Preparation and Characterization of New Room Temperature Ionic Liquids

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Abstract: A new series $[C_nO_m\text{mim}][X]$ of imidazolium cation-based room temperature ionic liquids (RTILs), with ether and alcohol functional groups on the alkyl side-chain has been prepared. Some physical properties of these RTILs were measured, namely solubility in common solvents, viscosity and density. The solubility of LiCl, $HgCl_2$ and $LaCl_3$ in room temperature ionic liquids was also determined. The features of the solid–liquid phase transition were analysed, namely the glass transition temperature and the heat capacity jump associated with the transition from the non-equilibrium glass to the metastable supercooled liquid. These properties were compared with those reported for the 1-*n*-alkyl-3-methylimidazolium $[C_n\text{mim}][X]$ series. While the density and solid–liquid phase transition properties are similar for both series, the new RTILs present a considerably lower viscosity and an increased ability to dissolve $HgCl_2$ and $LaCl_3$ (up to 16 times higher).

Keywords: alkylation · green chemistry · ionic liquids · phase transitions · solvent effects

Introduction

Although known since the beginning of the 21st century, only recently have room temperature ionic liquids (RTILs) attracted significant and growing interest, especially those based upon the 1-*n*-alkyl-3-methylimidazolium cation.[1, 2] They have intrinsically useful properties, such as thermal stability, high ionic conductivity, negligible vapour pressure and a large electrochemical window. Depending on the anion and alkyl group of the imidazolium cation, the RTILs can solubilise carbonyl compounds, alcohols, alkyl halides, supercritical CO_2 ($scCO_2$), and also transition metal complexes. Furthermore, they can have low miscibility with dialkyl ethers, alkanes, water and can be insoluble in $scCO_2$.[1, 3, 4] The RTILs can be used as an alternative recyclable and environmentally benign reaction media for chemical processes. Examples of their usefulness in biocatalysis[5] and catalysis have been reported, for example hydroformylation, hydrogenation, olefin oligomerisation, Heck reactions, alkylation, Friedel–Crafts reactions, Diels–Alder reactions and Baylis–Hillman reactions.[6] Moreover, RTILs have successfully replaced traditional organic solvents (OS) in aqueous-OS biphasic systems, including selective extraction of metal ions[7, 8] and for OS-$scCO_2$ extraction.[9, 10] Applications have also been found in different areas, including gas chromatography[11] as stationary phases, in electrochemistry[12] as solvents and electrolytes, and in pervaporation.[13]

Future applications of RTILs to other important processes may require the synthesis of new ionic liquids with suitable properties. For instance, improved solubility of more specific solutes including very polar substrates or catalysts may be called for. This can be achieved by including different substituent groups R with potential complexation properties in the basic ionic liquid structure.

Herein, we report the preparation of a new series of ionic liquids $[C_nO_m\text{mim}][X]$, based on the imidazolium cation that contains additional functional groups, such as ether and alcohol, on the alkyl group R. This new series of RTILs was prepared, characterised, and some physical properties were studied.

Results and Discussion

The structures of the ionic liquids $[C_nO_m\text{mim}][X]$ prepared and studied in the present work are shown in Table 1. A previously reported methodology[1, 14] was used for the preparation of these new ionic liquids. Alkylation of methylimidazole with an alkyl halide is followed by halogen (Cl^- or Br^-) exchange with slight excess (1.1 equiv) KPF_6, $NaBF_4$ or $NaCF_3CO_2$ (NaTFA) in order to reduce the amount of remaining halogen content. The volatile components are then

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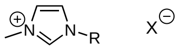
Table 1. Structure of room temperature ionic liquids of the series [$C_nO_m$mim][X].



Ionic liquid	Cation R	Anion X^-
[C_2OHmim][Cl]	$(CH_2)_2OH$	Cl^-
[C_2OHmim][PF_6]	$(CH_2)_2OH$	PF_6^-
[C_2OHmim][BF_4]	$(CH_2)_2OH$	BF_4^-
[C_2OHmim][TFA]	$(CH_2)_2OH$	$CF_3CO_2^-$
[C_3Omim][Cl]	$(CH_2)_2OMe$	Cl^-
[C_3Omim][PF_6]	$(CH_2)_2OMe$	PF_6^-
[C_3Omim][BF_4]	$(CH_2)_2OMe$	BF_4^-
[C_4OHmim][Br]	$(CH_2)_4OH$	Br^-
[C_5O_2mim][Cl]	$(CH_2)_2O(CH_2)_2OMe$	Cl^-
[C_5O_2mim][PF_6]	$(CH_2)_2O(CH_2)_2OMe$	PF_6^-
[C_5O_2mim][BF_4]	$(CH_2)_2O(CH_2)_2OMe$	BF_4^-

Table 2. Solubility of new RTILs in some common solvents.

Entry	Ionic liquid	H_2O [g L^{-1}]	Et_2O	EtOAc	EtOH[a]
1	[C_2OHmim][PF_6]	misc	imisc	pm	misc
2	[C_2OHmim][BF_4]	misc	imisc	pm	misc
3	[C_2OHmim][TFA]	misc	imisc	pm	misc
4	[C_3Omim][PF_6]	misc	imisc	pm	pm
5	[C_3Omim][BF_4]	misc	imisc	pm	pm
6	[C_5O_2mim][PF_6]	0.38[b]	imisc	imisc	pm
7	[C_5O_2mim][BF_4]	0.43[b]	imisc	imisc	pm
8	[C_4mim][PF_6]	0.57[b]	imisc	imisc	misc
9	[C_4mim][BF_4]	misc	imisc	imisc	misc
10	[C_8mim][PF_6]	0.22[b]	imisc	imisc	misc
11	[C_8mim][BF_4]	0.30[b]	imisc	imisc	misc
12	[C_{10}mim][BF_4]	0.59[b]	imisc	imisc	misc

[a] Ethanol 96% (v/v). [b] Determined by UV spectroscopy; misc: miscible; imisc: immiscible; pm: partially miscible.

removed by stirring the RTIL at 70–90 °C for 24–48 h under vacuum. Stirring is essential, otherwise removal of the volatile components is incomplete as a result of slow diffusion of the volatile molecules in the viscous RTIL. The remaining water content in the RTIL is higher in case of BF_4^- anion [2.3 to 4.7 µg (H_2O) mL^{-1} (RTIL)] than for PF_6^- [0.9 to 2.0 µg (H_2O) mL^{-1} (RTIL)] which is in agreement with the observed contents for the [$C_n$mim][X] series.[3c] The samples used for microanalysis and calorimetric experiments were further purified by filtration through silica and left under high vacuum (6×10^{-6} mbar) at room temperature in order to remove traces of halogen and volatile components, respectively.

