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ARTICLE *in* CHEMISTRY · FEBRUARY 2007

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# Comparison of Physicochemical Properties of New Ionic Liquids Based on Imidazolium, Quaternary Ammonium, and Guanidinium Cations

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**Abstract:** More than 50 ionic liquids were prepared by using imidazolium, quaternary ammonium, and guanidinium cations and various anions. In these series, different cationic structures such as 1-benzyl-3-methylimidazolium [Bzmim]<sup>+</sup>, 1,3-dibenzylimidazolium [BzmiBz]<sup>+</sup>, 1-octyl-3-methylimidazolium [C<sub>8</sub>mim]<sup>+</sup>, 1-decyl-3-methylimidazolium [C<sub>10</sub>mim]<sup>+</sup>, tricapryl-methylammonium [Aliquat]<sup>+</sup>, benzyltriethylammonium [BzTEA]<sup>+</sup>, phenyltrimethylammonium [PhTMA]<sup>+</sup>, and dimethyldihexylguanidinium [DMG]<sup>+</sup> were combined with anions, *p*-toluenesulfonate [TSA]<sup>−</sup>, dicyanoamide [DCA]<sup>−</sup>, sac-

charine (2-sulfobenzoic acid imide sodium salt) [SAC]<sup>−</sup>, trifluoroacetate [TFA]<sup>−</sup>, bis(trifluoromethanesulfonyl)-imide [Tf<sub>2</sub>N]<sup>−</sup>, trifluoromethanesulfonate [TfO]<sup>−</sup>, and thiocyanate [SCN]<sup>−</sup>. Important physical data for these ionic liquids are collated, namely solubility in common solvents, viscosity, density, melting point and water content. Apart from the viscosity, the Newtonian and non-Newtonian behavior of these ionic

**Keywords:** green chemistry • ionic liquids • phase transition • rheology • thermal and chemical stability

liquids is also disclosed. Stability of these ionic liquids under thermal, basic, acidic, nucleophilic, and oxidative conditions was also studied. The features of the solid–liquid phase transition were analyzed, namely the glass transition temperature and the heat capacity jump associated with the transition from the non-equilibrium glass to the metastable supercooled liquid. A degradation temperature of each ionic liquid was also determined. Comparisons of the properties of various ionic liquids were made.

## Introduction

Ionic liquid or molten salt preparation, characterization, and properties are rapidly growing areas of the current research interest. The low melting (12°C), ethylammonium nitrate salt was synthesized by Walder<sup>[1]</sup> in 1914. Hurley and Wier<sup>[2]</sup> prepared low-melting salts with chloroaluminate ions for the electroplating of aluminum in 1951. However, ionic liquids only received wide attention after the mid 1980s when low

melting ionic liquids were proposed as solvents for organic synthesis by Fry and Pienta<sup>[3]</sup> and Boon et al.<sup>[4]</sup>

Thereafter, ionic liquids that exhibit air and water compatibility but are liquid at temperatures below 100°C were discovered.<sup>[5–8]</sup> Since then a large number of ionic liquids has been reported with a diverse range of structures and properties. In 2004, Poole, published an excellent review in which he reported nearly 300 ionic liquids that consisted of cations such as, 1,3-dialkylimidazolium (ca. 170), tetraalkylammonium (ca. 30), 1-alkyl or aryl imidazolium (ca. 20), tetraalkylphosphonium (ca. 15), mono-, di-, or trialkylammonium (ca. 15), *N,N*-dialkylpyrrolidinium (ca. 10), tetraalkyldimethylguanidinium (ca. 10), *N*-alkylisoquinolinium (ca. 10), *N*-alkylpyridinium (ca. 5), 1,2,4-triazolium (ca. 5), and other heterocycles (e.g., piperidinium, indolium, pyrazolium, pyrrolium, 1,2,4-triazolium, ca. 10) and anions such as, NTf<sub>2</sub> (ca. 60), BF<sub>4</sub> (ca. 60), halogenates (X = Cl, Br and I, ca. 35), PF<sub>6</sub> (ca. 30), alkyl sulfonates (ca. 30), carboxylates (ca. 20), alkyl sulfates (ca. 15), nitrate (ca. 15), thiocyanate (ca. 10), and dicyanamide (ca. 10).<sup>[9]</sup>

Subsequently, more ionic liquids have been reported, including chiral,<sup>[10–21]</sup> biodegradable ones based on imidazoli-

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um [im] and ammonium cations,<sup>[22]</sup> task-specific ionic liquids<sup>[23]</sup> based on [im] containing amino,<sup>[24]</sup> silyl,<sup>[25]</sup> and sulfonate<sup>[26,27]</sup> dications.<sup>[28]</sup> Moreover, ionic liquids consisting of ammonium ions have also been reported, namely, Aliquat 336,<sup>[29]</sup> long alkyl chain ones,<sup>[30]</sup> and others,<sup>[31]</sup> as well as more biodegradable,<sup>[32]</sup> task-specific ionic liquids<sup>[23]</sup> containing sulfonate.<sup>[33]</sup> Apart from these, other cations such as imidazolium,<sup>[34]</sup> phosphazene,<sup>[35]</sup> guanidinium,<sup>[36–38]</sup> combinations of phosphonium-acesulfame<sup>[39]</sup> and phosphonium amino acids,<sup>[40]</sup> and other anions such as trihalides,<sup>[41]</sup> 3,5-dinitro-1,2,4-triazolate,<sup>[42]</sup> perfluoralkyltrifluoroborate,<sup>[43]</sup> and tricyanomethanide<sup>[44]</sup> have also been reported, recently.

The extensive range of combinations of cation and anion that ionic liquids provide allows a great variety of tunable interactions and applications.<sup>[45,46]</sup> Their peculiar properties such as high thermal and electrochemical stability, negligible vapor pressure,<sup>[47]</sup> and high ionic conductivity have made their use in the areas of organic chemistry,<sup>[48,49]</sup> chemical engineering,<sup>[50]</sup> material science,<sup>[51]</sup> physical chemistry,<sup>[52,53]</sup> analytical chemistry,<sup>[54,55]</sup> and biotechnology.<sup>[56]</sup> Their ability to solubilize a large array of diverse molecules along with the immiscibility both in water and nonpolar organic solvents further adds to their usefulness.<sup>[57]</sup>

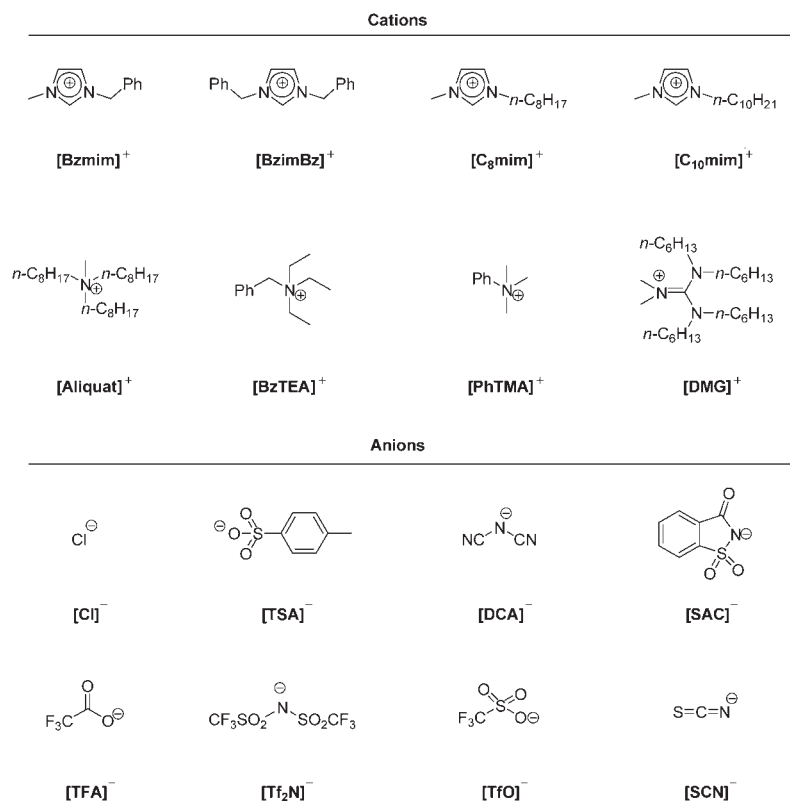
The basic difference in the properties of imidazolium and quaternary ammonium ionic liquids is that the former has a labile proton which limits its use in organic reactions<sup>[58]</sup> and it cannot be used as an electrolyte for high-energy electrochemical devices because of the electrochemical instability of the 1,3-dialkylimidazolium cations. The saturated quaternary ammoniums are more resistant against oxidation and reduction, thereby their ionic liquids with electrochemically stable anions, such as [Tf<sub>2</sub>N]<sup>−</sup>, have larger electrochemical windows than the corresponding 1,3-dialkylimidazolium compounds.<sup>[59]</sup> Also, the quaternary ammonium ionic liquids are easy to prepare and less expensive.<sup>[29,30]</sup> Further, there are many differences in the solubility, viscosity, and density of these two classes of ionic liquids. In comparison with these two classes, ionic liquids based on guanidinium<sup>[36–38]</sup> and phosphonium<sup>[39,40,60]</sup> have been less explored.

