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Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation

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A series of hydrophilic and hydrophobic 1-alkyl-3-methylimidazolium room temperature ionic liquids (RTILs) have been prepared and characterized to determine how water content, density, viscosity, surface tension, melting point, and thermal stability are affected by changes in alkyl chain length and anion. In the series of RTILs studied here, the choice of anion determines water miscibility and has the most dramatic effect on the properties. Hydrophilic anions (*e.g.*, chloride and iodide) produce ionic liquids that are miscible in any proportion with water but, upon the removal of some water from the solution, illustrate how sensitive the physical properties are to a change in water content. In comparison, for ionic liquids containing more hydrophobic anions (*e.g.*, PF_6^- and $N(SO_2CF_3)_2^-$), the removal of water has a smaller affect on the resulting properties. For a series of 1-alkyl-3-methylimidazolium cations, increasing the alkyl chain length from butyl to hexyl to octyl increases the hydrophobicity and the viscosities of the ionic liquids increase, whereas densities and surface tension values decrease. Thermal analyses indicate high temperatures are attainable prior to decomposition and DSC studies reveal a glass transition for several samples. ILs incorporating PF_6^- have been used in liquid/liquid partitioning of organic molecules from water and the results for two of these are also discussed here. On a cautionary note, the chemistry of the individual cations and anions of the ILs should not be overlooked as, in the case of certain conditions for PF_6^- ILs, contact with an aqueous phase may result in slow hydrolysis of the PF_6^- with the concomitant release of HF and other species.

Introduction

The continued use of large quantities of organic solvents as liquid media for chemical reaction, extraction, and formulation is a major concern in today's chemical processing industry. The perceived deleterious effects of these materials on human health, safety, and the environment combined with their volatility and flammability has lead to increasing pressure for minimizing their use both from a public relations and a cost perspective. Concepts, such as Environmental Stewardship,[1] have placed a renewed emphasis on careful solvent selection and a search for less harmful alternatives. In the past, the emphasis in industrial chemistry was placed on product yield and quality. Increasingly, solvent use during manufacture is viewed in terms of avoiding the costs associated with disposal, legal liabilities, and regulatory constraints.[2]

Recent regulatory controls have aggressively targeted the reduction of the volume of industrial pollutants, a major component of which comprise spent solvents unsuitable for recycling. Approaches to reduce the reliance on traditional solvents will be of tremendous importance in cleaning up industrial problems. Currently, treatment of solvent-laden wastes is a cost borne by industry, human health, and the environment. Although alternative approaches such as heterogeneous catalysis[3,4] and aqueous reaction media exist,[5–7] they may not represent generic solutions to these problems.

The ideal opportunity for waste reduction occurs before any reagents are mixed, during process design. In this approach, basic chemistry must play an important role in formulating alternative manufacturing processes with minimized hazards and decreased waste generation. This shift in the manufacturing paradigm is the basis of 'Green Chemistry', rather than pollute and remediate.[8] Green Chemistry also proposes optimized synthetic methodologies for high product yields and the generation of substances that offer little harm to the environment. In view of the heavy reliance on organic solvents in current manufacturing processes, the development of new technologies for pollution prevention can assist in the reduction of VOC usage and the associated volatility, environmental, and human health concerns that accompany exposure to organic solvents.

Green Context

Ionic liquids (ILs) are non-volatile, non-flammable and thermally stable solvents and as such as very promising replacements for the traditional volatile organic solvents. Their quite rapid emergence as alternative solvents has involved a rapidly growing number of examples of application but the understanding and study of their physical properties has lagged behind. It is very important that we accumulate a substantial body of physical data for these fascinating substances so that their true potential as solvents can be realised. Here the effects of the alkyl chain length of the cation and the identity of the anion on the key properties of hygroscopicity, density, viscosity, surface tension, melting point and thermal stability are studied. The anion identity is shown to be of foremost importance. *JHC*

Ionic liquids (ILs) as solvents

One of the most promising areas of research in new 'green' technologies is the application of neoteric solvents,[9] a category which includes supercritical CO_2,[10–12] aqueous biphasic systems,[13–15] and ionic liquids (ILs).[16–20] ILs offer a highly solvating, yet non-coordinating medium in which a number of organic and inorganic solutes may be dissolved.[12,21] In the ideal case, ILs are non-volatile, non-flammable, have high thermal stability,[22] and are relatively undemanding and inexpensive to manufacture. Many ILs fulfill these requirements and are liquids over a wide temperature range (some can exceed 300 °C). Melting points as low as −96 °C are known,[23] thus the usable liquid range may cover that used for conventional synthetic chemistry and low temperature extractions.

In the current understanding, ILs contain large, organic cations (Fig. 1) with a variety of anions and melt at or below about 150 °C (adopted as an arbitrary upper temperature limit for ionic liquids). We prefer to work with those ILs which have a liquid phase at ambient temperature and refer to these as room temperature ionic liquids (RTILs). ILs are usually composed of organic cations such as quaternary ammonium cations,[24,25] heterocyclic aromatic compounds,[26] pyrrolidinium cations,[27] derivatives of natural products,[28] and some more esoteric cations.[29,30] The properties of both cation and anion are useful tools for fine-tuning the properties of the resulting IL for desired 'solvent' properties. Clearly, many different ILs may be synthesized having a wide range of physical and chemical properties.

$CH_3CH_2CH_2CH_2 = [C_4mim]^+$
$CH_3CH_2CH_2CH_2CH_2CH_2 = [C_6mim]^+$
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2 = [C_8mim]^+$

Fig. 1 Formula of 1-alkyl-3-methylimidazolium cations.

The urgency surrounding the chemistry of ILs is attributed to their unique set of chemical and physical properties. The low melting nature of ILs can be engineered by combining cationic and anionic species to produce salts that, largely due to the asymmetric cations, have low lattice energies. The overall properties of ILs result from the composite properties of the cations and anions and include those that are superacidic,[20,31,32] basic,[33] hydrophilic, water miscible,[34,35] water immiscible and hydrophobic.[20,32,34] The anion is currently used to control the water miscibility, but the cation can also influence the hydrophobicity[16,19,34,36] or hydrogen bonding ability.

