4$] and [BMIm][H$_2$PO$_4$] having the best catalytic activity

Scheme 11. Protection of Alcohol Groups
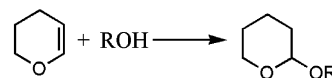
Scheme 12. Dehydration of Fructose
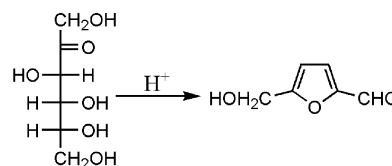

Scheme 13. Biginelli Reaction
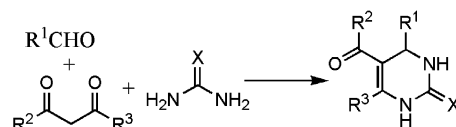
with yields of 94−96% in 30 min. The protic IL [HMIm]-BF$_4$ only had a yield of 71% in 4 h, while there was no reaction when the anion was TFA.[175]

6.4. Carbon−Carbon and Carbon−Oxygen Bond-Forming Reactions

6.4.1. Dehydration of Fructose

The acid-catalyzed dehydration of fructose into 5-hydroxymethylfurfural, shown in Scheme 12, has been conducted in [HMIm]Cl successfully. This PIL was used as the catalyst and solvent, with a 92% yield obtained after 15−45 min. In addition to environmental benefits, a particularly beneficial property of using the PIL was that the product did not undergo any decomposition, which occurs in other catalyst systems.[176] The imidazolium AILs [BMIm]BF$_4$ and [BMIm]PF$_6$ were trialed as cosolvents with DMSO for this reaction with much worse performance than the PIL. Additional proton-containing catalysts were required, and the yields were only 40−50%.[177]

6.5. Carbon−Carbon and Carbon−Nitrogen Bond-Forming Reactions

6.5.1. Biginelli Reaction

The Biginelli reaction, shown in Scheme 13, involves the condensation reaction of an aldehyde, β-ketoester, and urea, usually under strongly acidic conditions.[178,179] The PIL 1,1,3,3-tetramethylguanidinium TFA was successfully used as the catalyst and solvent for this reaction. Yields of 80−95% with reaction times of 5−50 min at 100 °C were achieved for aliphatic aldehydes and a range of aromatic

Scheme 14. Friedlander Reaction
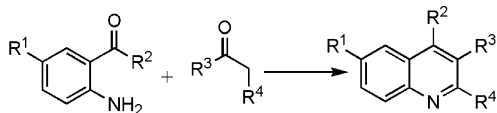
Scheme 15. Beckmann Rearrangement of Cyclohexanone
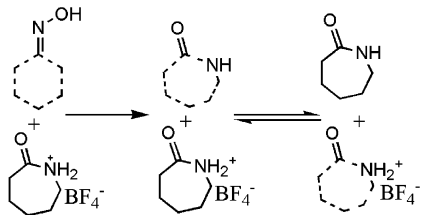
aldehydes, including those with electron-withdrawing or -donating substituents.[179]

A carboxylate functionalized imidazolium Brønsted acidic AIL was recently used as the catalyst and solvent for this reaction, with yields of 85−96% obtained after 15 min at 80 °C.[178] Similar to the guanidine PILs, this AIL promoted the Biginelli reaction for a wide range of aldehydes, though aromatic aldehydes containing strong electron-withdrawing groups and aliphatic aldehydes required longer reactions times.

The commonly used AILs [BMIm]BF$_4$ and [BMIm]PF$_6$ also displayed excellent catalytic activity for this reaction, leading to yields of 77−99% at 100 °C for 30 min.[180]

6.5.2. Friedlander Reaction

The Friedlander reaction, Scheme 14, is used to prepare biologically active substituted quinolines and fused polycyclic quinolines. The HBIm containing PILs trialed for this reaction led to yields from 50 to 96%, with a good correlation between the yield, the pK_a of the anion, and the chemical shift of the proton on the cation. In contrast, the BBIm AILs with the same anions had yields of only 37−75%. [HBIm]-BF$_4$ led to the highest yields of 90−98%, which were obtained under much milder conditions than in conventional systems. An additional advantage of the PILs was that, when unsymmetric ketones reactants were used, only the desired quinoline product formed, compared to only 80% for the AILs.[142]

6.6. Other Organic Synthesis Reactions

6.6.1. Beckmann Rearrangement

A few caprolactam containing PILs were successfully used as solvents and catalysts for the Beckmann rearrangement of cyclohexanone to produce caprolactam.[78] Unusually, the caprolactam product is the same as the neutral form of the cation in the PIL, shown in Scheme 15. The caprolactam BF$_4$ PIL under optimized conditions led to yields of 93% with 89% selectivity. In comparison, under the same conditions, [HMIm]BF$_4$ only had yields of 44% with 33% selectivity, showing the particular suitability of the caprolactam containing PILs for this reaction. Other anions were trialed with the caprolactam cation with good performance, though the BF$_4$ anion gave the best results.[78]

6.6.2. Isomerization

The cis−trans isomerization of dimethyl maleate to dimethyl fumerate is shown in Scheme 16 and is convention-

Scheme 16. (*Z*)- to (*E*)-Alkene Isomerization
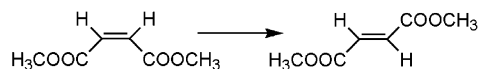
Scheme 17. Hydrolytic Reaction of 1,1,1,3-Tetrachloro-3-phenylpropane
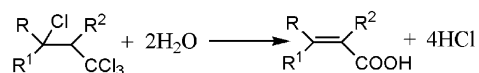
ally catalyzed by primary and secondary amines. Imidazolium PILs and AILs with DL-lactate, salicylate, or BF$_4$ anions were trialed as catalysts and solvents, with excellent conversions of 100% obtained at 90 °C after 4 h with most of the PILs, while the AILs did not promote the reaction at all.[61]

6.6.3. Ether Cleavage

The ionic media [HMIm]Br−HBr contains the anionic species Br$^-$, HBr$_2^-$, and H$_2$Br$_3^-$ and was used as the catalyst and solvent to cleave ethers to produce alcohols and bromides from cyclic and straight-chain dialkyl ethers and aryl alkyl ethers.[64] It was determined using NMR that the anionic proton was involved in the catalytic process, though the cationic proton was not. This PIL was well-suited to this reaction, enabling it to occur at room temperature with no side reactions and with easy separation of the product.

6.6.4. Chlorination

A catalyst−solvent system containing a PIL and HCl or two PILs was used for the chlorination of arene compounds to replace conventional Lewis acid catalysts. The PILs trialed were [HMIm]NO$_3$ and [HMIm]Cl. The best selectivity was obtained using [HMIm]NO$_3$ with HCl, with 99% conversion and 96% selectivity toward the monochloro derivative after 48 h.[181] The nitrate anion was determined to be involved in the reaction, with the IL being reformed afterward and being reusable.

6.6.5. Nitration of Aromatic Compounds

The nitration of aromatics has been conducted in a simple process using SO$_3$H functionalized imidazolium AILs, with nitric acid as the nitrate source. Conversions were obtained from 43 to 93% depending on the substituent on the aromatic ring. No dinitration occurred.[182] An earlier investigation in 2001 used a series of 1-ethyl-3-methylimidazolium AILs or the PIL protonated Hünig base [HNEt(*i*-Pr)$_2$][CF$_3$COO] in a nitrating system with a catalyst and NH$_4$NO$_3$ as a nitrate. The PIL and AILs all led to moderate-to-excellent yields, depending on the substituent on the aromatic ring.[58]

6.6.6. Hydrolytic Reaction

The hydrolytic reaction of 1,1,1,3-tetrachloro-3-phenyl-propane to make cinnamic acid is shown in Scheme 17 and has been reported to work well in ammonium PILs and imidazolium PILs and AILs, where the ILs were used as solvents and catalysts. The ammonium PILs were primary, secondary, or tertiary, though confusingly referred to as quaternary in the paper. It appears that the anion choice was of high importance, with excellent yields of 86−89% and conversions of mostly 100% obtained for the PILs and AILs containing the HSO$_4$ anion regardless of the cation.[183] AILs containing other anions, such as BF$_4$ and PF$_6$, still led to excellent performance, with yields of 82−85% and conversions from 87 to 98%, thus showing the proton is not required

for the catalysis process. Interestingly, it was mentioned that this process is being utilized within an agricultural chemical factory.