As part of our efforts to develop new ionic liquids based on tetraalkyldimethylguanidinium cations<sup>[38]</sup> (including chiral ones),<sup>[61]</sup> methylimidazolium-containing ether, and al-

cohol side chains<sup>[62]</sup> and their use as a simple reaction media for catalyst reuse<sup>[63–70]</sup> and as supported membranes for selective transport,<sup>[71–75]</sup> herein, we report on the extension of the known portfolio of ionic liquids to the ones based on cations containing long alkyl chains and/or phenyl groups and readily available anions, which are potentially more stable and less symmetric for use as a green media for organic vapor absorption above room temperature. Herein we report several types of imidazolium, quaternary ammonium, and guanidinium compounds. These were treated with the same set of anions to evaluate the difference in their properties. Various physicochemical properties of these ionic liquids were studied and the stability of these ionic liquids under thermal and chemical conditions was evaluated.

## Results and Discussion

The structures of the ionic liquids prepared and studied in the present work are shown in Scheme 1. The chloride salts of imidazolium and guanidinium were prepared in the laboratory using previously reported methodology,<sup>[9,38,62,76]</sup> whereas the quaternary ammonium salts were obtained commercially and were used as received. Subsequently, they were exchanged with a slight excess (1.2 equiv) of *p*-NaTSA (sodium *p*-toluenesulfonate), NaDCA (sodium dicyanamide), NaSAC (sodium 2-sulfobenzoic acid imide sodium salt or sodium saccharine), NaTFA (sodium trifluoroace-



Scheme 1. Structure of cations and anions used for the preparation of ionic liquids.

Table 1. Representative properties of new ionic liquids.

Ionic liquid	Physical state <sup>[a]</sup>	Water content <sup>[b]</sup> μg(H <sub>2</sub> O) mg <sup>-1</sup> (IL)	Viscosity η (Pa·s) <sup>[c]</sup>	$T_G$ <sup>[d]</sup> [°C]	DSC Analysis		$T_D$ <sup>[h]</sup> [°C]	Solubility	
					$\Delta C_p$ <sup>[f]</sup> [J g <sup>-1</sup> K <sup>-1</sup> ]	$\Delta C_{pm}$ <sup>[g]</sup> [J mol <sup>-1</sup> K <sup>-1</sup> ]		miscible <sup>[i]</sup>	immiscible <sup>[i]</sup>
[Bzmim][TSA]	Ss	–	–	–46.48	0.5904	216	183	w, ea(pm)	h, e
[Bzmim][DCA]	L	14.6	0.040	–77.75	0.8952	222	250	w	ea, h, e
[Bzmim][SAC]	L	14.8	26.75	–37.30	0.6254	222	205	w, ea(pm)	h, e
[Bzmim][TFA]	L	20.5	N-newt	–54.46	0.4941	159	180	w, ea	h, e
[Bzmim][Tf <sub>2</sub> N]	L	5.7	N-newt	–62.30	0.4357	200	> 300	w(pm), ea	h, e
[Bzmim][TfO]	Ss	–	–	–66.82	0.4718	152	> 300	w, ea	h, e
[Bzmim][SCN]	L	14.3	N-newt	–70.06	0.5797	139	169	w	ea, h, e
[BzimBz][TSA]	S	–	–	113.54 <sup>[e]</sup>			> 300	w	ea, h, e
[BzimBz][DCA]	L	6.5	0.202	–45.43	0.7431	234	252	w	ea, h, e
[BzimBz][SAC]	S	–	–	–9.65	0.4155	183	243	w	ea, h, e
[BzimBz][TFA]	S	–	–	–37.16	0.5858	233	180	w(pm), ea(pm)	h, e
[BzimBz][Tf <sub>2</sub> N]	L	5.4	N-newt	–50.24	0.469	275	> 300	ea	w, h, e
[BzimBz][TfO]	S	–	–	73.35 <sup>[e]</sup>			> 300	ea	w, h, e
[BzimBz][SCN]	L	7.7	0.625	–40.87	0.5385	167	163	w(pm)	h, e, ea
[C <sub>8</sub> mim][TSA]	S	–	–	89.48 <sup>[e]</sup>			> 300	w, ea	h, e
[C <sub>8</sub> mim][DCA]	L	11.1	0.034	–92.93	0.6369	172	250	w, ea	h, e
[C <sub>8</sub> mim][SAC]	L	13.3	0.389	–63.68	0.6295	242	245	w(pm), ea	h, e
[C <sub>8</sub> mim][TFA]	L	19.1	0.054	–88.90	0.5436	179	190	w(pm), ea	h, e
[C <sub>8</sub> mim][Tf <sub>2</sub> N]	L	5.8	0.087	–86.45	0.4229	210	> 300	ea	w, h, e
[C <sub>8</sub> mim][TfO]	L	4.5	0.100	–92.30	0.4686	161	> 300	ea	w, h, e
[C <sub>8</sub> mim][SCN]	L	12.2	0.070	–			226	w, ea	h, e
[C <sub>10</sub> mim][TSA]	S	–	–	78.99 <sup>[e]</sup>			278	w, ea(pm)	h, e
[C <sub>10</sub> mim][DCA]	L	4.7	0.076	–22.76	0.4556	136	270	w, ea	h, e
[C <sub>10</sub> mim][SAC]	L	5.7	0.884	–69.28	0.3315		251	w, ea	h, e
[C <sub>10</sub> mim][TFA]	L	3.0	N-newt	–			200	w, ea	h, e
[C <sub>10</sub> mim][Tf <sub>2</sub> N]	L	3.1	N-newt	–			> 300	ea	w, h, e
[C <sub>10</sub> mim][TfO]	L	5.6	0.194	–			> 300	w, ea	h, e
[C <sub>10</sub> mim][SCN]	L	9.2	N-newt	–			230	w, ea	h, e
[Aliquat][TSA]	S	–	–	77.98 <sup>[e]</sup>			241	e, ea	w, h
[Aliquat][DCA]	L	2.9	0.300	–89.94	0.7103		> 300	eo, ea	w, h
[Aliquat][SAC]	L	2.3	2.824	–54.02	0.2921		205	e, ea, h(pm)	w
[Aliquat][TFA]	L	7.7	0.740	–70.95	0.3576		183	e, h, ea	w
[Aliquat][Tf <sub>2</sub> N]	L	2.2	0.354	–81.42	0.3131		> 300	e, ea	w, h
[Aliquat][TfO]	Ss	–	–	–			> 300	e, ea	w, h
[Aliquat][SCN]	L	8.7	1.017	–				e, ea	w, h
[BzTEA][TSA]	S	–	–	–48.70	0.5375	198	280	w	ea, h, e
[BzTEA][DCA]	S	–	–	83.42 <sup>[e]</sup>			236	w	ea, h, e
[BzTEA][SAC]	S	–	–	151.32 <sup>[e]</sup>			209	w	ea, h, e
[BzTEA][TFA]	L	24.0	1.616	–48.90	0.6438	208	199	w, ea	e, h
[BzTEA][Tf <sub>2</sub> N]	Ss	–	–	–51.73	0.4616	235	> 300	ea	e, w, h
[BzTEA][TfO]	S	–	–	109.37 <sup>[e]</sup>			> 300	w	e, ea, h
[BzTEA][SCN]	S	–	–	87.82 <sup>[e]</sup>			88	w	e, ea, h
[PhTMA][TSA]	S	–	–	149.63 <sup>[e]</sup>			275	w	e, ea, h
[PhTMA][DCA]	S	–	–	117.37 <sup>[e]</sup>			195	w	e, ea, h
[PhTMA][SAC]	S	–	–	193.53 <sup>[e]</sup>			> 300	w	e, ea, h
[PhTMA][TFA]	L	20.6	–	–68.57	0.5201	139	182	w, ea(pm)	h, e
[PhTMA][Tf <sub>2</sub> N]	L	0.2	0.210	–58.01	0.3989	166	> 300	ea	w, h, e
[PhTMA][TfO]	S	–	–	82.97 <sup>[e]</sup>			> 300	w, ea	h, e
[PhTMA][SCN]	S	–	–	116.15 <sup>[e]</sup>			116	w	ea, h, e
[DMG][TSA]	L	5.5	0.398	–69.90	0.4563	271	200	e, ea, h(pm)	w
[DMG][DCA]	L	4.4	0.267	–77.18	0.2809		250	e, ea	h, w
[DMG][SAC]	L	4.6	1.175	–56.71			> 300	e, ea	h, w
[DMG][TFA]	L	5.0	0.194	–80.66	0.4055	222	190	e, ea	h, w
[DMG][Tf <sub>2</sub> N]	L	6.4	0.298	–72.11	0.3811	269	> 300	e, ea	h, w
[DMG][TfO]	L	1.7	0.178	–78.71	0.3909		> 300	e, ea	h, w
[DMG][SCN]	L	2.2	–	–72.43			275	e(pm), ea	h, w