Although the field of electrochemical applications of certain ILs is more mature, new RTILs have performed well in catalysis and synthetic experiments, oftentimes yielding unanticipated results, such as facilitated product recovery, enhanced separation,[20] or a preference for a particular isomer of the product.[37,38] The low temperatures typical of reactions in these systems tend to limit dissociation, disproportionation, and degradation reactions such that stability of otherwise transient species is often extended in the ionic environment. With an IL such as [C₄mim][BF₄], Beckmann rearrangement reactions can be performed under milder conditions to avoid the deactivation usually encountered in those reactions.[39]

We have demonstrated the utility of certain RTILs in a variety of separations with several RTILs which have solvent characteristics suitable for their incorporation in place of traditional volatile organic compounds (VOCs) in liquid/liquid separations.[16,18] For example, with a series of organic solutes, we have shown that the solute affinity for the RTIL ([C₄mim][PF₆]) phase increases in correlation with the solute's 1-octanol/water log *P* value (a traditional hydrophobicity probe).[16] Liquid/liquid extraction and reactive separations (where the reagents and products differ in IL solubility) offer excellent opportunities to reduce the reliance on VOCs in many industries.

In this paper we investigate and compare the properties of RTILs containing various 1-alkyl-3-methylimidazolium cations, due to the increasing number of reports in the literature utilizing RTILs of this type. Here the variations in alkyl chain, in conjunction with different anions, lead to a large matrix of materials. Characterization in terms of physical and chemical properties is thus an important first step toward their ultimate application.

Chemical and physical properties of new solvents

Before considering a new solvent for incorporation into an industrial application, a fundamental understanding must be established for the chemical and physical properties of the solvent. Ideally, if a new solvent is to be introduced as a 'green' solvent, it would be an improvement over the solvents currently available. Optimal physical properties would include low viscosity to facilitate mixing and a large density difference in comparison to other process fluids to hasten phase separation. Chemically, the solvent would have a high capacity for the solute. To encourage widespread use of the solvent, it would be inexpensive to produce, recyclable, and robust to endure various processing environments.

Of most interest to us at present are ionic liquids that are liquid at room temperature and represent potential replacements for traditional volatile organic solvents in separations processes. Recent developments have seen the investigation of classes of ionic liquids that are not only liquid at room temperature, but also air and water stable[34] which further increases the range of ionic liquids suitable for industrial application. Several physical and chemical properties of organic liquids merit their investigation when attempting selection for a particular application such as their use in dissolution or reaction media for various solutes.

Physical properties such as melting point, boiling point, density, and viscosity, are related to the mechanics and engineering components associated with a process. For example, densities, viscosities, and surface tensions will determine important parameters including rates of liquid–liquid phase separation, mass transfer, power requirements of mixing and pumping. Other physical properties, such as refractive index, are related to certain chemical properties despite providing a bulk property description. Chemical properties such as the structuredness, polarity, and relative hydrogen bonding donating and accepting ability are more obviously related to the molecular chemistry of their application.[40] Due to the obvious intermolecular interactions that these parameters measure, these chemical properties are belived to play a major role in determining solubilities, partition constants, and reaction rates.

Results

A series of hydrophilic and hydrophobic 1-alkyl-3-methylimidazolium salts of bis(trifluoromethylsulfonyl)imide (Tf₂N)⁻, PF₆⁻, BF₄⁻, Cl⁻ and I⁻ (Table 1) were prepared and their physical properties determined. The tabular results have been organized first by the most hydrophilic cation, decreasing in the series butyl, hexyl, octyl, and then arranged by the perceived increasing hydrophobicity of the anion from Cl⁻, I⁻, BF₄⁻, PF₆⁻ to Tf₂N⁻. Hydrophobic RTILs were studied both after equilibration with water corresponding to the maximum water concentration at ambient temperature, and after a moderate drying procedure which removed most of the water. The hydrophilic RTILs studied here are completely water soluble and were studied only after the drying procedure and referred to as 'dried', although many still contain some water.

Table 1 Ionic liquid cations and anions used in this study

Cations		Anions	
H_3C—N⊕N—C_4H_9	$[C_4mim]^+$	Hexafluorophosphate	PF_6^-
		Tetrafluoroborate	BF_4^-
H_3C—N⊕N—C_6H_{13}	$[C_6mim]^+$	Halides	Cl^-, I^-
		Bis(triflylmethyl-sulfonyl)imide	Tf_2N^-
H_3C—N⊕N—C_8H_{17}	$[C_8mim]^+$	$N(SO_2CF_3)_2^-$	

Water content

It is readily apparent from Table 2, that in the small series of RTILs studied here, the identity of the anion greatly influences the water miscibility and, if hydrophobic, the extent of which water is miscible in that IL. This also appears to be a factor in controlling the extent to which the RTILs may be dried, or the difficulty involved in drying to very low moisture contents.

Certain precautions are sometimes necessary, however, to account for the chemistry associated with the cations and anions. RTILs containing the PF_6^- anion are sparingly water soluble, but when used in liquid/liquid separations from acidic aqueous phases, the PF_6^- may undergo hydrolysis to produce HF and PO_4^{3-}.[19] Other anions may be better suited for such applications.

The current generation of air and water stable IL which remain in the liquid state at close to room temperature, are free from many of the difficulties involved in the application of, for example, the haloaluminate salts. Nevertheless, as may be judged from Table 2, they may contain significant amounts of water or be entirely miscible with water. While in this series this property is largely conveyed by the hydrophobicity of the anion, the water miscibility of the BF_4^- RTIL depends on the length of the alkyl chain or the temperature of the system. Holbrey and Seddon reported that, for $[C_nmim][BF_4]$, those with $n < 6$ are water soluble, although to varying degrees.[23] $[C_4mim][BF_4]$ at room temperature is completely water soluble but, at 0 °C, the solubility decreases.[36]

The presence of water may have a rather dramatic affect on reactivity, not only in the new biotechnology applications which have started to appear,[41–43] but also in many synthetic schemes using IL reaction media. Water is present in all RTILs of the type we studied, even after a moderate drying procedure. Organic solvents are known to contain varying degrees of water, unless rigorous drying protocols and inert environments are employed. There is little evidence in the current IL literature that such precautions are being taken for IL studies. Most authors do not yet report water content, drying procedures (if any), or impurity levels.