6.7. Transition Metal Catalysis

The use of PILs in palladium catalyst systems has been highly successful, though we believe there have been only two reported cases. AILs have also been used in similar circumstances.[140]

Dimerization and ring-closing metathesis reactions have been successfully conducted in 1-alkylimidazolium PILs using a palladium catalyst. The PIL was used as the solvent and source of protons. [HBIm]OTf led to 100% conversion and 100% selectivity for the ring-closing metathesis, compared to 30% conversion and 10% selectivity when the AIL [BMIm]BF$_4$ was used.[184] The dimerization reaction had >98% selectivity toward the desired product with the PILs.[184]

A catalytic system including the PIL 1,1,3,3-tetramethylguanidinium lactate was developed for hydrogenation reactions. The PIL was used to tether palladium nanoparticles onto the surface of a molecular sieve through adsorption of the PIL to the sieve and coordination to the metal particles. Excellent results were obtained with conversions from 100% at 20−40 °C.[185]

6.8. Industrial Applications and the BASIL Process

An update on the role of ILs as commercial solvents was given by Rogers and Seddon in 2003.[186] There was a strong expectation for these ILs to have increasing use in laboratory and industrial applications, with the replacement of many organic solvents currently used. In addition to their environmental benefits, ILs have a major advantage over conventional molecular solvents in the shear number of potential combinations of cations and anions that could be produced and, hence, the ability of ILs to be designed for specific applications.[186]

A significant commercial application of Brønsted acidic ILs has been by BASF with their range of BASIL processes, which involve ILs in industrial processes. These include the PIL [HMIm]Cl, where the PIL is produced from using 1-methylimidazolium as an acid scavenger of HCl, and the Brønsted acidic AIL [EMIm]HSO$_4$, used in liquid−liquid extraction.[187] In 2003, Rogers and Seddon reported that, for one particular BASIL process, the productivity had been increased by a factor of 80 000 compared to the conventional process![186]

7. Chromatography

PILs containing alkylammonium cations have been investigated for their potential use in chromatography, such as EAN,[50,73,76,188,189] ethylammonium acetate (EAA),[190] propylammonium nitrate (PAN),[50,73,76,188] tributylammonium nitrate (TBAN),[50,73] alkylammonium formates,[98] and various alkylammonium thiocyanates.[50,73,188] The early use of PILs in chromatography was primarily to characterize the solvent properties of the PILs, which was described in a comprehensive review by Poole in 2004.[12] The solvent properties of PILs that make them potentially useful in chromatography are that they are polar, are cheap, are easy to make, can be miscible with water, can be air/moisture stable, and have high selectivity toward solutes that are polar and/or hydrogen donors or acceptors.

The physicochemical properties of a number of alkylammonium based PILs were investigated to determine their suitability in chromatography. Throughout these experiments, it was demonstrated that the PILs were highly polar, have similar solvent behavior to solvents with high cohesive energy,[76] and are likely to have similar molecular interactions with polycyclic hydrocarbon solutes as organic solvents,[90] and the strongest interactions are proton donor−acceptor and orientation interactions, with dispersive interactions being weak.[73] The anion and the cation both influence the properties of the PILs in regards to their use in chromatography. Increasing the size of the alkyl groups (such as TBAN compared to EAN) made the PIL more organic-solvent like, whereas smaller alkyl groups led to more waterlike PILs.[73] Similarly, alkylammonium nitrates were more water-like, and alkylammonium thiocyanates were more organic-like.[73]

PILs are of interest as stationary phases in gas−liquid chromatography or as mobile phases in liquid chromatography. These two areas are discussed below, including the specific requirements on the PILs for the different types of chromatography. The PILs that have been identified as most useable for chromatography applications are EAN, PAN,[17] EAA[190] and EAF, PAF, and BAF.[98]

7.1. Liquid Chromatography

In liquid chromatography, PILs have been trialed as modifiers for the mobile phase, and as a stationary phase, when coated on a support, with moderate-to-good success. The PILs are unable to be used directly as the mobile phase because of their viscosities being too high and, hence, need to be mixed with either water or an organic solvent.[50]

The detection of the different chemicals in the solute is usually achieved using UV absorption spectroscopy. This imposes a limitation on the cations and anions that can be used for the mobile phase in liquid chromatography, with imidazolium cations and inorganic anions such as nitrate absorbing in the UV. In contrast, the use of organic anions with alkylammonium cations, such as EAA, has been shown to have no significant UV absorption above 260 nm.[190]

Alkylammonium nitrates, such as EAN and PAN, have been demonstrated to be potentially useful as mobile phases when mixed with another solvent of low viscosity.[50] Mixing with an organic solvent led to better solvent strength and selectivity than mixing with water.[73] However, alkylammonium formates, EAF, PAF, and BAF, when mixed with water, were found to be good replacements to organic solvents, with EAF being of particular interest because of its low viscosity of 11.5 ± 0.1 cP at 24 °C.[98] Alkylammonium thiocyanates were also trialed but were not useable since they led to corrosion of the chromatographic system, forming iron thiocyanate.[73] In more recent work, EAA−water mixtures were shown to be a potentially useful mobile phase, with the mixture having a polarity similar to that of methanol.[190]

EAN and PAN have also been used as the stationary phase in liquid chromatography when coated onto a stationary support and have been used with various organic solvent mobile phases.[17] The chromatographic system worked well, particularly for separating isomers of substances with hydrogen-bonding functional groups.

7.2. Gas Chromatography

The alkylammonium nitrates, particularly EAN and PAN, have been trialed for use as stationary phases in gas−liquid

chromatography. EAN has been demonstrated to be useful in separating solutes that are capable of hydrogen bonding,[76,189] though amines and other solutes capable of very strong hydrogen bonding were not eluted, presumably because they interacted too strongly.[189]

A commonly used method to characterize solvents for chromatography is to use the McReynolds phase constants, which are determined using gas chromatography. The McReynolds constants provide a scale for how strong the forces are, based on the retention index of 10 different probe compounds. However, this method has been shown to be inaccurate for PILs for two reasons. First, the McReynolds phase constants method has the assumption that the test probes are retained solely by gas−liquid partitioning, whereas some were definitely retained by adsorption mechanisms in the PILs.[76,188] Second, the PILs have an extremely low solubility toward hydrocarbons, which prevents the use of *n*-alkane probes and, hence, prevents the accurate determination of the McReynolds phase constants.[188]

8. Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry

A series of ILs, including AILs and PILs, were trialed as ionic matrices for use with matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS).[191−193] The ILs were of interest because of their high solubilizing power, negligible vapor pressure, and broad liquid temperatures.

Ionic matrices were made with the ILs and peptides, proteins, and poly(ethylene glycol) (PEG), which all easily dissolved in the ILs. All of the AILs trialed were found to be unsuccessful for use with the MALDI-MS, whereas many of the PILs were potentially useful. It was determined that the protic nature of the PILs was crucial, with the matrix requiring available protons to promote the ionization during the MS process.[191,193]

9. Biological Applications

EAN has been used as a solvent in a number of protein renaturation and crystallization studies.[194−197] The hydrophobic, ionic nature and ability to form hydrogen bonds makes EAN a good solvent for proteins.[197] The PILs used in the biological field have nearly exclusively involved EAN, with the exception of the antimicrobial work by Pernak et al. using imidazolium PILs.[68]

9.1. PILs as Solvents for Proteins

Potential applications have been identified for the use of EAN with proteins, such as dissolving hydrophobic ligands (e.g., ferrocene) to incorporate them into a protein crystal, improved solubility of some proteins, improved monodispersity of proteins, as a precipitating agent, and as an additive.[197]

Proteins can easily form aggregates during processing, which causes complications in their renaturation. EAN, however, has been shown to be useful in preventing this aggregation.[195,196] It was proposed that EAN prevents aggregation by having a weaker attraction to the hydrophobic part of the protein than conventional surfactants, and hence, for low concentrations, it can be displaced more easily during the refolding of the protein.[196] A compromise was needed in the concentration of EAN since, if it was too low, aggregation occurred, but if it was too high, the protein had

trouble displacing it to refold.[196] A secondary benefit of the EAN is that, unlike other surfactants used to prevent aggregation, EAN does not need to be removed before the protein can refold and the EAN was removed easily at the end of the refolding.[196]

The protein lysozyme was renatured using EAN, where the amount recovered was dependent on minimizing the amount of aggregation. Summers et al.[196] found that the presence of EAN was highly useful in the renaturation of proteins, since it led to the protein regaining between 75 and 90% of its original activity, and higher protein concentrations could be used compared to conventional methods. Lysozyme is soluble in EAN−water solutions, and denatured lysozyme does not precipitate, even at 100 °C with as little as 5% EAN present.[196] Lysozyme could be crystallized from an acetate solution using EAN as a precipitating agent, with variations in pH levels and EAN concentrations leading to monoclinic or tetragonal crystals.[197]

EAN−water solutions of different concentrations were used as solvents for the protein alkaline phosphatise.[198] The enzyme had a maximum activity when the solution contained 10% EAN and dropped to zero when there was 80% EAN. The activity of this enzyme is reliant on the ionic environment, and this study showed that solutions with a low concentration of EAN are suitably ionic to promote the activity of the enzyme. The enzyme was fairly stable in highly concentrated solutions of EAN.[198]