[a] Observed visual state at room temperature, where L=Liquid, Ss=Semisolid, S=Solid. [b] Water content of each ionic liquid. [c] Viscosity of ionic liquid, where Non-newtonian=N-newt. [d] Glass transition temperature ( $T_G$ ) determined as the onset temperature in the heating mode (10°Cmin<sup>-1</sup>). [e] Melting point determined by DSC. [f] Heat capacity jump ( $\Delta C_p$ ) in J g<sup>-1</sup> K<sup>-1</sup>. [g] Molar heat capacity jump ( $\Delta C_{pm}$ ) in J mol<sup>-1</sup> K<sup>-1</sup>. [h] Decomposition temperature is the temperature at which exothermic or endothermic behavior initiated after prolonged heating. [i] Observed complete solubilization (miscible), partial solubilization (pm) or non-solubilization (immiscible) by adding the solvent to a small amount of ionic liquid, where water=w, ethyl acetate=ea, ether=e, hexane=h.

tate),  $\text{LiTf}_2\text{N}$  (lithium bis(trifluoromethanesulfonyl)imide),  $\text{KTfO}$  (potassium trifluoromethanesulfonate), or  $\text{KSCN}$  (potassium thiocyanate) to reduce the amount of the residual halogen content. The exchange reaction was carried out at room temperature by using solvent dichloromethane for 48 h. The volatile components are then removed by stirring the product (ionic liquid) at 70–90 °C under vacuum for 24 h. Stirring is important in these reactions; too little stirring can result in the incomplete removal of the volatile components as a result of slow diffusion of the volatile molecules in the viscous ionic liquid. The samples used for microanalysis and calorimetric experiments were further purified by filtration through silica and left under high vacuum ( $6 \times 10^{-6}$  mbar) at room temperature to remove traces of halogen and volatile components, respectively.

All the new ionic liquids were obtained in medium-to-very high yields ( $\geq 70\%$ ). They are stable in air, water, and other common organic solvents, such as ethers, hexane, dichloromethane, ethyl acetate, and ethanol. No decomposition was observed in the range of temperatures tested (up to 100 °C). Physical properties of these ionic liquids, such as their solubility in common organic solvents and in water, their viscosity and their density, were studied. The analysis of the solid–liquid phase transition allowed the determination of the glass transition temperature,  $T_G$ , and of the heat capacity jump,  $\Delta C_p$  associated with the glass transition. A degradation temperature of each ionic liquid was also determined by differential scanning calorimetry (DSC). The properties of the different ionic liquids were compared with each other.

**Physical state, water content, and solubility:** The physical state of the ionic liquid varies from liquid–semisolid–solid depending on the type of cation and anion chosen. The solubility of the ionic liquids in the solvents ether, ethyl acetate, acetone, dichloromethane, hexane, and water was observed visually by adding each solvent to a small amount of ionic liquid. The water content of each ionic liquid was determined by a volumetric Karl Fischer titration. The physical state, water content, and solubility of the developed ionic liquids are presented in Table 1.

It can be observed that the  $[\text{Bzmim}][\text{X}]$  series are liquids and semisolids. They are soluble in water and insoluble in hexane and diethyl ether, while some of them are partly miscible with ethyl acetate. The water content of these ionic liquids was observed to be less than  $21 \mu\text{g mg}^{-1}$ . The  $[\text{BzimBz}][\text{X}]$  series have a lower water content than the  $[\text{Bzmim}][\text{X}]$  series, which may indicate that the replacement of the methyl group by a benzyl group decreases the affinity of water to the ionic liquids. However, there is no fixed trend available for the solubility of the  $[\text{BzimBz}][\text{X}]$  series. In the  $[\text{C}_8\text{mim}][\text{X}]$  series, all the ionic liquids are liquids except  $[\text{C}_8\text{mim}][\text{TSA}]$ . Their water content varies from 4.5 to  $19.1 \mu\text{g mg}^{-1}$ , with  $[\text{C}_8\text{mim}][\text{TFA}]$  having the highest value (see Table 1). All of them display a remarkable solubility in ethyl acetate and are insoluble in diethyl ether and hexane. As expected, ionic liquids in the  $[\text{C}_{10}\text{mim}][\text{X}]$  series, which

contain the longest alkyl chain tested have been found to have a lower water content ( $< 10 \mu\text{g mg}^{-1}$ ) than the other series of imidazolium compounds. This is in line with the reported trend for water-saturated ionic liquids based on  $[\text{C}_n\text{mim}][\text{X}]$  ( $n=4\text{--}10$ ;  $\text{PF}_6$ ,  $\text{BF}_4$ ).<sup>[77–79]</sup> The  $[\text{C}_n\text{mim}][\text{X}]$  series are soluble in ethyl acetate and insoluble in hexane and diethyl ether.

Ionic liquids of the quaternary ammonium series are more often found in the solid physical state than those ionic liquids based on imidazolium and guanidinium salts. Table 1 indicates that in the quaternary ammonium series, only ionic liquids of the form  $[\text{Aliquat}][\text{X}]$  have been shown to be liquids. They are all miscible in diethyl ether and their water content varies from 2.2 to  $8.7 \mu\text{g mg}^{-1}$ . In addition, they are also miscible in ethyl acetate and immiscible in water. The other two quaternary ammonium series,  $[\text{BzTEA}][\text{X}]$  and  $[\text{PhTMA}][\text{X}]$  are mainly solids at room temperature except the ionic liquids  $[\text{BzTEA}][\text{TFA}]$ ,  $[\text{PhTMA}][\text{TFA}]$ ,  $[\text{PhTMA}][\text{Tf}_2\text{N}]$  which are liquids. Apart from the  $[\text{Tf}_2\text{N}]^-$  ion, all of these show good solubility in water. All the ionic liquids of the guanidinium series  $[\text{DMG}][\text{X}]$  are liquids, and are found to be miscible in diethyl ether and ethyl acetate and immiscible in water. Their water content ranges from 1.7 to  $6.4 \mu\text{g mg}^{-1}$ , which is similar to those observed for other  $[\text{DMG}]$  ( $\text{X} = \text{BF}_4$ ,  $\text{PF}_6$ ,  $\text{Tf}_2\text{N}$ ) combinations.<sup>[38]</sup>

Moreover, all the ionic liquids studied were found to be miscible in acetone and dichloromethane. The water content studies reveal that ionic liquids containing  $[\text{TFA}]^-$  as an anion have very high values compared to the other anions tested. Amongst the cations studied, each with  $[\text{TFA}]^-$  as a constant, this order decreases as follows:  $[\text{BzTEA}]^+ > [\text{Bzmim}]^+ > [\text{PhTMA}]^+ > [\text{C}_8\text{mim}]^+ > [\text{Aliquat}]^+ > [\text{DMG}]^+ > [\text{C}_{10}\text{mim}]^+$ . The ionic liquid  $[\text{BzTEA}][\text{TFA}]$  has highest water content ( $24.0 \mu\text{g mg}^{-1}$ ), whereas the water content of the ionic liquids containing  $[\text{Tf}_2\text{N}]^-$  and  $[\text{TfO}]^-$  ions are generally found to be low.