Table 2 Water content of several water equilibrated (25 °C) and dried ILs[a]

Ionic liquid	Water equilibrated/ppm	Dried/ppm
$[C_4mim][Cl]$	Miscible	2200
$[C_4mim][I]$	Miscible	1870
$[C_4mim][BF_4]$	Miscible	4530
$[C_4mim][PF_6]$	11700	590
$[C_4mim][Tf_2N]$	3280	474
$[C_6mim][Cl]$	Miscible	1130
$[C_6mim][PF_6]$	8837	472
$[C_8mim][Cl]$	Miscible	890
$[C_8mim][PF_6]$	6666	388

[a] Water equilibrated refers to RTILs that have been stored in contact with water. Dried RTILs are water equilibrated RTILs that have been dried at 70 °C for 4 h on a vacuum line.

Melting point and glass transition

The solid–liquid phase transition of some of the current RTILs has been examined by DSC and the results are summarized in Tables 3 and 4. This behavior is relatively complex, as shown in Fig. 2. The DSC trace (exothermic up) shown in Fig. 2 is the heating curve for $[C_8mim][PF_6]$ where the glass transition is observed around −75 °C and the large peak at 0 °C can be attributed to the melting point of water. The broad exothermic transition between −25 and 0 °C may be due to the crystallization of water molecules or a simple reorganization of the water molecules prior to melting. Typically, the material in the solid crystalline state will exhibit a glass transition temperature on heating from low temperatures and may or may not be followed by a melting transiton (fusion) on further heating.

In our analyses, we observed melting points for only a few ILs. For the other samples, it is postulated that after passing through the glass transition temperature, the cations and anions must reorganize before a melting point will be observed. In the PF_6^- series, we did not observe melting points for $[C_6mim]^+$ or $[C_8mim]^+$, although the $[C_{10}mim]^+$ derivative melts slightly above room temperature.[17] Our analyses show a trend that has also been observed by Holbrey and Seddon.[23] These results and the crystal structure of $[C_{10} \text{ and } C_{12}mim][PF_6]$[17,44] suggest that

Table 3 Melting point data for several ILs

Ionic liquid	Melting point/°C (water equilibrated)	Melting point/°C (dried)	Lit. ref.
$[C_4mim][Cl]$		41	
$[C_4mim][I]$		−72	
$[C_4mim][PF_6]$	4	10	
$[C_4mim][Tf_2N]$	−25		
$[C_1mim][AlCl_4]$		125	45
$[C_2mim][AlCl_4]$		84	45
$[C_3mim][AlCl_4]$		60	45
$[C_4mim][AlCl_4]$		65	45
$[C_4C_4im][AlCl_4]$		55	45
$[C_2mim][NO_3]$		38	47
$[C_2mim][NO_2]$		55	47
$[C_2mim][CH_3CO_2]$		45	47
$[C_2mim][PF_6]$		58–60	47
$[C_2mim][TfO]$		9	34
$[C_2mim][NfO]$		28	34
$[C_2mim][Tf_2N]$		4	34
$[C_2mim][TA]$		14	34
$[C_3mim][PF_6]$		40	22
$[i\text{-}C_3mim][PF_6]$		102	22
$[C_4mim][BF_4]$		−81	36
$[C_6mim][PF_6]$		−61	36

Table 4 Glass transition temperatures of several ILs

Ionic liquid	T_g/°C (water equilibrated)	T_g/°C (dried)	Lit. ref.
$[C_4mim][BF_4]$		−97	
$[C_4mim][PF_6]$	−83	−80	
$[C_4mim][Tf_2N]$	−102	−104	
$[C_6mim][Cl]$		−75	
$[C_6mim][PF_6]$	−75	−78	
$[C_8mim][Cl]$		−87	
$[C_8mim][PF_6]$	−75	−82	
$[C_4mim][BF_4]$		−81	36
$[C_4mim][PF_6]$		−61	36
$[C_2mim][Tf_2N]$		−98	22
$[C_2mim][N(CF_2CF_3)_2]$		−85	22

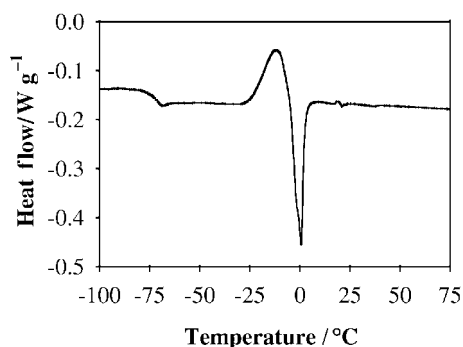**Fig. 2** Differential scanning calorimetry trace for water-equilibrated [C$_8$mim][PF$_6$] (exothermic up).

as the alkyl chain length increases, inter-chain hydrophobic packing affects and the formation of bilayer-type structures result in an increase in melting points for salts of [C$_n$mim]$^+$ with $n > 8$.

Ngo *et al.* have examined the properties of a series of imidazolium ILs and indicate that the melting points decrease with the larger more asymmetrical substituted cations.[22] ILs containing the nonaflate (NfO) anion (CF$_3$CF$_2$CF$_2$CF$_2$SO$_3$$^-$) were reported to melt closer to room temperature. The structure of both the cations and the anions has an obvious effect, for example, in the series of cations with AlCl$_4$$^-$ where smaller and more symmetrical cations result in higher melting points than ILs composed of unsymmetrical or larger cations.[45] Increased branching of the alkyl group results in melting points higher than the linear analogs. Appending an isopropyl group instead of an *n*-propyl group increases the melting point by 82 °C (Table 3).[22] Hagiwara and Ito[46] and Bonhôte *et al.*[34] have indicated that there is not an overall correlation between the composition of the IL and its melting point.

Explaining the anion effect is more difficult, owing to the presence of water and its interactions with the cation and anion. For ILs containing structurally similar anions such as triflate (TfO$^-$) and Tf$_2$N$^-$, the lower melting point of the Tf$_2$N$^-$ salt (Table 3) could be attributed to electron delocalization and the anion's inability to hydrogen bond.[34] This idea is substantiated by comparing the melting points for two similar cations, one containing a fluorinated methyl group, in combination with the TfO$^-$ anion. The fluorines act to distort the electron density on the imidazolium ring and promote hydrogen bonding and a corresponding 50 °C difference in the melting points between the two ILs.[34] In a similar manner, differences between [C$_2$mim][CF$_3$CO$_2$] and [C$_2$mim][CH$_3$CO$_2$], besides the tri-fluoroacetate (TA) moiety having a melting point 31 °C lower than CH$_3$CO$_2$$^-$, can undoubtedly be attributed to the presence of fluorine atoms on that anion and their interaction with other anions and the cation.[34,47] The melting point for [C$_2$mim][NO$_2$] is 17 °C higher than that for [C$_2$mim][NO$_3$], suggesting that anion structure also contributes to the thermal properties.[47] The combination of imidazolium cations and carborane anions has also been recently explored by Larson *et al.*[48] to determine the factors that influence the melting points.