A process was designed by Angell et al. to hyperquench glass-forming liquids containing molecules, such as proteins, that enabled internal structural changes to be observed over time, at a lower temperature than that at which they normally occur.[195] This process can be applied to proteins to observe refolding of denatured proteins. The solvents are required to not crystallize ice on heating or cooling, to not denature the proteins, and to allow the proteins to become thermally denatured without letting them form aggregates. EAN was included into the sucrose solution to prevent aggregation of the lyophilized lysozyme protein.[195]

9.2. Biocatalysis

A number of ILs, including EAN, were used as the reaction media for the enzyme *Candida Antarctica* lipase B (CaLB) in the transesterification of ethyl butonoate with 1-butanol.[194] EAN was not a good solvent, since the strongly coordinating nitrate anion dissolved the CaLB and caused denaturation, thus decreasing the activity of the enzyme by about 10 times.[194] The AILs [BMIm]BF$_4$ and [BMIm]PF$_6$ gave the highest reaction rates and did not dissolve the enzyme.[194] It was determined that a suitable reaction medium was one that had an anion with hydrogen bond-accepting properties, which were not so strong that they dissolved and denatured the protein but were strong enough to coordinate to it.[194] AILs have been trialed successfully as replacements for organic solvents, though PILs studied so far have not been suitable in this application.[199−201]

9.3. Antimicrobial

The biological activity of a variety of PILs of 1-alkyl- and 1-alkoxylmethylimidazole cations with lactate or salicylate anions were shown to have potentially useful antimicrobial properties.[68,69] These PILs were tested using different strains of rods, cocci, and fungi. The cations were chosen for their diffuse charge and the anions were chosen for being

highly asymmetric and nontoxic, to produce PILs with large packing disorder and, consequently, low melting points. The lactates with an alkoxymethyl substituent were more effective than those with just an alkyl substituent. The minimum concentration to inhibit growth generally decreased as the alkyl chain length increased.[68] These PILs showed similar antimicrobial properties to AILs but were more environmentally friendly, especially in comparison to AILs containing fluorinated anions.[68]

9.4. Immunotoxins

The protein toxin mistletoe lectin 1 (ML1) and ricin can be modified using aqueous EAN solutions to generate potentially useful immunotoxins,[202−204] or using butylammonium nitrate or 2-hydroxylethylamonium nitrate.[204] To generate an immunotoxin, the sugar-binding sites of the proteins need to be blocked, which can be achieved by a structural change of the protein. For the immunotoxin generated from ML1 in EAN, the structural change is described as a partially denatured state.[202] As the concentration of EAN increased, the distances between hydrophobic regions of the protein ML1 increased and the globular structure became more unfolded, resulting in a partially denatured state.[202]

A couple of changes in the properties of the proteins ML1 and rictin after treatment with EAN were that the proteins became unstable, the toxicity was drastically decreased, and they lost their sugar-binding ability.[203] Overall, the EAN treated proteins of ML1 and ricin were identified as potentially useful immunotoxins.[203]

9.5. Bacterial Endospore Detection

A current method for detecting bacterial endospores involves dissolving terbium dipicolinate in either water or a water−glycerol mixture, shining a UV beam on the sample, and observing the luminescence, which, if present, indicates the presence of endospores.[205]

Room-temperature ionic liquids (RTILs) have been recognized as potentially useful solvents for this application because of the low evaporation rate and the ability of some RTILs to dissolve terbium salts. EAN has been trialed as a solvent with little success. The characterization of the UV behavior when terbium monodipicolinate was dissolved in EAN was effectively the same as that in water.[205] However, in comparison to water, EAN has a much higher absorption of UV radiation, and hence, there is a much shorter path length, which means EAN is only useful as a solvent for specific applications where the solvent is present as a thin layer and not for most applications that use a bulk amount.[205]

10. Nonaqueous Electrolytes

PILs are potentially very useful as ionic-conducting electrolytes in electrochemical systems and as proton-conducting electrolytes in polymer membrane fuel cells (PEMFCs). While the properties and use of EAN as a liquid electrolyte have been investigated over a number of years, it was only recently that the potential application of PILs as electrolytes in fuel cells was identified. The use of PILs as electrolytes are described below, and their use in PEMFCs is described in the following section.

PILs that have had their electrolytic behavior investigated are EAN, PAN, and two alkylammonium picrates. The minimum cathodic potential for liquid EAN is −1.6 V,

because of the reduction of the nitrate ions.[206] At 25 °C, the mass transfer is very slow in EAN, causing slow diffusion,[206] though it is nearly ideal.[207] EAN and PAN were used as the electrolyte solutions for cyclic voltammetry experiments on ferrocene based complexes,[207] the reduction of uranium complexes,[208] and the reduction of a variety of metal ions.[206] Hexavalent uranium was irreversibly reduced by EAN at 20 °C, while tetravalent uranium was unstable and formed hexavalent uranium within 5 h.[208,209] The metal ions Cd^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, and Tl^+ all reversibly reduced in EAN, while Ni^{2+} was irreversibly reduced, with very stable potentials observed.[206] It was also observed that the addition of water to EAN shifted the redox potentials from −0.228 V to 0.327 V for ferrocene.[207]

The 1:2 salt formed from 2-methylpyridine and trifluoroacetic acid to form α-picoline trifluoroacetate has been claimed as a PIL with the assumption that the trifluoroacetate anion is present as the dimer $H(CF_3CO_2)_2^-$.[210] The evidence for this dimer is limited to the boiling point having a maximum at the 1:2 composition,[22] and the absence of smell at this composition,[210] while in contrast, the melting point and glass transition are both maximum at the 1:1 composition. However, this salt, which is possibly a PIL, has been used as an electrolyte with a RuO_2 electrode, where the salt shows pseudocapacitance and, hence, is potentially useful as an electrolyte in capacitors.[210]

11. Polymer Membrane Fuel Cells

A large number of stoichiometric imidazolium, alkylammonium, and other heterocyclic amine based PILs were developed and characterized, with particular emphasis on their ionic conductivity.[22,60,62,211,212] Some of these PILs were identified as having potential uses as electrolytes in fuel cells, with preliminary fuel cell tests conducted.[28,30,53,86]

Extensive research is continuing to be conducted into ways to improve polymer membrane fuel cells (PEMFCs), as outlined in recent reviews.[213,214] One particular problem associated with PEMFCs is that the proton-conducting membranes require the use of aqueous electrolyte solutions to obtain high proton conductivity, which causes their proton conductivity to be affected by changes in temperature and humidity, limits their use to <100 °C, and requires the constant replacement of lost water. A potential benefit of using PILs as electrolytes in PEMFCs is that the solutions can be anhydrous and, hence, can be operated at temperatures in excess of 100 °C.

Many PILs have good thermal and chemical stability and, hence, are stable above 100 °C. The PILs that have so far been investigated as potential electrolytes for polymer membrane fuel cells generally have lower proton conductivity than the aqueous solutions conventionally used, but recent PILs developed by Angell et al. have comparable conductivities.[86,211]

A recent review was written by Ohno et al. into the future use of ILs in advanced electrochemical devices. The general view stated was that, while there is a lot of potential for AILs to be used in lithium batteries and for PILs in proton-conducting fuel cells, at the moment there are not suitable ILs for these applications.[215]

In related fields, some protic acid−base combinations have recently been utilized to make polymeric materials that are good proton conductors,[86,211,216] and nonstoichiometric acid−base combinations have been used to obtain good ionic conductivity.[28,30,53,217] So far, a significant proportion of the

investigations have involved nonstoichiometric combinations of Brønsted acids and Brønsted bases to optimize their properties. These nonstoichiometric and polymeric Brønsted acid−base materials are briefly covered in this review, since they describe an area where the protic natures of these liquids and solids are essential.

11.1. Stoichiometric Combinations (PILs)

Pure salts, including ILs, are not generally expected to be good conductors at moderate temperatures because of electrostatic interactions between their ions, which causes a decrease in mobility. Usually the maximum ionic conductivity is obtained for electrolyte concentrations around 1 M. Angell et al. proved this is not always true, showing that the neat PILs of EAN, dimethylammonium nitrate, and ethylammonium formate have good conductivities, which are less than those for lithium salts in aqueous solutions but higher than those for nonaqueous lithium salts.