**Density ( $\rho$ ):** Figure 1 displays the densities of several ionic liquids measured at 25 °C. The densities range from 0.89 to  $1.46 \text{ g mL}^{-1}$ . In the imidazolium group, ionic liquids with a long alkyl chain have lower densities than the ones having aromatic rings. This is similar to the reported observations for the  $[\text{Tf}_2\text{N}]^-$  series.<sup>[80,81]</sup> An extra benzyl group in place of the methyl group in the imidazolium ring further increases the density of the ionic liquid, which may be attributed to the increase in the packing ability afforded by the phenyl group. Ionic liquids containing  $\text{C}_8$  and  $\text{C}_{10}$  alkyl chains, but having the same anion, have nearly same densities. Previously, it was observed that the increase in alkyl chain length leads to a decrease in the density of ionic liquids,<sup>[77]</sup> but, in the present case, it seems the effect is minimized at higher alkyl chain lengths ( $> \text{C}_8$ ). There is a very little difference between the densities of the  $[\text{C}_8\text{mim}]^+$  and  $[\text{C}_{10}\text{mim}]^+$  series. In the imidazolium group, the density increases in the order  $[\text{C}_{10}\text{mim}]^+ < [\text{C}_8\text{mim}]^+ < [\text{Bzmim}]^+ < [\text{BzimBz}]^+$  regardless of the anion.

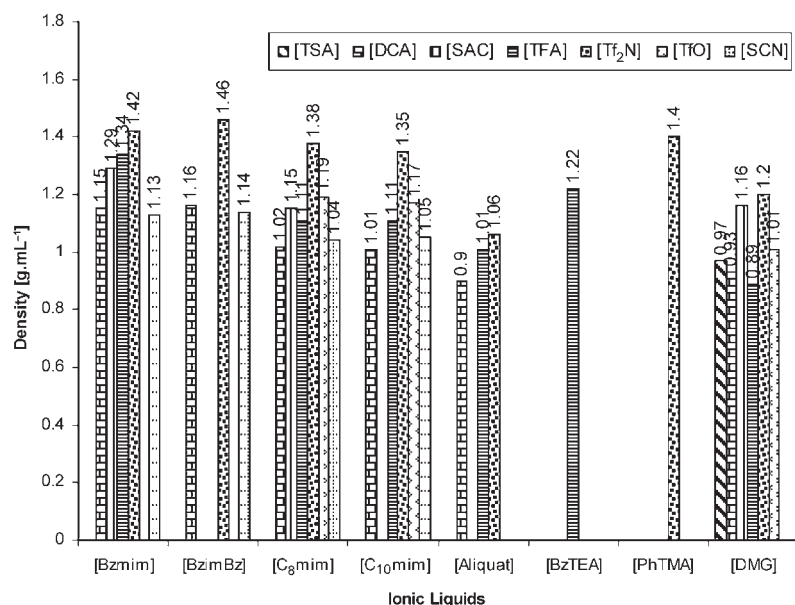


Figure 1. Densities at 25 °C of several ionic liquids.

In the quaternary ammonium group, the [Aliquat]<sup>+</sup> series have lower densities than their [BzTEA]<sup>+</sup> and [PhTMA]<sup>+</sup> counterparts.<sup>[29]</sup> However, the densities of [BzTEA][TFA] and [PhTMA][Tf<sub>2</sub>N] are lower than the corresponding [Bzmim]<sup>+</sup> and [BzimBz]<sup>+</sup> units. The density of the guanidinium series was also very low, which is quite interesting since it corresponds to the largest cation used (four *n*-hexyl groups) and is extremely less prone to crystallize. Thus, it appears that this cation is more capable to suppress the effect of the anion than the other cation series.<sup>[38,61]</sup> For the anions studied, ionic liquids containing the [Tf<sub>2</sub>N]<sup>−</sup> ion exhibit higher densities than the other anions. When the cation is kept constant, the order of densities increases as follows for the counter anions; [DCA]<sup>−</sup> < [SCN]<sup>−</sup> < [TFA]<sup>−</sup> < [TfO]<sup>−</sup> < [SAC]<sup>−</sup> < [Tf<sub>2</sub>N]<sup>−</sup>. This order indicates that the density of the ionic liquids increases with the increase in the bulkiness of the anion and the increase in the number of fluorine atoms.<sup>[43]</sup> Overall, it is observed that the ionic liquid [DMG][TFA] has the lowest (0.89 g mL<sup>−1</sup>) and [BzimBz][Tf<sub>2</sub>N] has the highest (1.46 g mL<sup>−1</sup>) density of the ionic liquids tested. These results demonstrate that the nature of the cation and anion play an important role in determining the densities of ionic liquids. They also show how the density can be fine-tuned through slight variations in the structures of the cation and anion.

**Viscosity ( $\eta$ ):** Viscosities of all the ionic liquids were measured at 20 °C and are shown in Table 1. From the steady-state flow measurements of the ionic liquids analyzed under a wide range of shear conditions, seven ionic liquids were found to be non-Newtonian, exhibiting shear-thinning behavior. Therefore, only the viscosity values of the ionic liquids showing Newtonian behavior are listed in Table 1.

As can be seen from the example of the flow curve obtained for [Bzmim][SAC] (Figure 2 A), a Newtonian liquid is the one for which the shear stress ( $\tau$ ) is a linear function of shear rate ( $\dot{\gamma}$ ). Consequently, the viscosity can be calculated by fitting the Newton equation ( $\tau = \eta\dot{\gamma}$ ) to the results obtained. The shear viscosity is the ratio of the shear stress to the shear rate, that is,  $\eta = \tau/\dot{\gamma}$ . For these Newtonian liquids the viscosity does not vary with the applied shear stress (Figure 2 B).

In contrast, for the seven non-Newtonian ionic liquids, the viscosity versus shear stress plots show a constant value of viscosity at low shear stresses (<100 Pa), but with the further increase in the shear stresses,

the viscosity was found to decrease significantly (Figure 3). This decrease of viscosity with shear stress is called shear-thinning behavior. For the studied ionic liquids with non-Newtonian behavior, Figure 3 illustrates the severe problems associated with using single measurements for the viscosity to describe the flow of shear-thinning fluids. To be useful,

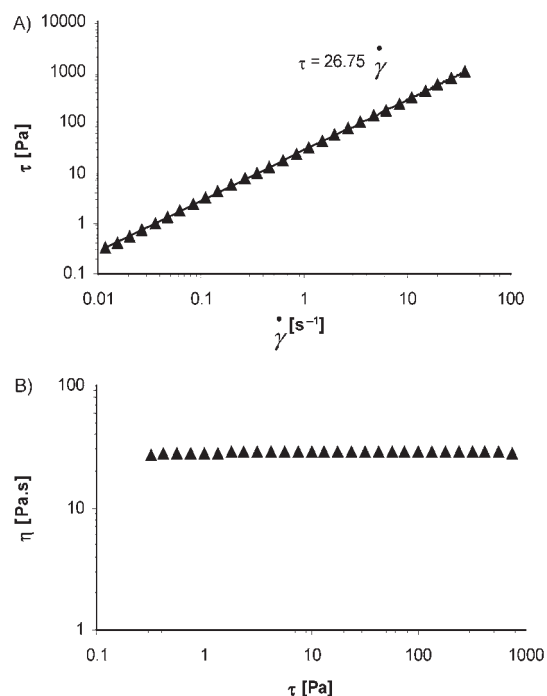


Figure 2. A steady-state flow curve based on the Newton equation (A), and a plot of viscosity versus shear stress (B) for the ionic liquid [Bzmim][SAC] obtained at 20 °C.