Supercooling, or glass formation, is a common characteristic associated with many, but not all, of the imidazolium ILs.[22,34,44,46,49] Literature reports indicate that dialkylimidazolium cations combined with Tf$_2$N$^-$, TA$^-$, and heptafluoro-butanoates (HB) are generally liquid up to −30 to −50 °C, but become increasingly viscous and turn finally into glasses without the observation of a melting point.[34] The ILs examined here exhibited glass transition temperatures between −104 and −75 °C, a slightly wider range than what is reported in the literature.[22,49] Tf$_2$N$^-$ and BF$_4$$^-$ anions produce the lowest glass transition temperatures and those for Cl$^-$ and PF$_6$$^-$ are similar.

Thermal stability

The RTILs under study here have no distinguishable vapor pressure and, as a result, the first thermal event on heating of the ILs is thermal decomposition. In general, most ILs have a high thermal stability, often beginning to decompose around 400 °C with minimal vapor pressure below their decomposition temperature, as determined by thermal gravimetric analyses. Recent reports have described the TGA of imidazolium salts and noted that the thermal decomposition is heavily dependent on the salt structure and, for certain samples, the type of sample pan (*i.e.*, aluminium or alumina) used in the analysis.[22] Literature reports indicate that experiments performed under N$_2$ or air produce the same results.[34]

Thermal stability data are shown in Table 5. The onset of thermal decomposition temperatures are similar for the different cations but appear to decrease as the anion hydrophilicity increases. In general it also appears that drying improves the thermal stability of this class of ILs, although the results for [C$_4$mim][PF$_6$] appear to be anomalous and, as yet, unexplained. The role of water in either situation, and the effect on ILs, has yet to be determined.

Table 5 Thermal decomposition temperatures of several ILs

Ionic liquid	Temp. onset for decomposition/°C (water equilibrated)	Temp. onset for decomposition/°C (dried)	Lit. ref.
[C$_4$mim][Cl]		254	
[C$_4$mim][I]		265	
[C$_4$mim][BF$_4$]		403	
[C$_4$mim][PF$_6$]	360	349	
[C$_4$mim][Tf$_2$N]	394	439	
[C$_6$mim][Cl]		253	
[C$_6$mim][PF$_6$]	390	417	
[C$_8$mim][Cl]		243	
[C$_8$mim][PF$_6$]	374	376	
[C$_2$mim][Cl]		285	22
[C$_2$mim][I]		303	22
[C$_2$mim][PF$_6$]		375	22
[C$_2$mim][BF$_4$]		412	22
[C$_2$mim][Tf$_2$N]		455	22
[C$_2$mim][Tf$_2$N]		~440	34
[C$_2$mim][CF$_3$COO]		~150	34
[C$_2$mim][CF$_3$SO$_3$]		~440	34
[C$_3$mim][Cl]		282	22
[C$_3$mim][PF$_6$]		335	22
[C$_3$mim][Tf$_2$N]		452	22
[C$_4$mim][BF$_4$]		360	23
[C$_{18}$mim][BF$_4$]		360	23

Bonhôte *et al.* found that [C$_2$mim][CF$_3$SO$_3$] and [C$_2$mim][Tf$_2$N] were stable up to 400 °C and decomposed rapidly between 440 and 480 °C. On the other hand, [C$_2$mim][TA] was only stable to 150 °C and then decomposed rather slowly to 250 °C.[34] Larger fluorinated organic anions (*e.g.*, N(SO$_2$CF$_2$CF$_2$CF$_2$CF$_3$)$_2$$^-$) combined with [C$_2$mim]$^+$ produced similarly stable ILs, beginning to decompose above 400 °C.[49] Substituting the ring hydrogens with methyl groups, especially the C2 hydrogen, added to the stability of the cation[46] and one proposed decomposition mechanism involves proton abstraction to produce both volatile acids from the anion and carbene derivatives of the cation.

Halide anions dramatically reduce the thermal stability with the onset of decomposition occurring at least 100 °C below the corresponding ILs with non-halide anions.[22] Relative anion stabilities have been suggested as PF$_6$$^-$ > Tf$_2$N$^-$ ~ BF$_4$$^-$ > halides,[22] concurrent with the results in Table 5. Increasing the cation size from [C$_4$mim]$^+$ to [C$_8$mim]$^+$ doesn't appear to have a large effect, since even more dramatic changes in cation size ([C$_4$mim]$^+$ to [C$_{18}$mim]$^+$) produced the same results.[23]

Viscosity

Viscosity data for a number of these RTILs are presented in Table 6. Hagiwara and Ito have determined that the viscosities of imidazolium ILs with fluorinated anions are much greater than that of water and, as can be expected, the longer alkyl substituents produce more viscous RTILs.[46] In our results, the viscosities in this type of RTILs are two or more orders of magnitude greater than that found for most traditional organic liquids (solvents) and are more comparable to a typical oil.[50] At a particular temperature, they seem to be actually more viscous than soybean oil but somewhat less viscous than glycerin.[50] These viscosities are also higher than those found for alkylammonium nitrate and thiocyanate salts by Poole et al.[24] and tetrachloroaluminates.[47]

Changing the experimental conditions allows further exploration of the nature of IL behavior. An increase in temperature shows that the viscosity increases in a non-Arrhenius fashion for the $[C_n mim][PF_6]$ ILs, as shown in Fig. 3. Other studies have investigated how the shear rate affects the viscosity.[51] Thus, ILs can be classified in terms of being a Newtonian fluid whose viscosity remains constant with increasing shear rates, or a thixotropic fluid whose viscosity decreases as the shear rate increases. For $[C_n mim][BF_4]$ (n = 4, 6, 8), the shear rate produced no difference in the viscosity.[51] Longer alkyl chains, (e.g., $[C_{12}mim][BF_4]$) show non-Newtonian behavior, although temperature has a significant effect on the results.[51]