In a recent patent application, Angell et al. described a series of alkylammonium PILs, which are potentially useful as nonaqueous electrolytes in high-temperature polymer membrane fuel cells.[86] The PILs investigated were stable to temperatures between 200 and 250 °C, had conductivities comparable to aqueous solutions, and could be enhanced through the addition of a base with a pK_a value intermediate between that of the acid and the base.[86]

A study by Ogihara et al. compared imidazolium cations with acidic anions, including PILs (HMIm and HEIm cations) and AILs (EMIm cation).[63] It was found that, generally, the PILs had higher ionic conductivities than the AILs, but not always, and this was attributed to the proton conduction resulting mainly from the acidic anions (HSO_4^-, $H_2PO_3^-$, $H_2PO_4^-$, or $H_3P_2O_7^-$).[63] The highest ionic conductivity at 30 °C was 6.5 mS/cm, obtained with [HMIm]HSO_4^-.[63]

More recently, Tigelaar et al. have developed an alternative polymer membrane to Nafion that contains rigid sulfonated aromatic backbones linked with diamine-terminated poly-(ethylene oxide) (PEO) oligomers.[218] This polymer was developed to increase the amount of ionic liquid in the membrane, where in Nafion, the perfluorinated nature was thought to be reducing the uptake. The polymer membranes were soaked with a 1:1 mixture of a PIL and water, where the PILs trialed contained the imidazolium cation with either sulfate, triflate, or TFSI anions. The highest conductivity obtained with these polymer membranes was 50 mS/cm at 150 °C with imidazolium−CF_3SO_3H.[218]

11.2. Nonstoichiometric Acid−Base Combinations

In many cases, higher ionic conductivities can be obtained by using nonstoichiometric ratios of acids to bases compared to the stoichiometric PIL. Studies have used the strong acid HTFSI with the bases 4,4′-trimethylenedipyridine (TMDP),[28] Im,[30] and organic amines.[53] Changes in composition had a significant affect on the melting points, as shown for TMDP and HTFSI, where the 1:1 composition has a melting point of 160 °C, while the eutectic composition of 85:15 had a melting point of 62.0 °C.[28] In comparison, related AILs were shown by Noda et al. to not display proton conduction.[30]

Three imidazolium based PILs have been trialed by Sun et al. as potential solvents for use with the polymer membrane Nafion.[216] These PILs were treated as salts and diluted with an imidazolium solution. The solution−salt combinations used were Im-ImH TFA, Me$_2$Im-Me$_2$ImH TFA, and Me$_2$Im-Me$_2$ImH TFSI, with salt concentrations between 5 and 15%.[216] Ionic conductivities of Nafion swollen with the salt solutions were in the range of 3−4 mS/cm at 100 °C.[216] The ionic conductivities of imidazolium and dimethylimidazolium solutions and each of the salts were individually measured, and all showed significantly poorer ionic conductivities than the salt solutions, indicating that both the salt and the solution contribute to the conductivity.[216] The ionic conductivity of Nafion swollen with nonaqueous AILs showed lower conductivity at 100 °C compared to the PIL solutions.[216]

The series of nonstoichiometric mixtures produced through the combination of organic amines with HTFSI include potential electrolytes for fuel cells, with many of them having good proton conductivities, and liquid below 100 °C.[53] The proton conductivity of the HTFSI−Im electrolytes increased with excess Im, with proton conduction occurring by fast proton transfer between the protonated Im and the excess Im. The proton-conduction mechanism was determined to be the Grotthuss- and vehicle-mechanisms for Im rich compositions.[30] The HTFSI−Im and HTFSI−TMDP electrolytes were tested in fuel cells and showed clear evidence that power was being generated in the cell.[28,30,53]

A nonstoichiometric mixture was produced from a polyoxometalate and a heteropolyacid to make a proton conductor with the general formula of $H_{3-x}M_xPOM$.[217] On the Walden plot, this mixture is above the line predicted by the classical Walden rule and in the superionic liquid region, indicating conduction is occurring by a more efficient conduction mechanism than the Walden mechanism, possibly by the Grotthus mechanism.[217]

A series of nonstoichiometric protic mixtures were made from various molar ratios of 2,5-diphenyl-1,3,4-oxadiazole (DOD) with HTFSI and with a polymerizable version of the base.[29] The stoichiometric salt had a melting point of 80 °C and a decomposition temperature of 200 °C, and because of features in the DSC traces that corresponded to the acid and the base, it was concluded that there was incomplete proton transfer. The highest ionic conductivity was for the salt with DOD/HTFSI of 8:2. When a polymerizable version of the base was used, the resulting polymeric systems had very low ionic conductivity.

11.3. Molten Salts

The protic molten salt [NH_4][HF_2] has a melting point of 125 °C and was shown by Angell et al. to have a very high ionic conductivity, which is comparable to 7.7 M LiCl solutions at high temperatures.[211] The extremely high conductivity is due to the dianion, which has also been used extensively with 1-ethyl-3-methylimidazolium to make an AIL with high conductivity.[219−221] A suggestion was made by Angell et al. that, while [NH_4][HF_2] is a molten salt not a PIL, it could be possible to design and make a similar complex with a melting point below 100 °C, based on the trend that melting points decrease with increasing alkyl chain lengths and substitution.[211]

More recently, Angell et al. have used mixtures of ammonium salts with organic anions, such as EAN with ammonium trifluoroacetate, to produce electrolytes for fuel cells suitable for operation between 100 and 200 °C.[222] An advantage of these electrolytes over aqueous ones is that they can be neutral, unlike aqueous electrolytes, which are either acidic or basic, and hence, there are more possible catalysts that can be used and cell designs can be simpler.

11.4. Proton-Conducting Analogues

One of the current goals within the field of PEMFCs is to find a nonaqueous, proton-conducting solid electrolyte–membrane system for fuel cells. While these are not PILs, they have similarities. Proton-exchange materials have been produced from imidazolium cations with inorganic anions,[223] such as benzimidazole with TFSI,[224] formed into a polymer with many similarities to PILs.

Imidazolium based PILs have been developed by Ohno et al. as monomers in the production of ion-conducting polymers[62,66,67,225] and in similar studies using AIL monomers.[62,226] Ohno et al. have shown that the ionic conductivity of the polymer can be comparable to the monomer by tethering the imidazolium groups on side branches off the main polymer backbone.[62] The high ionic conductivity was achieved through having flexible alkyl spacers between the imidazole and the polymer backbone so that the flexibility of the imidazolium was not reduced.[62,67,226]

A nonstoichiometric mixture was produced from imidazole and HTFSI and incorporated into the plastic crystal phase of succinonitrile to produce a plastic crystal electrolyte.[227] Additions of 2.5% Im_2I to the succinonitrile resulted in a solid with relatively good conductivities of 1.5 mS/cm at 25 °C.[227] The mechanical strength of the succinonitrile was poor, but the addition of a polymer to improve its strength caused a severe reduction in the conductivity.

A number of proton-conducting acid–base solid composites were made by Yamada et al.,[228–230] such as from the surfactants monododecyl phosphate (MDP) and 2-unidecylimidazole (UI).[229] Varying the acid–base ratios of UI–MDP and benzimidazole–MDP composites led to a maximum proton conductivity of 1 mS/cm at 150 °C under anhydrous conditions. Proton conduction occurred by the desirable proton-hopping Grotthuss mechanism, because of the proton-conducting pathways in the lamellar structure.[228,229] In comparison, imidazole–MDP composite materials had much poorer proton conductivity, even when heavily doped with MDP, which was attributed to it not forming a well-ordered lamellar structure.[229]

An acid–base composite biopolymer was produced by Yamada et al. from alginic acid and imidazole, which had relatively good proton conductivity of 2×10^{-3} S/cm at 130 °C, under anhydrous conditions, probably using the Grotthuss mechanism.[230] This biopolymer has slightly lower proton conductivity than the composites mentioned above, which has been attributed as possibly due to the carboxylic acid groups in the alginic acid leading to weaker acid–base pairs. This composite material does have the advantage of good mechanical strength and, hence, does not require an additional supporting material, whereas the other composites investigated by Yamada et al. do.[230]

12. Explosive Formulations

The alkylammonium nitrate PILs are well-known for their highly explosive exothermic decomposition when heated. The main decomposition products of methylammonium nitrate (MAN), dimethylammonium nitrate (DMAN), and trimethylammonium nitrate (TMAN) were reported as H_2O, N_2, NO, NO_2, and N_2O, with MAN also producing CH_3NH_2 and NH_3.[47] In contrast, heating these three complexes at low pressures of 0.5 mmHg led to them decomposing endothermically, most likely with the first part of the process involving proton transfer to make the amine and nitric acid.[47]

At low pressures, the decomposition of MAN produced the gases of $CH_2CH_3NH_3$, N_2, NO, N_2O, CH_4, O_2, NH_3, H_2O, and NO_2.[46] The thermal reactivity of the alkylammonium nitrates of MAN, DMAN, and TMAN have been shown to decrease with increasing substitution, though there is more complete decomposition when there is more substitution.[47] It has been reported that 1,2,3-guanidinium nitrate has a multistage decomposition, with the products HNO_3 and NH_3 being produced first, followed at a slightly higher temperature by NO_2, N_2O, and HCN, and then followed, after another small temperature increase, by CO_2, H_2O, and NO.[56]

A range of explosives and propellants have been developed based on the explosive nature of alkylammonium nitrate salts and of other nitrogen containing PILs. In early work in this field, alkylammonium nitrate salts, with the alkyl chain having 1–8 carbon atoms, were developed into explosive devises using a slurry of the PIL, an inorganic nitrate, water, a nonexplosive sensitizer, and a thickening agent.[231] A distinguishing feature of these devices was that the sensitizer was nonexplosive, unlike in other devices that require something like trinitrotoluene (TNT).[231] A liquid monopropellant was produced through the combination of the PIL isopropylammonium nitrate with hydroxylammonium nitrate and water.[232]