All new RTILs were obtained in medium-to-high yields (75–95%). They are stable in air, water and in 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 90 °C).

Some physical properties of this new series of RTILs were studied, namely their solubility in some common organic solvents and in water, solubility of inorganic salts in the RTIL, viscosity and density. The analysis of the solid–liquid phase transition allowed the determination of the glass transition temperature, T_g, and of the heat capacity jump, ΔC_p associated with the glass transition. Some of these properties were compared with those previously reported for the RTIL series [$C_n$mim][X] ($n = 4$, 6, 8 and 10) containing different anions ($X^- = Cl^-$, PF_6^- and BF_4^-).

Solubility of RTILs in some solvents: In Table 2 we present the solubilities of the new RTILs [$C_nO_m$mim][X] together with those of with the RTIL series [$C_n$mim][X]. It can be observed that the new RTILs [C_2OHmim][PF_6], [C_2OHmim][BF_4], [C_2OHmim][TFA], [C_3Omim][PF_6] and [C_3Omim][BF_4] (entries 1–5) are miscible with water, as is the case for the RTIL [C_4mim][BF_4] (entry 9). For the others, RTILs (entries 6–8 and 10–12) the solubility in water was determined by UV spectroscopy and it was found that the RTILs with PF_6^- anion have lower solubility in water when compared to those with the BF_4^- anion. The RTIL [C_5O_2mim][PF_6] has lower solubility in water than the RTIL [C_4mim][PF_6] (entry 6 vs entry 8). Among all RTILs studied, [C_8mim][PF_6] presents the lowest water solubility (entry 10). In ethyl acetate, the RTILs of entries 1–5 are partially miscible while the others (entries 6–12) are immiscible. On the other hand, in 96% ethanol (*v*/*v*) the RTILs of entries 4–7 are partially miscible while all the others (entries 1–3 and 8–12) are miscible. Additionally, all RTILs studied are immiscible in diethyl ether, and miscible in acetone and in dichloromethane. They also show low solubility in hexane and petroleum ether.

In general, the introduction of hydroxyl or ether functional groups in the alkyl chain considerably modifies the solubility behaviour, while modification of the anion (PF_6^-, BF_4^-, TFA^-) does not seem to have any significant influence.

Viscosity: Table 3 gives viscosity data for some RTILs at different temperatures (10, 20 and 30 °C). From this data it can be concluded that both RTIL series (the new [$C_nO_m$mim][X] and the [$C_n$mim][X]) display qualitatively similar viscosity behaviour.

Table 3. Viscosity (*cP*) data for several RTILs at different temperatures.

Entry	Ionic liquid	*cP* (30 °C)	*cP* (20 °C)	*cP* (10 °C)
1	[C_2OHmim][PF_6]	82.7	148.8	279.5
2	[C_2OHmim][BF_4]	70.9 (25 °C)	90.9	157.6
3	[C_3Omim][PF_6]	148.1	283.6	607.5
4	[C_3Omim][BF_4]	138.0	262.8	374.3
5	[C_5O_2mim][Cl]	283.7	613.4	1515.8
6	[C_5O_2mim][PF_6]	212.3	425.8	1034.9
7	[C_5O_2mim][BF_4]	189.2	377.0	860.4
8	[C_4mim][PF_6]	172.8[a]	308.3[b]	615.0
9	[C_4mim][BF_4]	65.2[c]	104.9[d]	185.9
10	[C_8mim][Cl]	337.0 (25 °C)		
11	[C_8mim][PF_6]	425.2[e]	857.4[f]	1922.4
12	[C_8mim][BF_4]	82.1	135.0	294.3
13	[C_{10}mim][BF_4]	223.1	416.6	846.3
14	[C_2mim][BF_4]	43.0[g]	66.5[g]	
15	[C_6mim][Cl]	716.0 (25 °C)[g]		
16	[C_6mim][PF_6]	363.0[g]	680.0[g]	
17	[C_6mim][BF_4]	177.0[g]	314.0[g]	

[a] 204.0;[15] [b] 371.0;[15] [c] 91.4;[15] [d] 154.0;[15] [e] 452.0;[15] [f] 866.0;[15] [g] literature values.[15, 16]

The viscosity of ionic liquids is essentially influenced by their hydrogen bonding ability and by the strength of their van der Waals interactions, being strongly dependent of the anion type. We observe that all the RTILs containing the BF_4^- anion have lower viscosity than the RTILs with PF_6^- anion, which is in agreement with reported data.[3c] This difference is even more noticeable at the lower temperature (10 °C). For example, in the $[C_n\text{mim}][PF_6]$ series, RTILs with PF_6^- have viscosities that are more than twice the value of the viscosity of RTILs with BF_4^- (entries 8, 11, 16 vs 9, 12, 17). This significant difference of viscosities between PF_6^- and BF_4^- anions is less pronounced for the $[C_nO_m\text{mim}][X]$ series (entries 1, 3, 6 vs 2, 4, 7).

The structure of the cation also influences the viscosity of the ionic liquid. In our studies we concluded that the viscosity of the RTIL $[C_2OH\text{mim}][PF_6]$ is less than half as large as the RTILs $[C_3O\text{mim}][PF_6]$ and $[C_4\text{mim}][PF_6]$ (entry 1 vs entries 3 and 8). The RTIL $[C_2OH\text{mim}][BF_4]$ presents an intermediary viscosity between the RTILs $[C_2\text{mim}][BF_4]$ and $[C_4\text{mim}][BF_4]$ (entry 14 < entry 2 < entry 9). The viscosity of the RTIL $[C_5O_2\text{mim}][Cl]$ is lower than the viscosity of the RTILs $[C_6\text{mim}][Cl]$ and $[C_8\text{mim}][Cl]$ (entry 5 vs entries 15 and 10).