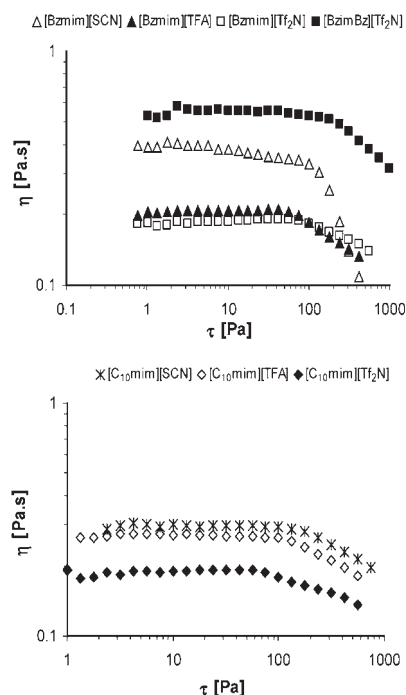


Figure 3. Plots of viscosity versus shear stress for non-Newtonian ionic liquids obtained at 20°C.

the variation in viscosity within a meaningful range of shear stress is needed.<sup>[82,83]</sup>

The viscosity results obtained for the [Bzmim]<sup>+</sup> series (Table 1) show evidence that saccharine induces an increase in viscosity compared with the other anions. In particular, the viscosity of the ionic liquid [Bzmim][SAC] is found to be 26.750 Pa·s. This effect of [SAC]<sup>−</sup> was also observed in all the other series of ionic liquids, such as [C<sub>8</sub>mim]<sup>+</sup>, [C<sub>10</sub>mim]<sup>+</sup>, [Aliquat]<sup>+</sup>, and [DMG]<sup>+</sup>, and it can be attributed to the larger size of saccharine compared with the other anions studied. Ionic liquids containing the [DCA]<sup>−</sup> ion exhibited the lowest viscosity, which is in line with the reported behavior with the [Tf<sub>2</sub>N]<sup>−</sup> ion for [C<sub>2</sub>mim]<sup>+</sup> and pyrrolidinium cations,<sup>[84]</sup> whereas the ionic liquids containing fluorine ions revealed intermediate viscosity values (Table 1). This can be attributed to interactions between hydrophobic groups. Anions that are more hydrophobic tend to interact through intra- and inter-chain electrostatic interactions, which, in turn, lead to an increase in the viscosity of the ionic liquid. In general, the delocalization of the charge over the anion favors lower viscosity by weakening hydrogen bonding with cation.<sup>[43]</sup>

The imidazolium ring containing two benzyl groups [BzmBz][DCA] was found to be more viscous than [Bzmim][DCA] which has only one benzyl group, due to the strong hydrophobic nature of the former. Amongst the [C<sub>8</sub>mim]<sup>+</sup> and [C<sub>10</sub>mim]<sup>+</sup> series with [DCA]<sup>−</sup> and [SAC]<sup>−</sup> ions (Table 1), the viscosity increases with the increase in the carbon chain length. A similar effect was described by others<sup>[8,62]</sup> for the ionic liquids [C<sub>4</sub>mim][PF<sub>6</sub>] and [C<sub>8</sub>mim][PF<sub>6</sub>], and was attributed to their tendency to form hydro-

gen bonds and the strength of their van der Waals interactions.

It was also observed that the flow behavior may change from Newtonian to non-Newtonian on increasing the length of the alkyl chains. This can be explained by the formation of a network due to the hydrophobic blocks from associative interactions, which are disrupted when high shear stresses are applied, leading to shear-thinning behavior. Thus, the series of ionic liquids containing the [C<sub>10</sub>mim]<sup>+</sup> ion may have a stiffer confirmation than those with the [C<sub>8</sub>mim]<sup>+</sup> ion. Accordingly, they dissociate faster when high shear stresses are applied, resulting in non-Newtonian behavior.

The viscosity values of the quaternary ammonium series [Aliquat]<sup>+</sup> and guanidinium [DMG]<sup>+</sup> are also compared and reported in Table 1. It is observed that the commercially available cation [Aliquat]<sup>+</sup> has a higher viscosity than the laboratory-synthesized [DMG]<sup>+</sup> ion (0.300 to 2.824 Pa·s as compared to 0.178 to 1.175 Pa·s, respectively). This again shows the influence of the strong hydrophobic nature of the [DMG]<sup>+</sup> ion compared to that of the [Aliquat]<sup>+</sup> ion, which itself shows quite unique properties owing to the presence of one extra long alkyl chain.

These results seem to indicate that ionic liquids that provide the lowest viscosity are [Bzmim][DCA], [C<sub>8</sub>mim][DCA], and [C<sub>10</sub>mim][DCA], which is in accord with reported data for other cations,<sup>[84,85]</sup> and which should facilitate mixing for potential use in many applications. However, it is important to note that highly viscous ionic liquids are preferred in applications such as stationary phases for gas-liquid chromatography.<sup>[86]</sup> With respect to the non-Newtonian ionic liquids, the rheological behavior must be taken into account in technical applications, since viscosity will decrease at a certain point of applied shear stress.

The effect of temperature on the viscosity of ionic liquids was also evaluated. Generally speaking all the data show the same variation of viscosity with temperature. As expected, the viscosity of all ionic liquids decreases with an increase in temperature between 20 and 90°C (0.5°Cmin<sup>−1</sup>), as shown, for example, for the series of [C<sub>8</sub>mim]<sup>+</sup> and [C<sub>10</sub>mim]<sup>+</sup> ions (Figure 4). This effect is attributed to the increase in Brownian motion of the constituent molecules of the ionic liquids.<sup>[82]</sup> The higher the viscosity, the greater is the rate of decrease, as observed for the ionic liquids containing saccharine, which show a marked decrease in viscosity on increasing the temperature.<sup>[82]</sup>

With this information, we can summarize that ionic liquids reported here display a very large range of viscosities, which are dependent on the cation/anion combination.

**Phase transitions:** Table 1 illustrates the solid-liquid phase transition of new ionic liquids that are calculated by differential scanning calorimetry (DSC) in the temperature range −120 to 50°C for a heating rate of 10°Cmin<sup>−1</sup>. A significant feature arising from the DSC study is that most of the ionic liquid salts described here, along with many of those previously reported,<sup>[30,38,41,62,77,80,81,87–89]</sup> are very good glass-formers, which indicates their weak tendency for crystallization.

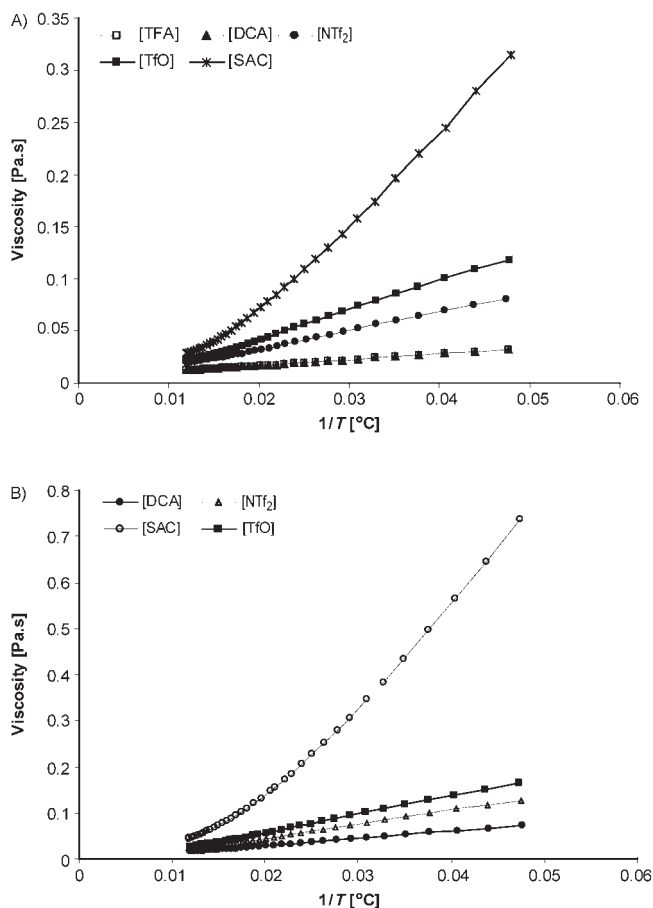


Figure 4. Plots of viscosity of a series of [C<sub>8</sub>mim]<sup>+</sup> (A) and [C<sub>10</sub>mim]<sup>+</sup> (B) ionic liquids as a function of 1/T.