Monopropellants have been made from solutions containing water, hydrogen peroxide, and either hydroxylammonium nitrate or hydrazinium mononitrate. The fuel used was a hydrocarbon that could be a short-chain alkylammonium nitrate or alkanolammonium nitrate.[233–235]

Liquid monopropellants incorporating the PIL into the solution have also been produced, consisting of water, ammonium nitrate, and alkyl-, dialkyl-, or trialkyl ammonium nitrate or alkanol-, dialkanol-, or trialkanolammonium nitrate.[236] These materials were easy to handle, were nonflammable, had zero organic vapor emission, were less corrosive than conventional monopropellants, and did not contain hydrazine or hydroxylammonium nitrate. In addition, the costs were expected to be about one-third compared to conventionally used monopropellants.[236]

Recent work has involved the development of PILs specifically designed for use as propellants or explosives.[71,72,237] These have been prepared through the combination of the nitrogen rich cation 1,5-diamino-1H-tetrazolium combined with a nitrate or perchlorate anion.[71,72] The perchlorate form results in a PIL with a melting point of 97 °C,[71] whereas the nitrate produces a molten salt with a melting point of 138 °C.[72] Imidazolium cations with cyano- or nitro-substituted groups have been shown as potentially useful explosives or propellants, with this range of energetic salts being developed to replace hydrazine based compounds, which are carcinogenic and less stable under normal conditions.[237]

13. Lubricants

A series of alkylammonium PILs and imidazolium AILs were trialed as lubricants for steel on aluminum applications. The PILs mostly had superior properties to the AILs, with a lower friction coefficient than the conventional hydrocarbon oils but a higher wear of the aluminum.[35] The reduction in friction of the PILs compared to the AILs was attributed to their ability to react quicker with the fresh metallic surfaces exposed by the friction and the ability to form a boundary film. Consistent with this, the fast reaction also meant more material was used, and hence, there was higher wear of the

aluminum. As a brief part of the investigation, the PIL $[C_8H_{17}]_3NH$ TFSI was trialed as a 10% additive in mineral oil, and there was reduced friction and wear, indicating that PILs are potentially very useful as additives in lubricants.[35]

14. Conclusion and the Future of PILs

In this review, the known range of protic ionic liquids has been discussed, including their reported physicochemical properties and the applications where they have been used. In comparison to the vast amount of literature for AILs, there have been relatively few papers on PILs, despite the fact that PILs can be used for many of the same applications as AILs, such as in chromatography, in organic synthesis, as amphiphile self-assembly media, in electrochemistry, and as explosives, as well as additional applications where having an available proton is essential such as many biological uses and as proton-conducting media for polymer membrane fuel cells.

There are a vast number of potential acid−base combinations that can be used to prepare new PILs. As a class of solvents, PILs have a range of properties, though they share in common that they are usually highly polar solvents, capable of hydrogen bonding (donation and acceptance). The physicochemical properties and correlations reported herein have the potential to assist in the design of future PILs.

It is anticipated that there will be strong growth in the field of PILs as they become more widely known, which will lead to their use in many more applications, as well as those identified within this review.

15. Summary of Abbreviations

IL	ionic liquid
PIL	protic ionic liquid
AIL	aprotic ionic liquid
EAN	ethylammonium nitrate
Im	imidazolium
HMIm	1-methylimidazolium
HEIm	1-ethylimidazolium
HBIm	1-butylimidazolium
EMIm	1-ethyl-3-methylimidazolium
TFA	trifluoroacetate
TfO	trifluoromethanesulfonate $[CF_3SO_3]$
TFSI	bis(trifluoromethanesulfonyl)imide $[(CF_3SO_2)_2N]$
BETI	bis(perfluoroethylsulfonyl)imide $[(CF_3CF_2SO_2)_2N]$
PEMFC	polymer membrane fuel cell

16. Acknowledgments

17. References

(1) Macfarlane, D. R.; Forsyth, M. *Adv. Mater.* **2001**, *13*, 957.
(2) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *Chem. Phys. Chem.* **2004**, *5*, 1106.
(3) Hagiwara, R.; Ito, Y. *J. Fluorine Chem.* **2000**, *105*, 221.
(4) Antonietti, M.; Kuang, D. B.; Smarsly, B.; Yong, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 4988.
(5) Jain, H.; Thomas, J. O.; Whittingham, M. S. *MRS Bull.* **2000**, *25*, 11.
(6) Shi, F.; Gu, Y. L.; Zhang, Q. H.; Deng, Y. Q. *Catal. Surv. Asia* **2004**, *8*, 179.
(7) Kubisa, P. *Prog. Polym. Sci.* **2004**, *29*, 3.
(8) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A. C.; Plaquevent, J. C. *Tetrahedron: Asymmetry* **2003**, *14*, 3081.
(9) Zhao, H.; Malhotra, S. V. *Aldrichim. Acta* **2002**, *35*, 75.
(10) Gordon, C. M. *Appl. Catal., A* **2001**, *222*, 101.
(11) Wilkes, J. S. *Green Chem.* **2002**, *4*, 73.
(12) Poole, C. F. *J. Chromatogr.* **2004**, *1037*, 49.
(13) Gabriel, S. *Ber.* **1888**, *21*, 2669.
(14) Cottrell, T. L.; Gill, J. E. *J. Chem. Soc.* **1951**, 1798.
(15) Walden, P. *Bull. Acad. Imp. Sci.* **1914**, 1800.
(16) Evans, D. F.; Yamauchi, A.; Roman, R.; Casassa, E. Z. *J. Colloid Interface Sci.* **1982**, *88*, 89.
(17) Shetty, P. H.; Poole, S. K.; Poole, C. F. *Anal. Chim. Acta* **1990**, *236*, 51.
(18) Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G. *Chem. Rev.* **2003**, *103*, 3857.
(19) Kreher, U. P.; Rosamilia, A. E.; Raston, C. L.; Scott, J. L.; Strauss, C. R. *Molecules* **2004**, *9*, 387.
(20) Schroth, W.; Andersch, J.; Schändler, H. D.; Spitzner, R. *Chem. Ztg.* **1989**, *113*, 261.
(21) Schroth, W.; Schadler, H. D.; Andersch, J.; Wiegeleben, A.; Wedler, W.; Krahnstover, J.; Radeglia, R.; Kolbe, A.; Schwarz, W. *Z. Chem.* **1989**, *29*, 129.
(22) Yoshizawa, M.; Xu, W.; Angell, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 15411.
(23) MacFarlane, D. R.; Pringle, J. M.; Johansson, K. M.; Forsyth, S. A.; Forsyth, M. *Chem. Commun.* **2006**, 1905.
(24) Kohler, F.; Atrops, H.; Kalall, H.; Liebermann, E.; Wilhelm, E.; Ratkovics, F.; Salamon, T. *J. Phys. Chem.* **1981**, *85*, 2520.
(25) Kohler, F.; Gopal, R.; Götze, G.; Atrops, H.; Demeriz, M. A.; Liebermann, E.; Wilhelm, E.; Ratkovics, F.; Palagyl, B. *J. Phys. Chem.* **1981**, *85*, 2524.
(26) Kohler, F.; Liebermann, E.; Miksch, G.; Kainz, C. *J. Phys. Chem.* **1972**, *76*, 2764.
(27) Nuthakki, B.; Greaves, T. L.; Krodkiewska, I.; Weerawardena, A.; Burgar, M. I.; Mulder, R. J.; Drummond, C. J. *Aust. J. Chem.* **2007**, *60*, 21.
(28) Susan, M. A. B. H.; Yoo, M. Y.; Nakamoto, H.; Watanabe, M. *Chem. Lett.* **2003**, *32*, 836.
(29) Matsuoka, H.; Nakamoto, H.; Susan, M. A. B. H.; Watanabe, M. *Electrochim. Acta* **2005**, *50*, 4015.
(30) Noda, A.; Susan, M. A. B. H.; Kudo, K.; Mitsushima, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2003**, *107*, 4024.
(31) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 19593.
(32) Greaves, T. L.; Weerawardena, A.; Fong, C.; Krodkiewska, I.; Drummond, C. J. *J. Phys. Chem. B* **2006**, *110*, 22479.
(33) MacFarlane, D. R.; Seddon, K. R. *Aust. J. Chem.* **2007**, *60*, 3.
(34) Belieres, J.-P.; Angell, C. A. *J. Phys. Chem. B* **2007**, *111*, 4926.
(35) Qu, J.; Truhan, J. J.; Dai, S.; Luo, H.; Blau, P. J. *Tribol. Lett.* **2006**, *22*, 207.
(36) Gao, H. X.; Han, B. X.; Li, J. C.; Jiang, T.; Liu, Z. M.; Wu, W. Z.; Chang, Y. H.; Zhang, J. M. *Synth. Commun.* **2004**, *34*, 3083.
(37) Du, Z. Y.; Li, Z. P.; Guo, S.; Zhang, J.; Zhu, L. Y.; Deng, Y. Q. *J. Phys. Chem. B* **2005**, *109*, 19542.
(38) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.
(39) Zhou, Z.-B.; Matsumoto, H.; Tatsumi, K. *Chem.−Eur. J.* **2004**, *10*, 6581.
(40) Zhou, Z. B.; Matsumoto, H.; Tatsumi, K. *Chem.−Eur. J.* **2005**, *11*, 752.
(41) Ding, C. G.; Taskila, T.; Laasonen, K.; Laaksonen, A. *Chem. Phys.* **2003**, *287*, 7.
(42) Re, S.; Osamura, Y.; Morokuma, K. *J. Phys. Chem.* **1999**, *103*, 3535.
(43) Arstila, H.; Laasonen, K.; Laaksonen, A. *J. Chem. Phys.* **1998**, *108*, 1031.
(44) Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature* **2006**, *439*, 831.
(45) Neto, B. A. D.; Santos, L. S.; Nachtigall, F. M.; Eberlin, M. N.; Dupont, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7251.
(46) Breisacher, P.; Takimoto, H. H.; Denault, G. C.; Hicks, W. A. *Combust. Flame* **1970**, *14*, 397.
(47) Jain, S. R.; Rao, M. V.; Pai, Verneker, V. R. *Propellants, Explos., Pyrotech.* **1978**, *3*, 83.
(48) Mirejovsky, D.; Arnett, E. *J. Am. Chem. Soc.* **1983**, *105*, 1112.
(49) Allen, M.; Evans, D. F.; Lumry, R. *J. Solution Chem.* **1985**, *14*, 549.
(50) Poole, C. F.; Kersten, B. R.; Ho, S. S. J.; Coddens, M. E.; Furton, K. G. *J. Chromatogr.* **1986**, *352*, 407.
(51) Duvivier, S.; Turmine, M.; Letellier, P. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3457.
(52) Sugden, S.; Wilkins, H. *J. Chem. Soc.* **1929**, 1291.
(53) Susan, M. A. B. H.; Noda, A.; Mitsushima, S.; Watanabe, M. *Chem. Commun.* **2003**, 938.
(54) Bicak, N. *J. Mol. Liq.* **2005**, *116*, 15.
(55) Tao, G. H.; He, L.; Sun, N.; Kou, Y. *Chem. Commun.* **2005**, 3562.