In Figure 1 we present the viscosity of some RTILs plotted as a function of the temperature, which allows a better comparison between the RTILs.

From this study, we can conclude that ionic liquids display a very large range of viscosities, depending on the cation/anion combination. On the other hand, the temperature coefficient of the viscosity at room temperature (that expresses the activation energy for the viscous flow) is high when compared to "normal" solvents.

From the data displayed in Figure 1, it can be concluded that with regard to the viscosity, the best RTILs are $[C_2OH\text{mim}][PF_6]$, $[C_2OH\text{mim}][BF_4]$, $[C_3O\text{mim}][BF_4]$ and $[C_4\text{mim}][BF_4]$, since they have a lower viscosity, which is an important issue in some applications.

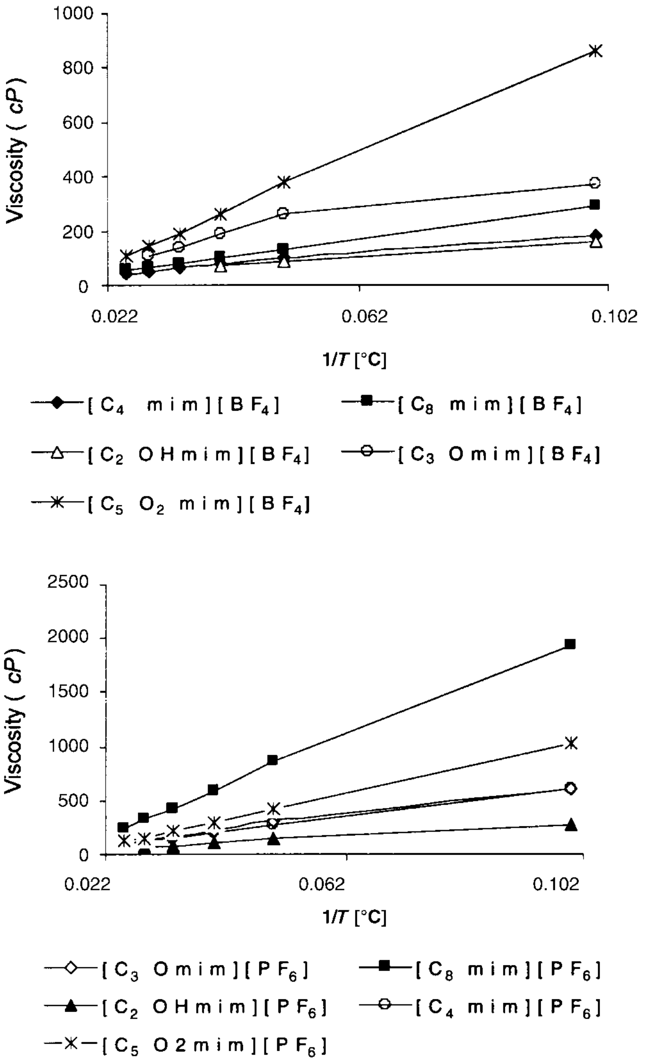


Figure 1. Viscosity of a series of RTILs as a function of the reciprocal of the temperature

Density: In Table 4 we present density data at 25 °C for the prepared RTILs. In general, the new RTIL $[C_nO_m\text{mim}][X]$ series have higher densities than the $[C_n\text{mim}][X]$ series. The RTILs containing the PF_6^- anion have higher densities than those with BF_4^- or Cl^- anions. As would be expected, a larger alkyl chain on the $[C_n\text{mim}]$ series results in a decrease of density (butyl > hexyl > octyl > decyl) (entries 8, 9 and 10 vs entries 13, 14 and 15).

Among the new RTIL $[C_nO_m\text{mim}][X]$ series, the densities decrease in the order $[C_2OH\text{mim}] > [C_3O\text{mim}] > [C_5O_2\text{mim}]$ (entries 1 and 2 vs entries 3 and 4 vs entries 6 and 7). The RTILs $[C_3O\text{mim}][X]$ and $[C_5O_2\text{mim}][PF_6]$ present a very similar density to those from the $[C_n\text{mim}][X]$ series with comparable chain size, respectively $[C_4\text{mim}][X]$ and $[C_6\text{mim}][PF_6]$.

Table 4. Densities at 25 °C of several RTILs.

Entry	Ionic liquid	Density [g mL^{-1}]
1	$[C_2OH\text{mim}][PF_6]$	1.48
2	$[C_2OH\text{mim}][BF_4]$	1.33
3	$[C_3O\text{mim}][PF_6]$	1.40
4	$[C_3O\text{mim}][BF_4]$	1.26
5	$[C_5O_2\text{mim}][Cl]$	1.14
6	$[C_5O_2\text{mim}][PF_6]$	1.32
7	$[C_5O_2\text{mim}][BF_4]$	1.22
8	$[C_4\text{mim}][Cl]$	1.08[a]
9	$[C_4\text{mim}][PF_6]$	1.31[b]
10	$[C_4\text{mim}][BF_4]$	1.26[c]
11	$[C_6\text{mim}][Cl]$	1.03[a]
12	$[C_6\text{mim}][PF_6]$	1.29[a]
13	$[C_8\text{mim}][Cl]$	1.00[a]
14	$[C_8\text{mim}][PF_6]$	1.19[d]
15	$[C_8\text{mim}][BF_4]$	1.08
16	$[C_{10}\text{mim}][BF_4]$	1.04

[a] Reported value;[3c] [b] 1.36;[3c] [c] 1.12;[3c] [d] 1.22.[3c]

Melting point and glass transition temperature: The solid–liquid phase transition of these RTILs has been studied by differential scanning calorimetry (DSC, Table 5). One of the features arising from this study is that most of these molten salts are very good glass-formers (they present a weak tendency to crystallise). They can be cooled from the equilibrium liquid state down to low temperatures without crystallising, entering the metastable supercooled liquid state, and suffering a glass transition leading to an out-of-equilibrium glassy state. Consequently, these RTILs, that are easily

Table 5. Thermal data of several RTILs obtained by DSC analysis.