Hence, they can be cooled from the equilibrium liquid state down to low temperatures without crystallizing. Furthermore, on entering the metastable supercooled liquid state, they undergo a glass transition leading to an out-of-equilibrium glassy state. Accordingly, these ionic liquids, which are easily manipulated in the supercooled liquid state, show a strong indication in the DSC trace of a glass transition (on cooling, as well as on heating). Among the ionic liquids examined, only [C<sub>8</sub>mim][SCN], [C<sub>10</sub>mim][TFA], [C<sub>10</sub>mim][Tf<sub>2</sub>N], [C<sub>10</sub>mim][TfO], [C<sub>10</sub>mim][SCN], and [Aliquat][TfO] readily crystallize on cooling. As a result, no glass transition signal was observed in these cases. The ionic liquids [C<sub>8</sub>mim][SCN], [C<sub>10</sub>mim][TFA], [C<sub>10</sub>mim][Tf<sub>2</sub>N], and [C<sub>10</sub>mim][SCN] showed exothermic effects with onset points of  $-57.03^{\circ}\text{C}$  ( $\Delta H = -52.3402 \text{ J g}^{-1}$ ),  $-31.07^{\circ}\text{C}$  ( $\Delta H = -69.88 \text{ J g}^{-1}$ ),  $-78.18^{\circ}\text{C}$  ( $\Delta H = -11.3181 \text{ J g}^{-1}$ ), and  $-18.99^{\circ}\text{C}$  ( $\Delta H = -84.67 \text{ J g}^{-1}$ ), respectively. However, the ionic liquid [C<sub>10</sub>mim][TfO] showed two crystalline onset points of  $-22.49^{\circ}\text{C}$  ( $\Delta H = -49.76 \text{ J g}^{-1}$ ) and  $-47.60^{\circ}\text{C}$  ( $\Delta H = -1.5654 \text{ J g}^{-1}$ ), thereby indicating polymorphism behavior. Interestingly, the quaternary ammonium compound [Aliquat][TfO], which has a tendency to form liquid crystals, has not shown any such effects.

The DSC thermogram recorded on heating some of the studied ionic liquids, namely [C<sub>8</sub>mim][DCA], [C<sub>8</sub>mim][TFA], and [C<sub>8</sub>mim][TfO], shows three different signals: the heat flow jump arising from the glass transition, a broad exothermic signal caused by cold recrystallization (crystallization on heating), and the melting (endothermic) peak. The ionic liquids [C<sub>8</sub>mim][DCA], [C<sub>8</sub>mim][TFA], and [C<sub>8</sub>mim][TfO] show cold recrystallization peaks at  $-46.06^{\circ}\text{C}$  ( $\Delta H = -97.0943 \text{ J g}^{-1}$ ),  $-54.88^{\circ}\text{C}$  ( $\Delta H = -55.9044 \text{ J g}^{-1}$ ), and  $-66.32^{\circ}\text{C}$  ( $\Delta H = -57.59 \text{ J g}^{-1}$ ), respectively, and melting peaks at  $-6.24^{\circ}\text{C}$  ( $\Delta H = 103.7812 \text{ J g}^{-1}$ ),  $-25.85^{\circ}\text{C}$  ( $\Delta H = 58.1345 \text{ J g}^{-1}$ ), and  $-20.51^{\circ}\text{C}$  ( $\Delta H = 61.27 \text{ J g}^{-1}$ ).

The other characteristic of the ionic liquids studied in the present work is that they show a strong jump in the molar heat capacity associated with the glass transition. Actually, the sigmoidal change in the heat flux, that is the DSC mark of the glass transition, arises from a change in the heat capacity,  $\Delta C_p$ , when the sample is heated from the glassy state to the metastable supercooled liquid (or cooled from the supercooled liquid to the glassy state). The jump in the molar heat capacity,  $\Delta C_{pm}$ , is observed to be higher than  $135 \text{ J K}^{-1} \text{ mol}^{-1}$  for all the ionic liquids investigated in the present work. These high values of  $\Delta C_{pm}$  indicate that many degrees of freedom are released on heating above  $T_g$ . A very high value of the heat capacity jump at the glass transition appears to be a salient feature of ionic liquids. The  $\Delta C_{pm}$  values of the common organic solvents glycerol and toluene are reported to be  $23 \text{ J K}^{-1} \text{ mol}^{-1}$  ( $T_g = 185 \text{ K}$ ) and  $53 \text{ J K}^{-1} \text{ mol}^{-1}$  ( $T_g = 113 \text{ K}$ ), respectively.<sup>[90]</sup> The higher  $\Delta C_{pm}$  values of the ionic liquids at  $T_g$  occurred due to the fact that each molecular unit is indeed composed by two subunits (cation and anion), which have, in the supercooled liquid state, an appreciable relative mobility.

**Thermal stability:** In the present study, the thermal stability of all the ionic liquids was examined by DSC<sup>[91]</sup> and each sample was tested up to  $300^{\circ}\text{C}$  (Table 1). A typical series of [Bzmim][X] shows that the thermal stability decreases in the order of  $[\text{TF}_2\text{N}]^- = [\text{TfO}]^- > [\text{TSA}]^- > [\text{DCA}]^- > [\text{SAC}]^- > [\text{TFA}]^- > [\text{SCN}]^-$ . It indicates that the thermal stability of each ionic liquid is heavily dependent on the type of anion.<sup>[30, 33, 77, 80, 81, 84, 86–88, 92]</sup> Amongst the groups, the ionic liquids containing [TfO]<sup>-</sup> and [TF<sub>2</sub>N]<sup>-</sup> ions were found to be stable above  $300^{\circ}\text{C}$  regardless of the cation. Apart from these 16 ionic liquids, the ionic liquids [Bzmim][TSA], [C<sub>8</sub>mim][TSA], [Aliquat][DCA], [PhTMA][SAC] were also stable above  $300^{\circ}\text{C}$ . The ionic liquids containing the [SCN]<sup>-</sup> ion show the lowest decomposition temperature, which was also observed for [C<sub>2</sub>mim]<sup>+</sup>, ammonium-, and pyrrolidinium-based cations.<sup>[93]</sup> In the imidazolium series, with a constant anion, the stability is observed to increase from [C<sub>8</sub>mim]<sup>+</sup> to [C<sub>10</sub>mim]<sup>+</sup>. This is in line with other reported examples<sup>[86]</sup> in which an increase in the stability of the ionic liquid is observed on increasing the length of the alkyl chain length. However, for a constant anion, it appears that the variation in [Bzmim]<sup>+</sup> and [Bzmim]<sup>+</sup> and quaternary ammonium cations has a smaller effect on the stability of the



corresponding ionic liquids. The values of degradation temperatures may be useful in the high-temperature applications of ionic liquids.

**Melting point:** A capillary melting point apparatus was used for the determination of the melting points of the ionic liquids that are solid at room temperature. The melting points of the solid ionic salts were also determined by DSC. Figure 5 shows the agreements between the values of the melting points measured by DSC and normal capillary apparatus. It is found that some of the quaternary ammonium ionic salts have a very high melting point ( $>100^{\circ}\text{C}$ ). Table 1 shows that the formation of room-temperature solid ionic salts is generally more prevalent in the quaternary ammonium group than in the imidazolium group. However, all the guanidinium salts are room-temperature ionic liquids. Amongst all the groups, it is seen that the  $[\text{TSA}]^{-}$  ion has a highest tendency to form solid ionic salts at room temperature. The tendency of formation of solid ionic salts amongst the anions decreases in the order of  $[\text{TSA}]^{-} > [\text{TfO}]^{-} > [\text{DCA}]^{-} = [\text{SAC}]^{-} = [\text{SCN}]^{-} > [\text{TFA}]^{-} = [\text{Tf}_2\text{N}]^{-}$ . It should be noted that the anions  $[\text{TFA}]^{-}$  and  $[\text{Tf}_2\text{N}]^{-}$  have no tendency to form solids.