(56) Oyumi, Y.; Brill, T. B. *J. Phys. Chem.* **1985**, *89*, 4325.
(57) Ito, N.; Huang, W.; Richert, R. *J. Phys. Chem.* **2006**, *110*, 4371.
(58) Laali, K. K.; Gettwert, V. J. *J. Org. Chem.* **2001**, *66*, 35.
(59) Oyumi, Y.; Brill, T. B. *J. Phys. Chem.* **1987**, *91*, 2657.
(60) Hirao, M.; Sugimoto, H.; Ohno, H. *J. Electrochem. Soc.* **2000**, *147*, 4168.
(61) Janus, E.; Lozynski, M.; Pernak, J. *Chem. Lett.* **2006**, *35*, 210.
(62) Ohno, H.; Yoshizawa, M. *Solid State Ionics* **2002**, *154*, 303.
(63) Ogihara, W.; Kosukegawa, H.; Ohno, H. *Chem. Commun.* **2006**, 3637.
(64) Driver, G.; Johnson, K. E. *Green Chem.* **2003**, *5*, 163.
(65) Ohno, H.; Yoshizawa, M.; Ogihara, W. *Electrochim. Acta* **2004**, *50*, 255.
(66) Hirao, M.; Ito, K.; Ohno, H. *Electrochim. Acta* **2000**, *45*, 1291.
(67) Yoshizawa, M.; Ogihara, W.; Ohno, H. *Polym. Adv. Technol.* **2002**, *13*, 589.
(68) Pernak, J.; Goc, I.; Mirska, I. *Green Chem.* **2004**, *6*, 323.
(69) Pernak, J.; Goc, I.; Fojutowski, A. *Holzforschung* **2005**, *59*, 473.
(70) Duan, Z. Y.; Gu, Y. L.; Zhang, J.; Zhu, L. Y.; Deng, Y. Q. *J. Mol. Catal., A: Chem.* **2006**, *250*, 163.
(71) Galvez-Ruiz, J. C.; Holl, G.; Karaghiosoff, K.; Klapotke, T. M.; Loehnwitz, K.; Mayer, P.; Noeth, H.; Polborn, K.; Rohbogner, C. J.; Suter, M.; Weigand, J. J. *Inorg. Chem.* **2005**, *44*, 4237.
(72) Drake, G. W.; Hawkins, T. W.; Boatz, J.; Hall, L.; Vij, A. *Propellants, Explos., Pyrotech.* **2005**, *30*, 156.
(73) Shetty, P. H.; Youngberg, P. J.; Kersten, B. R.; Poole, C. F. *J. Chromatogr.* **1987**, *411*, 61.
(74) Hadded, M.; Bahri, H.; Letellier, P. *J. Chim. Phys. Phys.−Chim. Biol.* **1986**, *83*, 419.
(75) Oleinikova, A.; Bonetti, M. *J. Solution Chem.* **2002**, *31*, 397.
(76) Arancibia, E. L.; Castells, R. C.; Nardillo, A. M. *J. Chromatogr.* **1987**, *398*, 21.
(77) Kumelan, J.; Kamps, I. P. S.; Tuma, D.; Maurer, G. *J. Chem. Thermodyn.* **2006**, *38*, 1396.
(78) Guo, S.; Du, Z. Y.; Zhang, S. G.; Li, D. M.; Li, Z. P.; Deng, Y. Q. *Green Chem.* **2006**, *8*, 296.
(79) Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, *35*, 1168.
(80) Widegren, J. A.; Laesecke, A.; Magee, J. W. *Chem. Commun.* **2005**, 1610.
(81) Tokuda, H.; Ishii, K.; Susan, M. A. B. H.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 2833.
(82) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103.
(83) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593.
(84) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. *J. Chem. Thermodyn.* **2005**, *37*, 559.
(85) Xu, W.; Cooper, E. I.; Angell, C. A. *J. Phys. Chem. B* **2003**, *107*, 6170.
(86) Angell, C. A.; Xu, W.; Belieres, J.-P.; Yoshizawa, M. Patent WO114445, 2004.
(87) Domanska, U.; Bogel-Lukasik, R. *J. Phys. Chem. B* **2005**, *109*, 12124.
(88) Bagno, A.; Butts, C.; Chiappe, C.; D'amico, F.; Lord, J. C. D.; Pieraccini, D.; Rastrelli, F. *Org. Biomol. Chem.* **2005**, *3*, 1624.
(89) Zhou, Z. B.; Matsumoto, H.; Tatsumi, K. *Chem. Lett.* **2004**, *33*, 1636.
(90) Street, K. W.; Acree, W. E.; Poole, C. F.; Shetty, P. H. *Analyst* **1988**, *113*, 1869.
(91) Reichardt, C. *Green Chem.* **2005**, *7*, 339.
(92) Schrödle, S.; Annat, G.; MacFarlane, D. R.; Forsyth, M.; Buchner, R.; Hefter, G. *Chem. Commun.* **2006**, 1748.
(93) Halder, M.; Headley, L. S.; Mukherjee, P.; Song, X.; Petrich, J. W. *J. Phys. Chem. A* **2006**, *110*, 8623.
(94) Chiappe, C.; Pieraccini, D. *J. Phys. Chem. A* **2006**, *110*, 4937.
(95) Siddiqui, S. A.; Potewar, T. M.; Lahoti, R. J.; Srinivasan, K. V. *Synthesis* **2006**, *17*, 2849.
(96) Harrod, W. B.; Pienta, N. J. *J. Phys. Org. Chem.* **1990**, *3*, 534.
(97) Poole, S. K.; Shetty, P. H.; Poole, C. F. *Anal. Chim. Acta* **1989**, *218*, 241.
(98) Waichigo, M. M.; Hunter, B. M.; Riechel, T. L.; Danielson, N. D. *J. Liq. Chromatogr. Relat. Technol.* **2007**, *30*, 165.
(99) Herfort, I. M.; Schneider, H. *Liebigs Ann. Chem.* **1991**, *1*, 27.
(100) Ogihara, W.; Aoyama, T.; Ohno, H. *Chem. Lett.* **2004**, *33*, 1414.
(101) Evans, D. F.; Yamauchi, A.; Wei, G. J.; Bloomfield, V. A. *J. Phys. Chem.* **1983**, *87*, 3537.
(102) Evans, D. F.; Chen, S.-H.; Schriver, G. W.; Arnett, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 481.
(103) Bleasdale, T. A.; Tiddy, G. J. T.; Wynjones, E. *J. Phys. Chem.* **1991**, *95*, 5385.
(104) Velasco, S. B.; Turmine, M.; Di Caprio, D.; Letellier, P. *Colloids Surf., A* **2006**, *275*, 50.
(105) Turmine, M.; Duvivier, S.; Mayaffre, A.; Letellier, P. *J. Phys. Chem. B* **2003**, *107*, 125.
(106) Araos, M. U.; Warr, G. G. *J. Phys. Chem. B* **2005**, *109*, 14275.