Ionic liquid	T_G[a] [°C]	ΔC_P[b] [$J g^{-1} K^{-1}$]	ΔC_{Pm}[c] [$J mol^{-1} K^{-1}$]	T_f[d] [°C]
[C$_2$OHmim][PF$_6$]	−72	0.46	125	
[C$_2$OHmim][Cl]	−111	0.72	117	
[C$_2$OHmim][BF$_4$]	−84	0.56	120	
[C$_2$OHmim][TFA]	−89	0.74	178	
[C$_3$Omim][PF$_6$]	–	–	–	26
[C$_3$Omim][Cl]	−60	0.52	92	
[C$_3$Omim][BF$_4$]	−88	0.56	128	
[C$_4$OHmim][Br]	−83	0.63	148	
[C$_5$O$_2$mim][PF$_6$]	−69	0.46	151	
[C$_5$O$_2$mim][Cl]	−85	0.79	174	
[C$_5$O$_2$mim][BF$_4$]	−86	0.65	177	
[C$_4$mim][Cl]				41[e]
[C$_4$mim][PF$_6$]	−80[e]			10[e]
[C$_4$mim][BF$_4$]	−97[e]			−81[e]
[C$_6$mim][Cl]	−75[e]			
[C$_6$mim][PF$_6$]	−78[e]			−61[e]
[C$_6$mim][BF$_4$]	−82.4[e]			
[C$_8$mim][Cl]	−87[e]			
[C$_8$mim][PF$_6$]	−82[e]			
[C$_8$mim][BF$_4$]	−80.5[e]			
[C$_{10}$mim][BF$_4$]	−24.7[e]			

[a] Glass transition temperature (T_G) determined as the onset temperature in the heating mode (10 °C min^{-1}); [b] heat capacity jump (ΔC_P); [c] molar heat capacity jump (ΔC_{Pm}); [d] melting temperature (T_f); [e] reported values.[3a,c]

manipulated in the supercooled liquid state, show a strong DSC signature of a glass transition (on cooling, as well as on heating). Among the ionic liquids studied, only [C$_3$Omim][PF$_6$] readily crystallises on cooling. As a consequence, no glass transition signal was observed in this case. For a heating rate of 10 °C min^{-1}, the onset of the melting peak appeared at 15 °C, and the maximum of this peak occurred at 26 °C. The molar melting enthalpy was found to be $\Delta H_m = 14.3$ kJ mol^{-1}.

The DSC thermogram recorded on heating of some of the studied molten salts, namely of [C$_3$Omim][Cl] and [C$_5$O$_2$mim][PF$_6$], show three different signals: the heat flow jump arising from the glass transition, a broad exothermic signal caused by cold recrystallisation (crystallisation on heating), and the melting (endothermic) peak. In most cases, the melting peak of these ionic liquids appears above room temperature. This means that, when manipulated as liquids near room temperature, they are, in fact, in the metastable supercooled liquid state, rather than in the equilibrium liquid state.

Another feature of the room temperature ionic liquids studied in the present work is that they show a strong jump in the molar heat capacity associated with the glass transition. In fact, the sigmoidal change in the heat flux, that is the DSC signature of the glass transition, arises from a change in the heat capacity, ΔC_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, ΔC_{Pm}, is higher than 90 J K^{-1}mol^{-1} for all the RTILs studied in the present work. These high values of ΔC_{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 as a specific feature of ionic liquids. Indeed, values of ΔC_{Pm} of 23 J K^{-1}mol^{-1} and 53 J K^{-1}mol^{-1} are reported respectively for glycerol ($T_g = 185$ K) and toluene ($T_g = 113$ K),[17] while for polymeric systems we have $\Delta C_{Pm} = 10$ J K^{-1}mol^{-1} for polyethylene ($T_g = 140$ K) and $\Delta C_{Pm} = 36$ J K^{-1}mol^{-1} for poly(vinyl acetate) ($T_g = 302$ K).[18] The high ΔC_{Pm} at T_g found for ionic liquids arises from the fact the each molecular unit is in fact composed by two sub-units (the cation and the anion) that have, in the supercooled liquid state, an appreciable relative mobility.

No apparent correlation can be found between the heat capacity jump, ΔC_{Pm}, at the glass transition, and the glass transition temperature or the molar mass of the ionic liquids.

Solubility of inorganic salts in RTILs: Recently, ionic liquids have often been discussed as promising solvents for green chemistry and clean synthesis.

The use of RTILs as a new recyclable reaction media for a considerable range of organic transformations, including transition metal catalysis has already been demonstrated. Nonetheless, the use of RTILs has been mainly restricted to the [C$_n$mim][X] series. Meanwhile, in our experience, the extension of this medium to other organic transformations suffers from the drawback of the considerably low solubility of some substrates and catalysts on the RTIL [C$_n$mim][X] series. To circumvent this limitation, we performed a comparative study of solubility of Li, Hg and La chlorides between the [C$_n$mim][X] and [C$_n$O$_m$mim][X] series as a prospective study. The three salts tested were chosen in order to allow us to predict the potential solubility of each RTIL of different types of a diverse range of transition metals and inorganic species that could eventually be used in different applications.

Solubility data for LiCl, HgCl$_2$ and LaCl$_3$ in several RTILs is presented in Table 6.

Table 6. Observed solubility constants (K_s) of LiCl, HgCl$_2$ and LaCl$_3$ in several RTILs.