IL impurities have a significant affect on viscosity as well as other properties. Another report has measured the effect of water, sodium chloride, and organic solvents on IL physical properties.[52] For example, $[C_4mim][BF_4]$ with 0.01 molal Cl$^-$ has a viscosity of 154 (mPa s^{-1}) and an increase to 0.5 molal Cl$^-$ increases the viscosity to 201 (mPa s^{-1}).[52] This aspect raises the important point that, in consideration of ILs for use in processes where it would be in contact with another phase,
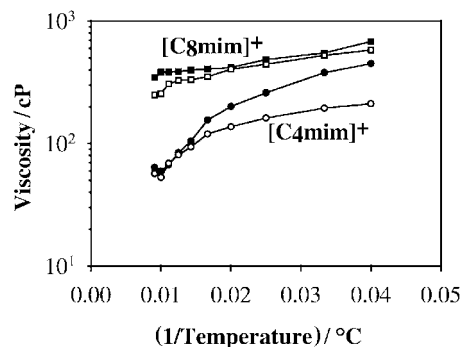

Fig. 3 Viscosity of a series of ILs as a function of increasing temperature: dried samples (filled symbols), water equilabrated samples (open symbols).

cross-contamination of the ILs may drastically affect the physical properties.

Such viscosities, as observed here and in the literature, will critically affect rates of mass transfer and power requirements for mixing in liquid reaction systems. The viscosities, especially for PF$_6^-$ ILs, are substantially higher than the majority of those found by Bonhôte et al., for a similar series of ILs,[34] but substantially lower than those reported for a series of tetraalkylammonium sulfonates.[53] That they are not in error is suggested by the close correspondence of our data for $[C_4mim][Tf_2N]$ (69 cP) and that given by Bonhôte et al. of 55 cP.[34] The data for $[C_4mim][PF_6]$ and $[C_2mim][CF_3CF_2CF_2CF_2SO_3]$ liquid organic salts indicate viscosities more comparable to those found here.

An increase in the viscosity of the various anion/cation combinations was attributed to an increase in van der Waals forces over hydrogen bonding.[34] Such an explanation might also be applicable to our own results, however, hydrogen bonding between cationic protons and anionic halides has been noted in the crystalline state from X-ray diffraction studies[17] and may represent an additional factor. In addition, the increased symmetry of the inorganic anions (e.g., PF$_6^-$ or BF$_4^-$) compared to the organic anion (Tf$_2$N$^-$) may play an important role. The results of Table 6 seems to indicate that the geometry and molar mass of the anions have a strong influence on the viscosity of this class of IL since $[C_4mim]^+$ combined with either PF$_6^-$ or Tf$_2$N$^-$ produces ILs with significantly different viscosities. These results suggest a complex relationship where the importance of cation–anion interactions as well as the presence of water cannot be overlooked.[52]

Surface tension

Surface tension data for several RTILs have been obtained and these are shown in Table 7. In general these liquid/air surface tension values are somewhat higher than for conventional solvents (e.g., hexane: 18 dyn cm^{-1}, toluene: 32 dyn cm^{-1}), but not so high as water (73 dyn cm^{-1})[50] which will tend to mitigate against liquid–liquid phase mass transfer but at the same time promote more rapid phase disengagement.

Table 6 Viscosity data (25 °C, unless indicated otherwise) for several ILs

Ionic liquid	Viscosity/cP (water equilibrated)	Viscosity/cP (dried)	Lit. ref.
$[C_4mim][I]$		1110	
$[C_4mim][BF_4]$		219	
$[C_4mim][PF_6]$	397	450	
$[C_4mim][Tf_2N]$	27	69	
$[C_6mim][Cl]$		716	
$[C_6mim][PF_6]$	452	585	
$[C_8mim][Cl]$		337	
$[C_8mim][PF_6]$	506	682	
$[C_4mim][Tf_2N]$		52	34
$[C_4mim][CF_3CO_2]$		73	34
$[C_4mim][CF_3SO_3]$		90	34
$[C_4mim][CF_3CF_2CF_2SO_3]$		373	34
$[C_2mim][BF_4]$		43	49
$[C_2mim][Tf_2N]$		28	49
$[C_4mim][BF_4]$		233	36
$[C_4mim][BF_4]$ (20 °C)		154	52
$[C_2mim][BF_4]$ (20 °C)		66.5	51
$[C_2mim][BF_4]$ (30 °C)		43	51
$[C_4mim][BF_4]$ (20 °C)		154	51
$[C_4mim][BF_4]$ (30 °C)		91.4	51
$[C_6mim][BF_4]$ (20 °C)		314	51
$[C_6mim][BF_4]$ (30 °C)		177	51
$[C_4mim][PF_6]$ (20 °C)		371	51
$[C_4mim][PF_6]$ (30 °C)		204	51
$[C_6mim][PF_6]$ (20 °C)		680	51
$[C_6mim][PF_6]$ (30 °C)		363	51
$[C_8mim][PF_6]$ (20 °C)		866	51
$[C_8mim][PF_6]$ (30 °C)		452	51
$[C_4mim][PF_6]$		312	36

Table 7 Surface tension data (25 °C) for several ILs

Ionic liquid	Surface tension/dyn cm^{-1} (water equilibrated)	Surface tension/ dyn cm^{-1} (dried)
$[C_4mim][I]$		54.7
$[C_4mim][BF_4]$		46.6
$[C_4mim][PF_6]$	49.8	48.8
$[C_4mim][Tf_2N]$	36.8	37.5
$[C_6mim][Cl]$		42.5
$[C_6mim][PF_6]$	36.8	43.4
$[C_8mim][Cl]$		33.8
$[C_8mim][PF_6]$	34.2	36.5

Density

It may be readily observed from the density data presented in Table 8, that the molar mass of the anion significantly determines the overall density found for each RTIL. Using halogenated carborane anions, the density can be as high as 2.151 g cm^{-3}.[48] Adding CH_2 groups to the alkyl chain on the $[C_n mim]^+$ cation decreases the density since CH_2 is less dense than an imidazolium ring. Dependence of the density on the carbon number of the anion (in this case) was also found for a series of alkylammonium sulfonate liquid organic salts.[54]

In our studies, the simple halide salts have significantly lower densities than the PF_6^- RTIL, and these lower densities are comparable to other solvents (*e.g.*, $[C_8 mim][Cl]$ is similar to water, $[C_6 mim][Cl]$ is similar to dioxane[50]). The contribution of the larger hydrophobic anions is significant for the water immiscible ILs and the densities found are comparable to carbon disulfide or glycerin.[50] Such densities would be advantageous to the phase separation of immiscible liquids mixtures but disadvantageous to the power requirements of mixing. However, for both hydrophobic and hydrophilic ILs, an increase in the water content causes the density to decrease and approach that of water, as shown in Table 8.