(107) Atkin, R.; Warr, G. G. *J. Am. Chem. Soc.* **2005**, *127*, 11940.
(108) Tamuralis, W.; Lis, L. J.; Quinn, P. J. *Biophys. J.* **1988**, *53*, 489.
(109) Tamuralis, W.; Lis, L. J.; Quinn, P. J. *J. Colloid Interface Sci.* **1992**, *150*, 200.
(110) Tamura-Lis, W.; Lis, L. J. *J. Phys. Chem.* **1987**, *91*, 4625.
(111) O'Leary, T. J.; Levin, I. W. *J. Phys. Chem.* **1984**, *88*, 4074.
(112) Evans, D. F.; Kaler, E. W.; Benton, W. J. *J. Phys. Chem.* **1983**, *87*, 533.
(113) Anderson, D. M. Patent WO106382-A2, 2003.
(114) Anderson, D. M. Patent WO000057-A1, 2003.
(115) Spicer, P. T.; Small, W. B.; Lynch, M. L. Patent WO066014-A2, 2002.
(116) Kraus, C. A. *J. Phys. Chem.* **1956**, *60*, 129.
(117) Perron, G.; Hardy, A.; Justice, J. C.; Desnoyers, J. E. *J. Solution Chem.* **1993**, *22*, 1159.
(118) Chagnes, A.; Tougui, A.; Carré, B.; Ranganathan, N.; Lemordant, D. *J. Solution Chem.* **2004**, *33*, 247.
(119) Hadded, M.; Biquard, M.; Letellier, P.; Schaal *Can. J. Chem.* **1985**, *63*, 565.
(120) Sonawane, P. D.; Kumar, A. *J. Solution Chem.* **2004**, *33*, 1097.
(121) Duvivier, S.; Turmine, M.; Letellier, P. *Can. J. Chem.* **1998**, *76*, 1210.
(122) Weingärtner, H.; Merkel, T.; Kashammer, S.; Schroer, W.; Wiegand, S. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 970.
(123) Heimburg, T.; Mirzaev, S. Z.; Kaatze, U. *Phys. Rev. E* **2000**, *62*, 4963.
(124) Mirzaev, S. Z.; Kaatze, U. *Phys. Rev. E* **2002**, *65*, 1.
(125) Weingärtner, H. Schroer, W. *J. Mol. Liq.* **1995**, *65−66*, 107.
(126) Schröer, W.; Wiegand, S.; Weingartner, H. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 975.
(127) Horn, R. G.; Evans, D. F.; Ninham, B. W. *J. Phys. Chem.* **1988**, *92*, 3531.
(128) Considine, R. F.; Drummond, C. J. *Langmuir* **2000**, *16*, 631.
(129) Lee, C. K.; Huang, H. W.; Lin, I. J. B. *Chem. Commun.* **2000**, 1911.
(130) Yamauchi, A.; Inoue, M.; Ohgi, H.; Mito, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1361.
(131) Greaves, T. L.; Weerawardena, A.; Fong, C.; Drummond, C. J. *J. Phys. Chem. B* **2007**, *111*, 4082.
(132) Greaves, T. L.; Weerawardena, A.; Fong, C.; Drummond, C. J. *Langmuir* **2007**, *23*, 402.
(133) Wang, L. Y.; Chen, X.; Chai, Y. C.; Hao, J. C.; Sui, Z. M.; Zhuang, W. C.; Sun, Z. W. *Chem. Commun.* **2004**, 2840.
(134) Lee, K. M.; Lee, C. K.; Lin, I. J. B. *Chem. Commun.* **1997**, 899.
(135) He, Y.; Li, Z.; Simone, P.; Lodge, T. P. *J. Am. Chem. Soc.* **2006**, *128*, 2745.
(136) Evans, D. F. *Langmuir* **1988**, *4*, 3.
(137) Binnemans, K. *Chem. Rev.* **2005**, *105*, 4148.
(138) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
(139) Muzart, J. *Adv. Synth. Catal.* **2006**, *348*, 275.
(140) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015.
(141) Sheldon, R. *Chem. Commun.* **2001**, 2399.
(142) Palimkar, S. S.; Siddiqui, S. S.; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. *J. Org. Chem.* **2003**, *68*, 9371.
(143) Du, Y.; Tian, F. *J. Chem. Res.* **2006**, *8*, 486.
(144) Fei, Z. F.; Zhao, D. B.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *Chem.—Eur. J.* **2004**, *10*, 4886.
(145) Zhang, P. P.; Du, J. Y.; Yang, F.; Zou, G.; Tang, J. *Chin. J. Chem.* **2005**, *23*, 581.
(146) Gui, J. Z.; Ban, H. Y.; Cong, X. H.; Zhang, X. T.; Hu, Z. D.; Sun, Z. L. *J. Mol. Catal., A: Chem.* **2005**, *225*, 27.
(147) Hangarge, R. V.; Jarikote, D. V.; Shingare, M. S. *Green Chem.* **2002**, *4*, 266.
(148) Hangarge, R. V.; Shingare, M. S. *Mendeleev Commun.* **2003**, 79.
(149) Hu, Y.; Wei. P.; Huang, H.; Le, Z.-G.; Chen, Z.-C. *Synth. Commun.* **2005**, *35*, 2955.
(150) Darvatkar, N. B.; Deorukhkar, A. R.; Bhilare, S. V.; Salunkhe, M. M. *Synth. Commun.* **2006**, *36*, 3043.
(151) Hu, Y.; Chen, J.; Le, Z. G.; Zheng, Q. G. *Synth. Commun.* **2005**, *35*, 739.
(152) Karthikeyan, G.; Perumal, P. T. *Can. J. Chem.* **2005**, *83*, 1746.
(153) Jaeger, D. A.; Tucker, C. E. *Tetrahedron Lett.* **1989**, *30*, 1785.
(154) Janus, E.; Goc-Maciejewska, I.; Lozynski, M.; Pernak, J. *Tetrahedron Lett.* **2006**, *47*, 4079.
(155) Wasserscheid, P.; Sesing, M.; Korth, W. *Green Chem.* **2002**, *4*, 134.
(156) Olah, G. A.; Mathew, T.; Goeppert, A.; Torok, B.; Bucsi, I.; Li, X. Y.; Wang, Q.; Marinez, E. R.; Batamack, P.; Aniszfeld, R.; Prakash, G. K. S. *J. Am. Chem. Soc.* **2005**, *127*, 5964.
(157) Jiang, T.; Gao, H. X.; Han, B. X.; Zhao, G. Y.; Chang, Y. H.; Wu, W. Z.; Gao, L.; Yang, G. Y. *Tetrahedron Lett.* **2004**, *45*, 2699.
(158) Zhu, A. L.; Jiang, T.; Wang, D.; Han, B. X.; Liu, L.; Huang, J.; Zhang, J. C.; Sun, D. H. *Green Chem.* **2005**, *7*, 514.
(159) Zhao, G. Y.; Jiang, T.; Gao, H. X.; Han, B. X.; Huang, J.; Sun, D. H. *Green Chem.* **2004**, *6*, 75.