Entry	Ionic liquid	K_s[a] (LiCl)[b]	K_s[a] (HgCl$_2$)[c]	K_s[a] (LaCl$_3$)[c]
1	[C$_2$OHmim][PF$_6$]	144.47	44.64	32.47
2	[C$_2$OHmim][BF$_4$]	18.46	84.73	54.01
3	[C$_3$Omim][PF$_6$]	12.44	50.13	37.61
4	[C$_3$Omim][BF$_4$]	14.43	220.86	180.27
5	[C$_5$O$_2$mim][Cl]	9.98	295.34	379.23
6	[C$_5$O$_2$mim][PF$_6$]	35.52	147.48	97.22
7	[C$_5$O$_2$mim][BF$_4$]	21.36	174.17	292.46
8	[C$_4$mim][PF$_6$]	12.08	4.06	6.58
9	[C$_4$mim][BF$_4$]	15.54	41.41	10.92
10	[C$_8$mim][PF$_6$]	35.32	32.98	8.49
11	[C$_8$mim][BF$_4$]	56.02	35.92	53.25
12	[C$_{10}$mim][BF$_4$]	12.64	2.12	47.12

[a] Observed K_s (10^{-6} g of salt g^{-1} of RTIL); [b] determined by flame photometry; [c] determined by inductively coupled plasma spectroscopy (ICP).

We found that LiCl has, in general, a low solubility in the RTILs studied, except for [C$_2$OHmim][PF$_6$] (entry 1). The solubility of LiCl in the RTIL with [C$_3$Omim] cation structure is similar to the solubility in the RTIL with the [C$_4$mim] cation structure (entries 3 and 4 vs entries 8 and 9). The same is observed between the RTILs [C$_5$O$_2$mim][PF$_6$] and [C$_8$mim][PF$_6$] (entry 6 vs entry 10).

Our results show that the solubility of LiCl in RTIL [C_5O_2mim][BF_4] is less than half of that in the RTIL [C_8mim][BF_4], which is unexpected on account of the presence of the ether functionality (entry 7 vs entry 11). In general, we did not detect a considerable difference in solubility for LiCl between the new RTIL [$C_nO_m$mim][X] and the [$C_n$mim][X] series. Among the RTILs, [C_2OH-mim][PF_6] is a notable exception which appears to be the appropriate RTIL to solubilise LiCl and comparable alkaline metals.

With regard to the solubility of $HgCl_2$, we verified that the new RTILs [$C_nO_m$mim][X] allow a higher dissolution than the [$C_n$mim][X] series: both [C_2OHmim][PF_6] and [C_3Omim]-[PF_6] solubilise an amount of $HgCl_2$ eleven or more times higher than [C_4mim][PF_6] (entries 1 and 3 vs entry 8). The RTIL [C_3Omim][BF_4] was found to solubilise $HgCl_2$ three and five times better than the RTILs [C_2OHmim][BF_4] and [C_4mim][BF_4], respectively (entry 4 vs entries 2 and 9). In the same line, RTILs containing the [C_5O_2mim] cation solubilise $HgCl_2$ five to six times better than those having the [C_8mim] cation (entries 5 and 6 vs entries 10 and 11). From the above observations, we can conclude that the new RTILs (in particular [C_3Omim][BF_4], [C_5O_2mim][BF_4] and [C_5O_2mim][PF_6]) are more efficient at solubilising $HgCl_2$ and possibly other transition metals.

Similar to $HgCl_2$, $LaCl_3$ is more soluble in the [C_nO_m-mim][X] series than in the [$C_n$mim][X] series: both [C_2OH-mim][PF_6] and [C_3Omim][PF_6] solubilise $LaCl_3$ five or more times better than [C_4mim][PF_6] (entries 1 and 3 vs entry 8). $LaCl_3$ has a solubility in [C_3Omim][BF_4] which is three to sixteen times higher than in [C_2OHmim][BF_4] and [C_4mim][BF_4], respectively (entry 4 vs entries 2 and 9). The RTILs containing the [C_5O_2mim] cation solubilise $LaCl_3$ five to eleven times better than those containing the [C_8mim] cation (entries 6 and 7 vs entries 10 and 11). From the above results obtained for $LaCl_3$, we expect that the most appropriate RTILs to solubilise lanthanides are [C_5O_2mim][BF_4] and [C_3Omim][BF_4].

In general, the solubility behaviour of $HgCl_2$ and $LaCl_3$ is similar for the RTILs [$C_nO_m$mim][X] and [$C_n$mim][X]. The RTILs containing BF_4^- are better solvents than the corresponding RTILs with the PF_6^- anion. The cation structure of the RTIL also influences the solubility of $HgCl_2$ and $LaCl_3$, which increases with chain size: [C_2OHmim] < [C_3Omim] < [C_5O_2mim] and [C_4mim] < [C_8mim]. In contrast, LiCl presents very different solubility behaviour in the RTILs studied.

The solubility profile presented here for LiCl, $HgCl_2$ and $LaCl_3$ should be valid for alkaline, transition metals and lanthanides salts, respectively.

Conclusion

The new [$C_nO_m$mim][X] RTILs described here show a set of properties (solubility in common solvents, viscosity, solid–liquid phase transition, density and solubility of inorganic salts) that could extend the range of applications this new media has to offer. We have shown that the presence of hydroxyl or ether functional groups promotes remarkable changes on the solubility of inorganic salts, arising from the possibility of new interactions occurring. Taking advantage of the general properties of RTILs and the presence of these extra potential complexing groups, new specific applications of the RTILs [$C_nO_m$mim][X] series presented here are expected to emerge.

Experimental Section

General remarks: All glassware was oven-dried and cooled in a desiccator (P_2O_5 desiccant) prior to use. Commercially supplied reagents were used as supplied.

All aqueous solutions were prepared with distilled water.

The room temperature ionic liquids (RTIL) 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6], 1-*n*-butyl-3-methylimidazolium tetrafluoroborate [C_4mim][BF_4], 1-*n*-octyl-3-methylimidazolium hexafluorophosphate [C_8mim][PF_6], 1-*n*-octyl-3-methylimidazolium tetrafluoroborate [C_8mim][BF_4], 1-*n*-decyl-3-methylimidazolium hexafluorophosphate [C_{10}mim][PF_6], 1-*n*-decyl-3-methylimidazolium tetrafluoroborate [C_{10}mim][BF_4] were prepared according to reported procedures.[1c, 14]

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX400 spectrometer. Chemical shifts are reported downfield in ppm from a tetramethylsilane reference. [D_6]toluene was used as an internal reference in the case of neat samples. IR spectra were recorded on a Mattson Instruments model Satellite FTIR as thinly dispersed films. The samples for elemental analysis were performed by Laboratório de Análises at Instituto Superior Técnico (Lisbon). The differential scanning calorimetry (DSC) experiments were performed with a 2920MDSC system from TA Instruments Inc. The water content of each RTIL was determined by a volumetric Aquastar Karl Fischer titration. Each RTIL sample (2 mL scale) used for elemental analysis and DSC experiments was further purified by flash column chromatography (eluent: dichloromethane) followed by removal of the volatile components under high vacuum (6×10^{-6} mbar) at room temperature for 24 h.