Table 8 Densities (25 °C) of several ILs

Ionic liquid	Density/g mL^{-1} (water equilibrated)	Density/g mL^{-1} (dried)	Lit. ref.
$[C_4 mim][Cl]$		1.08	
$[C_4 mim][I]$		1.44	
$[C_4 mim][BF_4]$		1.12	
$[C_4 mim][PF_6]$	1.35	1.36	
$[C_4 mim][Tf_2N]$	1.39	1.43	
$[C_6 mim][Cl]$		1.03	
$[C_6 mim][PF_6]$	1.24	1.29	
$[C_8 mim][Cl]$		1.00	
$[C_8 mim][PF_6]$	1.16	1.22	
$[C_4 mim][Tf_2N]$		1.429	34
$[C_4 mim][CF_3CO_2]$		1.209	34
$[C_4 mim][CF_3SO_3]$		1.290	34
$[C_4 mim][BF_4]$		1.17	36
$[C_4 mim][PF_6]$		1.37	36

Refractive index

The refractive index data are shown in Table 9. The refractive index is related to the polarizability/dipolarity of the medium and the excess molar refraction is used in the least squares energy relationships (LSERs) of Abraham *et al.* as a predictor of solute distribution.[55–57] These results are quite comparable with values for typical organic solvents and are similar to the values reported for the alkylammonium IL salts reported by Shetty *et al.*[25]

Table 9 Refractive index (25 °C) for several ILs

Ionic liquid	Refractive index (dried)	Lit. ref.
$[C_4 mim][I]$	1.572	
$[C_4 mim][PF_6]$	1.409	
$[C_6 mim][Cl]$	1.515	
$[C_8 mim][Cl]$	1.505	
$[C_8 mim][PF_6]$	1.423	
$[C_4 mim][Tf_2N]$	1.4271	34

Organic solute partitioning

We have previously demonstrated[16] that organic solute partitioning from water to $[C_4 mim][PF_6]$ in general follows the log
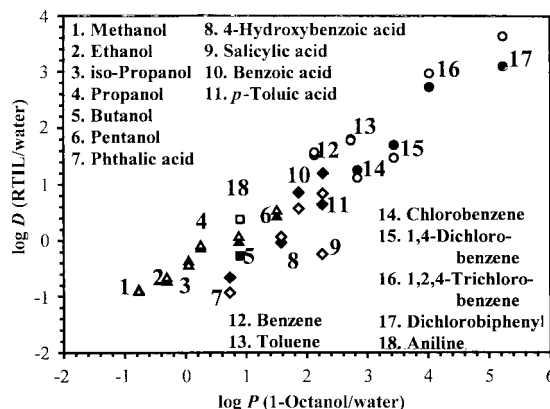

Fig. 4 Comparison of distribution ratios of selected organic molecules between $[C_4 mim][PF_6]$/water (filled symbols) or $[C_6 mim][PF_6]$/water (open symbols) with log *P* (1-octanol/water) data.

P (1-octanol/water) values for the solutes. Fig. 4 illustrates the trend in partitioning is very similar for $[C_6 mim][PF_6]$ and the actual distribution ratios vary only slightly, indicating that contacting $[C_4 mim][PF_6]$ or $[C_6 mim][PF_6]$ with water produces only small differences in the water content for the IL phase.

There are few reports concerning the miscibility with other solvents. Certain RTILs are reported to be miscible to 0.66 mole fraction with benzene although solutes with larger dipole moments are more soluble.[12] The contact of supercritical CO_2 (sc-CO_2) with $[C_4 mim][PF_6]$ represents a unique situation, as observed by Blanchard *et al.*,[10] because sc-CO_2 is readily soluble in the RTIL, although very little of that RTIL is miscible with the supercritical fluid. Other studies of sc-CO_2 in ILs have used attenuated total reflectance infrared spectroscopy to determine the anion effect in the Lewis acid–base interactions with CO_2.[11]

Studying the solute partitioning in IL systems unearths some inevitable comparisons to the partitioning behavior of the same solute in more traditional liquid/liquid separations systems. Indeed, ILs can be considered a novel class of solvents, but, in light of the profusion of traditional organic solvents available with their associated variations in solvent properties, to what class of solvents can ILs be likened in terms of their solvating power, *etc.*? Bonhôte *et al.* used pyrene and pyrenecarboxaldehyde to study the fluorescence of those probe molecules in ILs and, also, the phosphorescence of bromonaphthalene to investigate the microenvironments of ILs.[34] Other work has used Nile Red[58] to report on the solvatochromic response for a variety of ILs and, separately, fluorescence probes to study imidazolium and pyridinium ILs.[59] In a subsequent paper, we report the use of several different probe molecules to study the solvatochromic response of both hydrophobic and hydrophilic ILs leading to their classification in terms of more familiar solvents. This work also delves into the use of organic solute partitioning and LSERs, to model the partitioning of solutes in IL systems.[60]

Conclusions

For the set of $[C_n mim]^+$ RTILs examined here, the resulting physical properties show that anion identity is of foremost importance. Our observations show how sensitive the resulting properties are towards the water miscibility and content, sometimes shifting the results an order of magnitude. Water content and hydrophobicity are also connected to changes in cation substitution and can be a significant factor when considering the applications of a particular IL. As a result, simple variations in cation and anion structure and overall ionic composition illustrate the ease in which physical properties of a

class of ILs can be modified to produce a wide range of solvent media. A recent publication[61] has detailed a series of 58 ILs (38 represent new ILs) based on the imidazolium cation and, in the overall picture, illustrates the vast number of ILs available and the daunting task of their characterization. The report also includes the first published toxicity data (LD_{50}) for 3-hexyloxy-methyl-1-methylimidazolium BF_4.[61]

In light of how ILs are being proposed for use where traditional organic solvents have been the norm, it is interesting how the results reported here indicate several properties of ILs are quite different from traditional organic solvents. Most notable for the RTILs is the lack of significant vapor pressure despite their ability to solubilize materials. The ionic nature present in these neoteric solvents presents both a promising opportunity and a challenge; to explore the properties and applications of ILs, and to better understand how the ionic environment sustains the ILs while producing such novel properties.