**Stability tests:** Considering the potential applications of ionic liquids in different areas, their stability under different reaction conditions is an important issue to address. A comparative study of the stability to standard nucleophiles,<sup>[94]</sup>  $h\nu$ /oxidant<sup>[95]</sup> conditions, and thermal conditions<sup>[77,88,92]</sup> has been reported. Stability studies on the imidazolium and guanidinium cations were reported earlier under conditions

which mimic the standard potential applications as reaction media.<sup>[38]</sup> Hence, to assess whether the quaternary ammonium ionic liquids are good candidates, we selected the  $[\text{Aliquat}][\text{Cl}]$  as an example. The stability experiments were monitored by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy under the following representative conditions: acidic ( $\text{HCl}$ ), basic ( $\text{KOH}$ ), nucleophilic ( $\text{NH}_3$ ), reductive ( $\text{NaBH}_4$ ), and oxidative ( $\text{NaIO}_4$  and  $\text{O}_2$ ) and compared with the results obtained for 3-*n*-butyl-1-methylimidazolium chloride  $[\text{Bmim}][\text{Cl}]$  and  $[\text{DMG}][\text{Cl}]$  salts<sup>[38]</sup> under similar conditions (Table 2).

Interestingly, for all the conditions tested the  $[\text{Aliquat}]$

Table 2. Comparative stability by  $^1\text{H}$  and  $^{13}\text{C}$  NMR between the chlorides  $[\text{Bmim}][\text{Cl}]$ ,  $[\text{DMG}][\text{Cl}]$ , and  $[\text{Aliquat}][\text{Cl}]$ .<sup>[a]</sup>

Conditions	$[\text{Bmim}][\text{Cl}]$		$[\text{DMG}][\text{Cl}]$		$[\text{Aliquat}][\text{Cl}]$	
	RT	60 $^{\circ}\text{C}$	RT	60 $^{\circ}\text{C}$	RT	60 $^{\circ}\text{C}$
$\text{HCl}$ (1 equiv)	++	+	++	++	++	++
$\text{KOH}$ (1 equiv)	++	–	++	+	++	–
$\text{NH}_3$ (2 equiv)	++	+	++	++	++	++
$\text{NaBH}_4$ (3 equiv)	++	++	++	–	++	+
$\text{NaIO}_4$ (1 equiv)	++	++	++	++	++	++
$\text{O}_2$		++		++		–

[a] 500 mg of each salt was used; duration of the stability experiment: 24 h; ++: no change in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra was observed; +: no change in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra was observed, but a color change occurs; –: observed complete decomposition of the ionic liquid; RT = measurement at room temperature.

salts displayed similar stabilities to  $[\text{Bmim}][\text{Cl}]$  and  $[\text{DMG}][\text{Cl}]$  under thermal, acidic ( $\text{HCl}$ ), and nucleophilic conditions ( $\text{NH}_3$ ), ( $[\text{Bmim}][\text{Cl}]$  is unstable in solution), and in the presence of  $\text{NaIO}_4$ . However, it is unstable under basic conditions ( $\text{KOH}$ ) and stronger oxidative conditions ( $\text{O}_2$ ). In the presence of  $\text{NaBH}_4$  at  $60^{\circ}\text{C}$ , the neat guanidinium salt was unstable, whereas  $[\text{Bmim}][\text{Cl}]$  and  $[\text{Aliquat}][\text{Cl}]$  were stable.

## Conclusion

Imidazolium, quaternary ammonium, and guanidinium chloride salts were used and exchanged with the anions  $[\text{TSA}]^{-}$ ,  $[\text{DCA}]^{-}$ ,  $[\text{SAC}]^{-}$ ,  $[\text{TFA}]^{-}$ ,  $[\text{Tf}_2\text{N}]^{-}$ ,  $[\text{TfO}]^{-}$ , and  $[\text{SCN}]^{-}$  for the preparation of new ionic liquids. Various physicochemical properties, such as the solubility in common organic solvents, density, viscosity, solid–liquid phase transition, thermal stability, degradation temperature, and stability, have been explored for the ionic liquids synthesized. This study offers the possibility to extend the range of applications that this

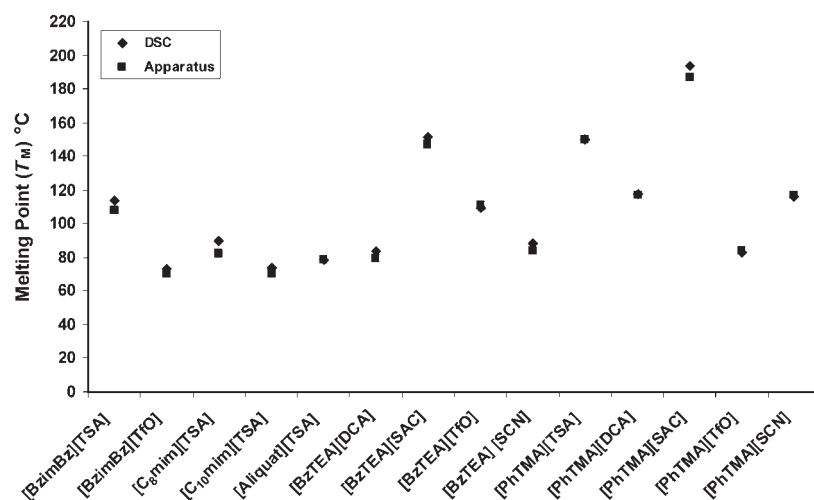


Figure 5. Observed melting points of the ionic liquids.

new media can offer, and the behavior observed for the ionic liquids studied provides some valuable hints about how the careful choice of the combination of cation and anions might be used to achieve some desired ultimate applications.

## Experimental Section

**General remarks:** Following chemicals were purchased from Aldrich and were used as supplied: Aliquat 336 [Aliquat]Cl; benzyl triethylammonium chloride [BzTEA]Cl; phenyl trimethylammonium chloride [PhTMA]Cl p-toluenesulfonic acid (TsOH); sodium dicyanoamide (NaDCA); sodium saccharine (NaSac); sodium trifluoroacetate (NaTFA); sodium thiocyanate (NaSCN); potassium trifluoromethanesulfonate (KTfO); lithium trifluoromethanesulfonimide (LiTf<sub>2</sub>N). The salts 1-benzyl-3-methylimidazolium chloride [Bzmim]Cl; 1,3-dibenzylmethylimidazolium chloride [BzimBz]Cl; 1-octyl 3-methylimidazolium chloride [C<sub>8</sub>mim]Cl; 1-decyl-3-methylimidazolium chloride [C<sub>10</sub>mim]Cl and tetra-*n*-hexyl-dimethylguanidinium chloride [DMG]Cl were prepared according to the reported procedures.<sup>[38,62,77,96]</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> or D<sub>2</sub>O were recorded on a Bruker AMX400 spectrometer. Chemical shifts are reported downfield in parts per million (ppm) from a tetramethylsilane reference. Elemental analysis (C, H, N, analyzer) of each synthesized ionic liquid was performed by the Laboratório de Análises at REQUIMTE. For the ionic liquids which are solid at room temperature the melting point determination was performed by using an Electrothermal Melting Point apparatus (uncorrected).

**Density:** The density of each ionic liquid was determined by using a DMA 38 model from Anton Paar Ltd., Austria. It is an oscillating U-tube density meter that enables the measurement of sample density values accurately up to 0.001 g cm<sup>-3</sup> in a temperature range from 15 to 40 °C. For each analysis approximately 1 mL of sample was used and the density of that volume of liquid was determined. The measurements were repeated three times and the average value is reported. All the measurements were recorded at room temperature ((25 ± 1) °C).

**Viscosity:** The viscosity of the ionic liquids was analyzed by using a Rheometer (RS-300, Haake, Germany). Steady-state flow measurements were carried out using a controlled-stress rheometer fitted with a cone-plate sensor C20/2°Ti. The torque amplitude was imposed by using a logarithmic ramp of shear stress, which was increased in 30 min intervals from 0.01 to 1000 Pa to decrease the initial acceleration and the effects due to instrument inertia. The temperatures of the samples were maintained at (20 ± 0.5) °C by means of a circulating water bath (DC30, Haake, Germany), and they were measured with a thermocouple attached to the stationary element.

The temperature dependence of the viscosity was also studied. The ionic liquids were heated from 20° to 90 °C (0.5 °C min<sup>-1</sup>), using a constant shear stress of 5 Pa. All the measurements were performed at least twice.

**Water content:** The water content of each ionic liquid was determined by a volumetric Aquastar Karl Fischer titration (method TitroLine KF). Samples of all compounds were dissolved in dichloromethane and titrated in steps of 250 µL.