Viscosity: The viscosity of each RTIL was measured with a Brookfield, Model RVT DV-II viscosimeter. For each analysis, an 8-mL sample was used and the measurements were performed in duplicate. The temperature of the samples was maintained to ±0.1 °C by means of an external temperature controller.

Density: The density of each RTIL was determined with a picnometer. For each analysis a 1-mL sample was used and the mass of that volume of liquid was determined. The measurements were repeated three times and the average value is reported. All measurements were taken at room temperature (25 ± 1 °C).

Solid–liquid phase transition analysis: The calorimetric measurements were performed with a 2920MDSC system from TA Instruments Inc. Dry high-purity He gas with a flow rate of 30 $cm^3 min^{-1}$ was purged through the sample. Cooling was accomplished with the liquid nitrogen cooling accessory (LNCA) which provides automatic and continuous programmed sample cooling down to −150 °C.

The baseline was calibrated by scanning the temperature domain of the experiments with an empty pan. The temperature calibration was performed taking the onset of the endothermic melting peak of several calibration standards: *n*-decane ($T_m = 243.75$ K), *n*-octadecane ($T_m = 301.77$ K), hexatriacontane ($T_m = 347.30$ K), indium ($T_m = 430.61$ K) and tin ($T_m = 506.03$ K). The organic standards were high-purity Fluka products, while the metal standards were supplied by TA Instruments Inc. The enthalpy was calibrated with indium (melting enthalpy $\Delta H_m = 28.71$ J g^{-1}).

Solubility of inorganic salts in RTILs: The solubility of inorganic salts in each RTIL was measured by Inductively Coupled Plasma spectroscopy (ICP) for Hg and La, and by flame photometry (Corning flame photometer 410) for Li.

For preparation of the samples we used 1.00 g of each ionic liquid followed by the addition of excess inorganic salt ($HgCl_2$, LiCl and $LaCl_3$). This mixture was stirred at room temperature for 48 h and then filtered, weighed (range: 150–380 mg) and diluted with distilled water (100 mL). By means of this procedure we prepared the initial solutions that, in a number of cases, were diluted to the calibration range of the method used.

Preparation of ionic liquids

[C$_2$OHmim][Cl]: 1-Chloroethanol (64 mL, 0.95 mol) and 1- methylimidazole (50 mL, 0.63 mol) were added to a round-bottomed flask fitted with a reflux condenser for 24 h at 80 °C with stirring until two phases formed. The top phase, containing unreacted starting material, was decanted and diethyl ether (50 mL) was added with thorough mixing. The diethyl ether was decanted followed by addition of fresh solvent and this step was repeated twice. The bottom phase was washed with diethyl ether (4 × 25 mL), heated at 80 °C and stirred under vacuum (0.5 mmHg) for 2 d. The product was obtained as a slightly yellow liquid which solidified on cooling (84.00 g, 82 %). ^{1}H NMR (400 MHz, D$_2$O, 25 °C): $\delta = 3.80$ (s, 3H), 3.84 (d, J(H,H) = 4.6 Hz, 2H) 4.22 (t, J(H,H) = 8.8 Hz, 2H), 7.36 (s, 1H), 7.41 (s, 1H), 8.66 (s, 1H); ^{13}C NMR (100 MHz, D$_2$O, 25 °C): $\delta = 35.73$, 51.52, 59.79, 122.43, 123.59, 136.37; IR (film): $\tilde{\nu}_{max} = 648.5$, 751.1, 840.8, 945.1, 1068.9, 1167.9, 1339.9, 1452.3, 1574.4, 1643.1, 2888.3, 2961.0, 3160.8, 3392.2 cm^{-1}; elemental analysis calcd (%) for C$_6$H$_{12}$N$_2$OCl (163.63): C 44.04, H 7.30, N 17.12; found: C 44.08, H 6.92, N 17.10.

[C$_2$OHmim][PF$_6$]: [C$_2$OHmim][Cl] (25.00 g, 0.15 mol) was transferred to a plastic Erlenmeyer flask (250 mL). Acetone (150 mL) was added followed by KPF$_6$ (31.00 g, 0.17 mol). This mixture was stirred at room temperature for 24 h. The resulting waxy solid precipitate was collected by filtration and washed with acetone (2 × 100 mL). The organic layer was collected, dried (MgSO$_4$), filtered and the solvent removed in vacuum to give the product [C$_2$OHmim][PF$_6$] (37.00 g, 91 %) as a colourless liquid; water content of 0.85 µg (H$_2$O) mL^{-1} (RTIL). ^{1}H NMR (400 MHz, neat, 25 °C): $\delta = 3.88$ (s, 3H), 3.91 (t, J(H,H) = 9.8 Hz, 2H), 4.29 (t, J(H,H) = 9.2 Hz, 2H), 4.74 (s, 3H), 7.42 (s, 1H), 7.48 (s, 1H), 8.69 (s, 1H); ^{13}C NMR (100 MHz, neat, 25 °C): $\delta = 36.10$, 52.00, 60.20, 122.90, 124.10, 136.80; IR (film): $\tilde{\nu}_{max} = 651.8$, 703.1, 750.2, 839.5, 943.0, 1068.4, 1170.2, 1247.3, 1360.3, 1452.3, 1579.2, 1705.0, 2896.2, 2967.5, 3172.3, 3412.6, 3591.4 cm^{-1}; elemental analysis calcd (%) for C$_6$H$_{12}$N$_2$OPF$_6$ (273.14): C 26.48, H 4.07, N 10.29; found: C 26.53, H 4.08, N 10.20.