Experimental

All aqueous solutions were prepared with deionized water that was purified with a Barnsted deionization system (Dubuque, IA) and polished to 18.3 MΩ cm. All salt and acid solutions were prepared as molar concentrations by transferring a known amount of material to a volumetric flask and diluting to the specified volume with deionized water. When needed, pH adjustments of the aqueous phase were made using H_2SO_4 or NaOH.

HPF_6 was supplied by Ozark Mahoning (Tulsa, OK) and was used as received. $LiN(CF_3SO_2)_2$ was supplied by 3M (Minneapolis, MN) and used as received. All other chemicals were of reagent grade, obtained from Aldrich (Milwaukee, WI) and used without further purification. Organic molecule partitioning was done with ^{14}C labeled solutes obtained from Sigma (St. Louis, MO).

Synthesis of ionic liquids

[C$_4$mim][Cl]. Equal molar amounts of chlorobutane and 1-methylimidazole were added to a round-bottomed flask fitted with a reflux condenser for 24–72 h at 70 °C with stirring until two phases formed. The top phase, containing unreacted starting material, was decanted and ethyl acetate (a volume approximately equal to half that of the bottom phase) was added with thorough mixing. The ethyl acetate was decanted followed by the addition of fresh ethyl acetate and this step was repeated twice. Washing with ethyl acetate should suffice to remove any unreacted material from the bottom phase. After the third decanting of ethyl acetate, any remaining ethyl acetate was removed by heating the bottom phase to 70 °C and stirring while on a vacuum line. The product, [C$_4$mim][Cl], is slightly yellow and may be crystalline at room temperature, depending on the amount of water present in that phase.

The H NMR spectrum for [C$_4$mim][Cl] (D_2O, ppm) consist of the following peaks: δ 0.95 (t), 1.38 (sextet), 1.80, (q), 3.70 (s), 4.00 (s), 4.30 (t), 7.00 (s), 7.15 (s), 7.55 (s). ^{13}C NMR results (ppm) include: δ 15.72, 34.21, 36.04, 38.69, 52.14, 124.16, 126.39 and 141.16.

[C$_4$mim][PF$_6$]. [C$_4$mim][Cl] was transferred to a 2 L plastic container (lined with a perfluorinated material) followed by the addition of 500 mL deionized water. An aqueous solution of 60% HPF_6 in a 1.1:1 molar ratio was added. **CAUTION**: the addition of HPF_6 should be done slowly to minimize the amount of heat generated. As HPF_6 was added, two phases formed, where [C$_4$mim][PF$_6$] was the bottom phase and HCl was the

upper phase. The upper phase was decanted and 500 mL of water was added followed by vigorous shaking and mixing. After the mixture settles, the upper aqueous phase was decanted and more deionized water was again added. This procedure was repeated until the pH of the upper phase was *ca.* 7.

The [C$_4$mim][PF$_6$] was stored in contact with water and is referred to as water-equilibrated or 'wet'. An aliquot of the wet [C$_4$mim][PF$_6$] was dried at 70 °C on a vacuum line for 4 h to produce the 'dried' version of the IL. (The IL was not extensively dried because, realistically, the results would not be practical towards our intended applications). In addition, despite being dried for several hours, when the IL is removed from the vacuum line it will readily reabsorb water from air since our analyses and characterization experiments were not carried out in a glove box.

Analysis of [C$_4$mim][PF$_6$] included H (360.13 MHz) and ^{19}F (470.56 MHz) NMR. Each H NMR spectrum contained peaks corresponding to the [C$_n$mim]$^+$ cation and indicated no residual reactants. The chemical shifts (ppm, neat sample) for the H NMR of [C$_4$mim][PF$_6$] appear as follows: δ 0.72 (t), 1.15 (sextet), 1.68 (qnt), 2.25 (s, br), 3.73 (s), 4.05 (t), 7.22 (s), 7.30 (s) and 8.26 (s). The ^{19}F NMR spectra consist of two peaks, one at δ −74 and the other at δ −72.5, corresponding to the splitting of ^{19}F ($I = \frac{1}{2}$) by ^{31}P ($I = \frac{1}{2}$). ^{13}C NMR (neat sample, ppm) shows peaks at δ 17.72, 24.03, 36.52, 40.58, 54.41, 127.16, 128.49 and 141.27. The H NMR analyses were performed on a Bruker AM 360 instrument (Houston, TX) while ^{19}F NMR analyses used a Bruker AM 500 instrument (Houston, TX).

[C$_4$mim][BF$_4$]. [C$_4$mim][Cl] was transferred to a 2 L plastic container (lined with a perfluorinated material) followed by the addition of aqueous HBF_4 (40%) at a 1.1:1 molar ratio. [C$_4$mim][BF$_4$] was separated from the HCl by extraction into a volume of methylene chloride approximately equal to the initial amount of [C$_4$mim][Cl]. The addition of methylene chloride was followed by thorough mixing and transfer of the solution to a separatory funnel where the organic phase was the upper phase. The [C$_4$mim][BF$_4$–methylene chloride mixture was put in a round-bottomed flask to rotovap at 95 °C under a vacuum to remove any residual methylene chloride.

The H NMR spectrum (ppm, acetone-d_6, dried) for [C$_4$mim][BF$_4$] showed peak locations remained essentially the same as those for [C$_4$mim][Cl], although the ^{19}F NMR spectra has a singlet at δ −152.,86. The ^{13}C NMR spectrum (*d*-acetone, ppm, dried) contains peaks at δ 13.12, 19.30, 31.94, 35.90, 54.45, 122.56, 123.84 and 136.67.

[C$_4$mim][I]. This synthesis followed the same procedure as for [C$_4$mim][Cl] described above, although iodobutane was used instead of chlorobutane. [C$_4$mim][I] was slightly darker and the yield was approximately 70%. All other steps remain the same. The H NMR spectrum (ppm, dried, neat sample) for [C$_4$mim][I] resulted in peak locations similar to those for [C$_4$mim][Cl].

[C$_4$mim][Tf$_2$N]. Approximately 100 g of [C$_4$mim][Cl] was transferred to a 250 mL plastic bottle and a 1.1:1 molar ratio of Li(Tf$_2$N) was added, followed by 50 mL of deionized water. After mixing, two phases formed where the bottom phase was [C$_4$mim][Tf$_2$N] and the top phase was aqueous LiCl. Both phases were colorless. After decanting the top phase, 50 mL of fresh deionized water was added and the solution was thoroughly mixed. This was repeated twice.