**Solid-liquid transition analysis and decomposition temperature (DSC):** The glass transition temperature (*T*<sub>G</sub>), melting temperature (*T*<sub>M</sub>), decomposition temperature (*T*<sub>D</sub>), and the enthalpy of fusion of ionic liquids were measured at the Laboratório de Análises at REQUIMTE by differential scanning calorimetry (DSC), using a differential scanning microcalorimeter (Setaram, Mod. DSC 131) at a scan rate of 10 °C min<sup>-1</sup>, a flow rate of 20 dm<sup>3</sup> h<sup>-1</sup> with a power sensitivity of 16 mJ s<sup>-1</sup> and a recorder sensitivity of 5 mV. Each time the instrument was used, it was calibrated with a 99.9999 mol % purity indium sample. The decomposition temperature was considered as the temperature at which exothermic or endothermic behavior began during the heating of sample.

The heat capacity per unit volume of melting was measured under atmospheric pressure using a Setaram model TG-DSC 111 differential scanning

calorimeter. The heat-capacity measurements were made during the heating process. The range is dependent on the melting point of the investigated compounds. The measurements were performed by the “step with reference” method, using a scanning rate of 0.5 K min<sup>-1</sup> over a wide range of temperatures. Al<sub>2</sub>O<sub>3</sub> was used as a reference sample of known heat capacity.

### Synthesis of ionic liquids (ILs)

**General procedure for the anion exchange of different ionic liquids:** The selected salt (3 g of [Bzmim]Cl, [BzimBz]Cl, [C<sub>8</sub>mim]Cl and [C<sub>10</sub>mim]Cl; 2 g of [(di-*h*)<sub>2</sub>dmg]Cl and 5 g of [Aliquat]Cl, [BzTEA]Cl, and [PhTMA]Cl) was dissolved in dichloromethane (20–50 mL) and then the desired organic anion (1.2 equiv) was added as a salt. The mixture was stirred at room temperature for 48 h. The resulting solid was collected by filtration and washed with dichloromethane (2 × 25 mL). The combined organic layers were collected, dried (MgSO<sub>4</sub>), and filtered. The salt was then recovered after passing through a column containing silica and activated charcoal, and the solvent was removed under vacuum. The product was stirred under vacuum overnight. Each ionic liquid sample (2 mL scale) used for elemental analysis, DSC measurements, and for the determination of the water content was further purified by flash column chromatography (eluent: dichloromethane) followed by removal of the volatile components under high vacuum (5 × 10<sup>-5</sup> mbar) at room temperature for 4–5 h.

[Bzmim][TSA]: yellow semisolid, 72 %; [Bzmim][DCA]: yellow liquid, 71 %; [Bzmim][Sac]: pale yellow viscous liquid, 84 %; [Bzmim][TFA]: colorless liquid, 89 %; [Bzmim][Tf<sub>2</sub>N]: colorless liquid, quantitative; [Bzmim][TfO]: colorless semisolid, 75 %; [Bzmim][SCN]: orange liquid, 79 %.

[BzimBz][TSA]: pale yellow solid, 72 %; [BzimBz][DCA]: yellow liquid, 76 %; [BzimBz][Sac]: white solid, 82 %; [BzimBz][TFA], white solid, 84 %; [BzimBz][Tf<sub>2</sub>N]: yellow liquid, 85 %; [BzimBz][TfO]: white solid, 81 %; [BzimBz][SCN]: orange liquid, 77 %.

[C<sub>8</sub>mim][TSA]: pale yellow solid, 78 %; [C<sub>8</sub>mim][DCA]: yellow liquid, 89 %; [C<sub>8</sub>mim][Sac]: yellow viscous liquid, 72 %; [C<sub>8</sub>mim][TFA]: yellow liquid, 75 %; [C<sub>8</sub>mim][Tf<sub>2</sub>N]: yellow liquid, quantitative; [C<sub>8</sub>mim][TfO]: yellow liquid, 73 %; [C<sub>8</sub>mim][SCN]: orange liquid, 82 %.

[C<sub>10</sub>mim][TSA]: pale yellow solid, 77 %; [C<sub>10</sub>mim][DCA]: yellow liquid, 78 %; [C<sub>10</sub>mim][Sac]: yellow viscous liquid, 98 %; [C<sub>10</sub>mim][TFA]: yellow liquid, 96 %; [C<sub>10</sub>mim][Tf<sub>2</sub>N]: yellow liquid, quantitative; [C<sub>10</sub>mim][TfO]: yellow liquid, 80 %; [C<sub>10</sub>mim][SCN]: yellow liquid, 97 %.

[Aliquat][TSA]: yellow solid, 88 %; [Aliquat][DCA]: yellow liquid, 90 %; [Aliquat][Sac]: yellow semisolid, 94 %; [Aliquat][TFA]: yellow viscous liquid, quantitative; [Aliquat][Tf<sub>2</sub>N]: yellow liquid, 86 %; [Aliquat][TfO]: yellow semisolid, 83 %; [Aliquat][SCN]: orange liquid, 81 %;

[BzTEA][TSA]: white solid, 90 %; [BzTEA][DCA]: white solid, 91 %; [BzTEA][Sac]: pale yellow solid, 98 %; [BzTEA][TFA]: yellow liquid, quantitative; [BzTEA][Tf<sub>2</sub>N]: semisolid, quantitative; [BzTEA][TfO]: white solid, quantitative; [BzTEA][SCN]: orange solid, 98 %.

[PhTMA][TSA]: white solid, 92 %; [PhTMA][DCA]: white solid, 71 %; [PhTMA][Sac]: white solid, 85 %; [PhTMA][TFA]: yellow liquid, 80 %; [PhTMA][Tf<sub>2</sub>N]: yellow liquid, 79 %. [PhTMA][TfO]: white solid, 100 %; [PhTMA][SCN]: yellow solid, 72 %.

[DMG][TSA]: yellow liquid, 81 %; [DMG][DCA]: yellow liquid, 72 %; [DMG][Sac]: brownish viscous liquid, 79 %; [DMG][TFA]: orange liquid, 85 %; [DMG][Tf<sub>2</sub>N]: orange viscous liquid, 91 %; [DMG][TfO]: orange viscous liquid, 83 %; [DMG][SCN]: orange viscous liquid, 87 %.

The spectral data (<sup>1</sup>H NMR and <sup>13</sup>C NMR) and elemental analysis of each ionic liquid is provided in the Supporting Information.

## Acknowledgements

We would like to thank Fundação para a Ciência e Tecnologia (POCI 2010) and FEDER for the financial support (Ref. POCI/QUI/57735/2004 and Ref. SFRH/BPD/14848/2003) and Professor Joaquim J. Moura

Ramos for the helpful discussions. We gratefully acknowledge *solchemar* company (<http://www.solchemar.com>) for providing the [C<sub>8</sub>mim]Cl and [C<sub>10</sub>mim]Cl salts.

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Received: January 31, 2007

Revised: June 25, 2007

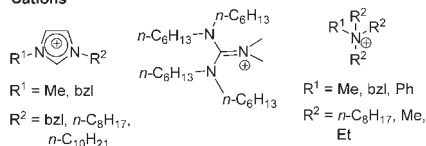
Published online: ■ ■ ■, 2007

## Ionic Liquids

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### Comparison of Physicochemical Properties of New Ionic Liquids Based on Imidazolium, Quaternary Ammonium, and Guanidinium Cations

#### Cations



Anions:  $\text{Cl}^-$ ,  $\text{TolSO}_3^-$ ,  $(\text{CN})_2\text{N}^-$ , Saccharine $^-$ ,  $\text{CF}_3\text{CO}_2^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{TF}_2\text{N}^-$ ,  $\text{SCN}^-$

**Key physico-chemical data on a series of new ionic liquids** based on the combination of imidazolium, quaternary ammonium, and guanidinium cations and the anions *p*-toluenesulfonate, dicyanoamide, saccharine, trifluoroacetate, bis(trifluoromethanesulfonyl)imide, trifluoromethanesulfonate, and thiocyanate has been collated. These data include their solubility in common solvents, viscosity, water content, solid–liquid phase transition, density and stability under thermal, basic, acidic, nucleophilic, and oxidative conditions.