[C$_2$OHmim][BF$_4$]: [C$_2$OHmim][Cl] (25.00 g, 0.15 mol) was transferred to a plastic Erlenmeyer flask (250 mL). Acetone (150 mL) was added followed by NaBF$_4$ (19.00 g, 0.17 mol). This mixture was stirred at room temperature for 24 h. The resulting waxy solid precipitate was collected by filtration and washed with acetone (2 × 100 mL). The combined layer was collected, dried (MgSO$_4$), filtered and the solvent removed in vacuum to give the product [C$_2$OHmim][BF$_4$] (30.00 g, 93 %) as a colourless liquid; water content of 4.68 µg (H$_2$O) mL^{-1} (RTIL). ^{1}H NMR (400 MHz, neat, 25 °C): $\delta = 3.75$ (m, 2H), 4.16 (t, J(H,H) = 10.0 Hz, 2H), 4.61 (s, 3H), 7.30 (s, 1H), 7.35 (s, 1H), 8.58 (s, 1H); ^{13}C NMR (100 MHz, neat, 25 °C): $\delta = 35.10$, 51.50, 59.70, 122.40, 123.60, 136.30; IR (film): $\tilde{\nu}_{max} = 652.2$, 702.7, 755.2, 846.2, 1059.1, 1169.6, 1252.2, 1287.3, 1340.3, 1452.9, 1575.4, 1705.0, 2894.3, 2966.2, 3123.4, 3164.8, 3546.5 cm^{-1}; elemental analysis calcd (%) for C$_6$H$_{12}$N$_2$OBF$_4$ · 0.5 H$_2$0 (223.99): C 32.17, H 5.60, N 12.51; found: C 32.31, H 5.36, N 12.53.

[C$_2$OHmim][TFA]: [C$_2$OHmim][Cl] (3.00 g, 0.013 mol) was transferred to a plastic Erlenmeyer flask (1000 mL). Acetone (20 mL) was added followed by NaCF$_3$CO$_2$ (2.81 g, 0.021 mol). This mixture was stirred at room temperature for 24 h. The resulting waxy solid precipitate was collected by filtration and washed with acetone (2 × 25 mL). The organic layer was collected, refiltered and the solvent removed in vacuum to give the product [C$_2$OHmim][TFA] (2.81 g, 94 %) as a colourless liquid. ^{1}H NMR (400 MHz, neat, 25 °C): $\delta = 3.73$ (m, 2H), 4.15 (brs, 2H), 4.59 (s, 3H), 7.35 (s, 1H), 7.43 (s, 1H), 8.86 (s, 1H); ^{13}C NMR (100 MHz, neat, 25 °C): $\delta = 36.06$, 48.36, 60.06, 119.13, 123.12, 135.16; IR (film): $\tilde{\nu}_{max} = 721.4$, 833.1, 945.3, 1075.9, 1135.3, 1341.1, 1426.7, 1574.2, 1689.7, 2885.9, 2964.3, 3286.3 cm^{-1}; elemental analysis calcd (%) for C$_8$H$_{12}$N$_2$O$_3$F$_3$ · 0.5 H$_2$O (250.19): C 38.37, H 5.18, N 11.11; found: C 38.22, H 5.20, N 11.17.

[C$_4$OHmim][Br]: The same procedure was followed as that described above for [C$_2$OHmim][Cl], except for the use of bromobutanol (133 mL, 0.95 mol) instead of chloroethanol. The product [C$_4$OHmim][Br] (114.00 g, 79 %) was obtained as a colourless liquid. ^{1}H NMR (400 MHz, neat, 25 °C): $\delta = 0.68$ (brs, 2H), 0.94 (m, 2H), 2.31 (m, 2H), 2.68 (brs, 2H), 3.23 (s, 1H), 4.60 (s, 3H), 6.87 (s, 1H), 6.94 (s, 1H), 8.46 (s, 1H); ^{13}C NMR (100 MHz, neat, 25 °C): $\delta = 26.23$, 28.44, 36.07, 44.81, 60.05, 119.13, 123.15, 135.17; IR (film): $\tilde{\nu}_{max} = 625.0$, 762.1, 831.6, 903.3, 1086.3, 1171.6, 1283.6, 1331.0, 1380.4, 1450.0, 1550.3, 1581.7, 1639.2, 2616.6, 2837.8, 2946.1, 3399.5 cm^{-1}; elemental analysis calcd (%) for C$_8$H$_{16}$N$_2$OBr (235.90): C 40.70, H 6.78, N 11.87; found: C 40.65, H 6.90, N 11.41.

[C$_3$Omim][Cl]: The same procedure was followed as that described above for [C$_2$OHmim][Cl], except for the use of 2-chloroethylmethyl ether (87 mL, 0.95 mol) instead of chloroethanol. The product [C$_3$Omim][Cl] (89.00 g, 80 %) was obtained as a slightly yellow oil that solidified on cooling. ^{1}H NMR (400 MHz, D$_2$O, 25 °C): $\delta = 3.28$ (s, 3H), 3.73 (t, J(H,H) = 12.0 Hz, 2H), 3.80 (s, 3H), 4.29 (t, J(H,H) = 12.0 Hz, 2H), 7.34 (s, 1H), 7.40 (s, 1H), 8.64 (s, 1H); ^{13}C NMR (100 MHz, D$_2$O, 25 °C): $\delta =$ 35.53, 48.73, 58.09, 69.72, 122.49, 123.55, 136.40; IR (film): $\tilde{\nu}_{max} = 653.9$, 760.2, 833.5, 968.3, 1013.8, 1083.2, 1171.0, 1285.1, 1453.1, 1572.9, 1572.9, 1640.4, 2834.3, 3433.7 cm^{-1}; elemental analysis calcd (%) for C$_7$H$_{14}$N$_2$OCl (177.65): C 47.33, H 7.90, N 15.75; found: C 47.29, H 7.65, N 15.55.