(160) Sahoo, S.; Joseph, T.; Halligudi, S. B. *J. Mol. Catal., A: Chem.* **2006**, *244*, 179.
(161) Gu, Y.; Ogawa, C.; Kobayashi, S. *Chem. Lett.* **2006**, *35*, 1176.
(162) Wang, H.; Cui, P.; Zou, G.; Yang, F.; Tang, J. *Tetrahedron* **2006**, *62*, 3985.
(163) Zhu, H. P.; Yang, F.; Tang, J.; He, M. Y. *Green Chem.* **2003**, *5*, 38.
(164) Joseph, T.; Sahoo, S.; Halligudi, S. B. *J. Mol. Catal., A: Chem.* **2005**, *234*, 107.
(165) Arfan, A.; Bazureau, J. P. *Org. Process Res. Dev.* **2005**, *9*, 743.
(166) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 5962.
(167) Fang, D.; Zhou, X.-L.; Ye, Z.-W.; Liu, Z.-L. *Ind. Eng. Chem. Res.* **2006**, *45*, 7982.
(168) Gu, Y. L.; Shi, F.; Deng, Y. Q. *J. Mol. Catal., A: Chem.* **2004**, *212*, 71.
(169) Forbes, D. C.; Weaver, K. J. *J. Mol. Catal., A: Chem.* **2004**, *214*, 129.
(170) Xing, H. B.; Wang, T.; Zhou, Z. H.; Dai, Y. Y. *Ind. Eng. Chem. Res.* **2005**, *44*, 4147.
(171) Gui, J.; Cong, X.; Liu, D.; Zhang, X.; Hu, Z.; Sun, Z. *Catal. Commun.* **2004**, *5*, 473.
(172) Du, Y. Y.; Tian, F. L. *Synth. Commun.* **2005**, *35*, 2703.
(173) Wu, H. H.; Yang, F.; Cui, P.; Tang, J.; He, M. Y. *Tetrahedron Lett.* **2004**, *45*, 4963.
(174) Zhang, F.; Xu, D. Q.; Luo, S. P.; Liu, B. Y.; Du, X. H.; Xu, Z. Y. *J. Chem. Res. Synop.* **2004**, 773.
(175) Duan, Z. Y.; Gu, Y. L.; Deng, Y. Q. *Synth. Commun.* **2005**, *35*, 1939.
(176) Moreau, C.; Finiels, A.; Vanoye, L. *J. Mol. Catal., A: Chem.* **2006**, *253*, 165.
(177) Lansalot-Matras, C.; Moreau, C. *Catal. Commun.* **2003**, *4*, 517.
(178) Zheng, R.; Wang, X.; Xu, H.; Du, J. *Synth. Commun.* **2006**, *36*, 1503.
(179) Shaabani, A.; Rahmati, A. *Catal. Lett.* **2005**, *100*, 177.
(180) Peng, J. J.; Deng, Y. Q. *Tetrahedron Lett.* **2001**, *42*, 5917.
(181) Chiappe, C.; Leandri, E.; Tebano, M. *Green Chem.* **2006**, *8*, 742.
(182) Qiao, K.; Yokoyama, C. *Chem. Lett.* **2004**, *33*, 808.
(183) Weng, J. Y.; Wang, C. M.; Li, H. R.; Wang, Y. *Green Chem.* **2006**, *8*, 96.
(184) Picquet, M.; Tkatchenko, I.; Tommasi, I.; Wasserscheid, P.; Zimmermann, J. *Adv. Synth. Catal.* **2003**, *345*, 959.
(185) Huang, J.; Jiang, T.; Gao, H. X.; Han, B. X.; Liu, Z. M.; Wu, W. Z.; Chang, Y. H.; Zhao, G. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 1397.
(186) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792.
(187) BASF−BASIL process, 2007; http://www2.basf.de/en/intermed/nbd/products/ionic_liquids.
(188) Kersten, B. R.; Poole, C. F. *J. Chromatogr.* **1987**, *399*, 1.
(189) Pacholec, F.; Butler, H. T.; Poole, C. F. *Anal. Chem.* **1982**, *54*, 1938.
(190) Waichigo, M. M.; Riechel, T. L.; Danielson, N. D. *Chromatographia* **2005**, *61*, 17.
(191) Armstrong, D. W.; Zhang, L. K.; He, L. F.; Gross, M. L. *Anal. Chem.* **2001**, *73*, 3679.
(192) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14247.
(193) Boehm, G.; Stahl, B.; Mank, M. Patent DE10238069, 2004.
(194) Lau, R. M.; Sorgedrager, M. J.; Carrea, G.; Van Rantwijk, F.; Secundo, F.; Sheldon, R. A. *Green Chem.* **2004**, *6*, 483.
(195) Angell, C. A.; Wang, L. M. *Biophys. Chem.* **2003**, *105*, 621.
(196) Summers, C. A.; Flowers, R. A. *Protein Sci.* **2000**, *9*, 2001.
(197) Garlitz, J. A.; Summers, C. A.; Flowers, R. A.; Borgstahl, G. E. O. *Acta Crystallogr., Sect D* **1999**, *55*, 2037.
(198) Magnuson, D. K.; Bodley, J. W.; Evans, D. F. *J. Solution Chem.* **1984**, *13*, 583.

(199) Maruyama, T.; Nagasawa, S.; Goto, M. *Biotechnol. Lett.* **2002**, *24*, 1341.
(200) Eckstein, M.; Sesing, M.; Kragl, U.; Adlercreutz, P. *Biotechnol. Lett.* **2002**, *24*, 867.
(201) Cull, S. G.; Holbrey, J. D.; Vargas-Mora, V.; Seddon, K. R.; Lye, G. J. *Biotechnol. Bioeng.* **2000**, *69*, 227.
(202) Bushueva, T. L.; Medvedeva, N. V.; Tonevitsky, A. G.; Pfuller, U.; Fiedler, S.; Franz, H. *Stud. Biophys.* **1990**, *138*, 229.
(203) Pfuller, U.; Franz, H.; Pfuller, K.; Jungham, I.; Bielka, H. *Lectins* **1988**, *6*, 299.
(204) Pfuller, U.; Franz, H. Patent DD262042-A, 1989.
(205) Rosen, D. L. *Appl. Spectrosc.* **2006**, *60*, 1453.
(206) Schneider, H.; Stroka, J. *Pol. J. Chem.* **1994**, *68*, 795.
(207) Shotwell, J. B.; Flowers, R. A. *Electroanalysis* **2000**, *12*, 223.
(208) Martinot, L.; Gubbels, F.; Michaux, C.; Nemeeger, C. *Radiochim. Acta* **1992**, *57*, 119.
(209) Martinot, L.; Bare, D.; Michaux, C. *J. Radioanal. Nucl. Chem. Art.* **1993**, *170*, 389.
(210) Rochefort, D.; Pont, A. L. *Electrochem. Commun.* **2006**, *8*, 1539.
(211) Xu, W.; Angell, C. A. *Science* **2003**, *302*, 422.
(212) Yoshizawa, M.; Ogihara, W.; Ohno, H. *Electrochem. Solid-State Lett.* **2001**, *4*, E25.
(213) Haile, S. M. *Acta Mater.* **2003**, *51*, 5981.
(214) Litser, S.; McLean, G. *J. Power Sources* **2004**, *130*, 61.
(215) Fernicola, A.; Scrosati, B.; Ohno, H. *Ionics* **2006**, *12*, 95.
(216) Sun, J. Z.; Jordan, L. R.; Forsyth, M.; Macfarlane, D. R. *Electrochim. Acta* **2001**, *46*, 1703.
(217) Bourlinos, A. B.; Raman, K.; Herrera, R.; Zhang, Q.; Archer, L. A.; Giannelis, E. P. *J. Am. Chem. Soc.* **2004**, *126*, 15358.
(218) Tigelaar, D. A.; Waldecker, J. R.; Peplowski, K. M.; Kinder, J. D. *Polymer* **2006**, *47*, 4269.
(219) Hagiwara, R.; Hirashige, T.; Tsuda, T.; Ito, Y. *J. Electrochem. Soc.* **2002**, *149*, D1.
(220) Matsumoto, K.; Tsuda, T.; Hagiwara, R.; Ito, Y. *Solid State Sci.* **2002**, *4*, 23.
(221) Tsuda, T.; Nohira, T.; Nakamori, Y.; Matsumoto, K.; Hagiwara, R.; Ito, Y. *Solid State Ionics* **2002**, *149*, 295.
(222) Belieres, J. P.; Gervasio, D.; Angell, C. A. *Chem. Commun.* **2006**, 4799.
(223) Masayoshi, T.; Toshihiko, Y.; Takumi, T.; Toshiyuki, O.; Toshihiko, M. Patent JP044550-A, 2005.
(224) Watanabe, M.; Noda, A.; Osawa, T.; Kishi, T.; Matsuda, T. Patent WO083981, 2003.
(225) Yoshizawa, M.; Ohno, H. *Chem. Commun.* **2004**, 1828.
(226) Yoshizawa, M.; Ohno, H. *Electrochim. Acta* **2001**, *46*, 1723.
(227) Abu-Lebdeh, Y.; Abouimrane, A.; Alarco, P. J.; Hammami, A.; Ionescu-Vasii, L.; Armand, M. *Electrochem. Commun.* **2004**, *6*, 432.
(228) Yamada, M.; Honma, I. *Electrochim. Acta* **2003**, *48*, 2411.
(229) Yamada, M.; Honma, I. *J. Phys. Chem. B* **2004**, *108*, 5522.
(230) Yamada, M.; Honma, I. *Polymer* **2004**, *45*, 8349.
(231) Minnick, J. J. Patent 3409484, 1968.
(232) Mueller, K. F.; Cziesla, M. J. Patent 5223057, 1993.
(233) Wagaman, K. L. U.S. Patent 6331220-B1, 2001.
(234) Wagaman, K. L. U.S. Patent 6328831-B1, 2001.
(235) Wagaman, K. L. U.S. Patent 6165295-A, 2000.
(236) Wagaman, K. L. U.S. Patent 6001197, 1999.
(237) Gutowski, K. E.; Holbrey, J. D.; Rogers, R. D.; Dixon, D. A. *J. Phys. Chem. B* **2005**, *109*, 23196.