Analysis of [C$_4$mim][Tf$_2$N] by H NMR (neat sample, ppm) produced a spectrum similar to that for [C$_4$mim][Cl]. The ^{13}C NMR spectrum is also similar to [C$_4$mim][Cl] with the addition of peaks at δ 115.56 and 122.66.

[C$_6$mim][Cl]. The same procedure was used as indicated for [C$_4$mim][Cl] with the exception of the use of chlorohexane

instead of chlorobutane. The product is a tan liquid that is markedly more colored than [C₄mim][Cl] or [C₈mim][Cl]. The yield is approximately 80%. Analysis of [C₆mim][Cl] by H NMR (neat sample, dried, ppm) resulting in a spectrum similar to that for [C₄mim][Cl] with the addition of a multiplet of peaks at δ 2.05.

[C₆mim][PF₆]. The same procedure was used as for [C₄mim][PF₆]. Here, the tan color associated with [C₆mim][Cl] was carried through in this step and is not removed by repeated washing. Analysis of [C₆mim][PF₆] by H NMR (neat sample, dried, ppm) gave a spectrum identical to that for [C₆mim][Cl] with the addition of a small, broad peak at δ 2.30. The impurity contributing to the tan color was not observed by NMR. The F NMR spectrum was very similar to that for [C₄mim][PF₆] with no additional peaks.

[C₈mim][Cl]. The same procedure was used as for [C₄mim][Cl] with the substitution of chlorooctane for chlorobutane. The product is a colorless liquid with a yield of *ca.* 80%. Analysis of [C₈mim][Cl] by H NMR (neat sample, dried, ppm) resulted in a spectrum containing the following peaks: δ 0.67 (t), 1.08 (m), 1.70 (m), 3.75 (s), 4.10 (t), 4.68 (s), 5.27 (s), 7.35 (d) and 8.40 (d). The ¹³C NMR (neat, dried, ppm) spectrum shows the following peak locations: δ 13.28, 21.96, 25.28, 29.51, 30.68, 35.37, 49.35, 53.86, 119.55, 122.06, 123.41 and 136.04.

[C₈mim][PF₆]. The same procedure was used as for [C₄mim][PF₆]. The product is a colorless liquid. Analysis of [C₈mim][PF₆] by H NMR (neat sample, dried, ppm) gave spectra containing no extraneous peaks that were not assigned to the [C₈mim][Cl] sample. The F NMR (neat sample, dried, ppm) showed the same peaks observed for both [C₄mim][PF₆] and [C₆mim][PF₆].

Water content

The water content of each RTIL was determined using a volumetric Aquastar Karl Fischer titrator (EM Science, Gibbstown, NJ) with Composite 5 solution as the titrant and anhydrous methanol as the solvent. Each sample was at least 1 g and duplicate measurements were performed on each sample with results agreeing to within 5%.

Melting point and glass transition temperature

Melting point and glass transition temperatures were determined by differential scanning calorimetry using a TA Instruments (New Castle, DE) model 2920 differential scanning calorimeter. Each sample was approximately 10 mg and analyzed in a hermetically sealed aluminium pan. For each experiment, an empty hermetically sealed pan was referenced as the blank. A ramp temperature of 10 °C min⁻¹ was employed over the temperature range of −150 to 100 °C. Temperature calibration was performed on a sample of indium.

Decomposition temperatures

The range of thermal decomposition temperatures for each IL was determined by thermogravimetric analysis using a TA Instruments (New Castle, DE) model 2950 thermogravimetric analyzer. Each sample was analyzed in a platinum pan with nitrogen as the purge gas. In each experiment, the temperature was linearly increased at 10 °C min⁻¹ over a temperature window of 30 to 600 °C.

Viscosity

The viscosity of each RTIL was measured with a Cole-Parmer (Vernon Hills, IL) 98936 series viscometer. For each analysis, an 8 mL sample was used and the measurements were performed in duplicate. The temperature of the sample was maintained to ±0.1 °C *via* an external temperature controller. A correction factor for each of the experimentally determined values was determined by measuring the viscosity of a Cannon (State College, PA) certified viscosity standard (S200). Each sample was analyzed in duplicate and the results agree to within 10 cP.

Surface tension

The surface tension of each RTIL was measured with a Fisher brand manual model 20 tensiometer with a 6 cm platinum–indium wire. A glass sample dish was used to hold the 40 mL sample volume used for each analysis. A correction factor for each measurement was determined by measuring the surface tension of DI water, dividing the result by its established value, and multiplying the results for the surface tension of RTILs by that value. All readings were taken at ambient temperature (25 ± 1 °C). Each sample was analyzed in triplicate and the average value is reported.

Density

The density of each RTIL was determined by gravimetric analysis. After calibrating a 1 mL pipet to dispense 1 g mL⁻¹ of water, that pipette was used to transfer 1 mL of each RTIL to determine the mass of that volume of liquid. Each measurement was repeated 10 times and the average value is reported. All measurements were taken at room temperature (25 ± 1 °C).

Refractive index

All measurements were made with a ABBE Bausch and Lomb refractive index instrument. The instrument was calibrated by measuring the refractive index of deionized water. The sample holder was rinsed with 80% ethanol–water solution between each sample, dried with a paper towel and rinsed with the sample to be measured a minimum of two times. All measurements were made at 25 °C.

¹⁴C-labelled solute partitioning

Liquid scintillation analyses were performed for analysis of ¹⁴C-labelled organics using Ultima Gold scintillation cocktail (Packard Instrument, Downers Grove, IL) and a Packard Tri-Carb 1900 TR Liquid Scintillation Analyzer.

The organic solute distribution ratios were determined by mixing 1 mL of RTIL and 1 mL of an aqueous phase followed by vortexing (2 min) and centrifuging (2000 *g*, 2 min) to equilibrate the phases. Addition of the organic tracer (*ca.* 0.005 μCi, 5 μL) was followed by two intervals of vortexing (2 min) and centrifuging (2000 *g*, 2 min) to ensure that the phases were fully separated. Each tube was uncapped and 100 μL of each phase was removed for radiometric analysis. Since equal volumes of both phases were removed for analysis, the distribution ratio for the organic solutes was determined as in eqn. (1):

$$D = \frac{\text{Activity in the RTIL lower phase}}{\text{Activity in the aqueous upper phase}} \quad (1)$$

Each experiment was carried out in duplicate and the results agreed to within 5%.

Acknowledgements

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