[C$_3$Omim][PF$_6$]: The same procedure was followed as that described above for [C$_2$OHmim][PF$_6$]: [C$_3$Omim][Cl] (25.00 g, 0.14 mol) and KPF$_6$ salt (29.00 g, 0.16 mol) were used, and the product [C$_3$Omim][PF$_6$] (37.00 g, 93 %) was obtained as a colourless liquid; water content of 1.74 µg (H$_2$O) mL^{-1} (RTIL); ^{1}H NMR (400 MHz, neat, 25 °C): $\delta = 3.27$ (s, 3H), 3.73 (brs, 2H), 3.88 (s, 3H), 4.30 (brs, 2H), 7.35 (s, 1H), 7.42 (s, 1H), 8.42 (s, 1H); ^{13}C NMR (100 MHz, neat, 25 °C): $\delta = 36.89$, 50.61, 59.19, 70.99, 124.27, 124.73, 138.12; IR (film): $\tilde{\nu}_{max} = 652.8$, 749.6, 836.9, 968.7, 1013.8, 1084.6, 1169.8, 1226.5, 1340.5, 1453.5, 1574.0, 2839.9, 2902.6, 2943.0, 3125.7, 3170.4, 3595.1, 3667.8 cm^{-1}; elemental analysis calcd (%) for C$_7$H$_{14}$N$_2$OPF$_6$ (287.17): C 29.38, H 4.58, N 9.79; found: C 29.30, H 4.60, N 9.80.

[C$_3$Omim][BF$_4$]: The same procedure was followed as that described above for [C$_2$OHmim][BF$_4$]: [C$_3$Omim][Cl] (25.00 g, 0.14 mol) and NaBF$_4$ salt (17.00 g, 0.16 mol) were used, and the product [C$_3$Omim][BF$_4$] (31.00 g, 96 %) was obtained as a colourless liquid; water content of 2.55 µg (H$_2$O) mL^{-1} (RTIL). ^{1}H NMR (400 MHz, neat, 25 °C): $\delta = 3.27$ (s, 3H), 3.72 (brs, 2H), 3.78 (s, 3H), 4.28 (brs, 2H), 7.33 (s, 1H), 7.39 (s, 1H), 8.50 (s, 1H); ^{13}C NMR (100 MHz, neat, 25 °C): $\delta = 38.06$, 51.27, 60.63, 72.25, 125.03, 126.09, 139.12; IR (film): $\tilde{\nu}_{max} = 653.5$, 756.7, 835.2, 1075.3,1171.3, 1286.5, 1340.1, 1454.3, 1574.4, 2838.7, 2902.6, 2943.1, 3123.2, 3163.1, 3563.8, 3635.4 cm^{-1}; elemental analysis calcd (%) for C$_7$H$_{14}$N$_2$OBF$_4$ · 0.5 H$_2$O(238.01): C 35.29, H 6.30, N 11.76; found: C 35.67, H 6.12, N 11.81.

[C$_5$O$_2$mim][Cl]: The same procedure was followed as that described above for [C$_2$OHmim][Cl], except for the use of 1-chloro-2-(2-methoxyethoxy)-ethane (98 mL, 0.95 mol) instead of 1-chloroethanol. The product [C$_5$O$_2$mim][Cl] (104.00 g, 75 %) was obtained as a slightly yellow liquid; water content of 4.31 µg (H$_2$O) mL^{-1} (RTIL). ^{1}H NMR (400 MHz, neat, 25 °C): $\delta = 3.30$ (s, 3H), 3.53 (brs, 2H), 3.65 (brs, 2H), 3.90 (brs, 2H), 3.99 (s, 3H), 4.44 (brs, 2H), 7.58 (s, 1H), 7.66 (s, 1H), 8.92 (s, 1H); ^{13}C NMR (100 MHz, neat, 25 °C): $\delta = 36.31$, 50.06, 58.57, 68.94, 71.43, 72.00, 123.52, 123.9, 137.71; IR (film): $\tilde{\nu}_{max} = 654.9$, 763.1, 846.8, 920.3, 1025.4, 1104.6, 1171.6, 1246.9, 1297.5, 1355.1, 1453.5, 1572.3, 1665.2, 1713.5, 2878.8, 2980.7, 3067.2, 3144.2, 3381.4 cm^{-1}; elemental analysis calcd (%) for C$_9$H$_{18}$N$_2$O$_2$Cl · 0.2 H$_2$O (225.31): C 47.93, H 8.08, N 12.43; found: C 47.90, H 8.13, N 12.80.

[C$_5$O$_2$mim][PF$_6$]: The same procedure was followed as that described above for [C$_2$OHmim][PF$_6$]: [C$_5$O$_2$mim][Cl] (25.00 g, 0.11 mol) and KPF$_6$ salt (23.00 g, 0.13 mol) were used, and the product was obtained [C$_5$O$_2$mim][PF$_6$] (34.00 g, 94 %) as a colourless liquid; water content of 2.02 µg (H$_2$O) mL^{-1} (RTIL). ^{1}H NMR (400 MHz, neat, 25 °C): $\delta = 3.48$ (s, 3H), 3.71 (brs, 2H), 3.82 (brs, 2H), 4.05 (brs, 2H), 4.10 (s, 3H), 4.51 (brs, 2H), 7.59 (s, 1H), 7.68 (s, 1H), 8.73 (s, 1H); ^{13}C NMR (100 MHz, neat, 25 °C): $\delta = 35.26$, 49.05, 57.45, 67.88, 69.47, 70.88, 122.46, 122.90, 136.45; IR (film): $\tilde{\nu}_{max} = 653.2$, 750.9, 842.7, 1025.0, 1104.2, 1170.4, 1198.7, 1247.9, 1299.2, 1354.2, 1435.7, 1575.2, 1620.3, 2884.6, 2929.7, 3122.8, 3167.9, 3413.0, 3645.4 cm^{-1}; elemental analysis calcd (%) for C$_9$H$_{18}$N$_2$O$_2$PF$_6$ · H$_2$0 (349.22): C 30.95, H 5.73, N 8.02; found: C 30.72, H 5.35, N 8.05.

[C$_5$O$_2$mim][BF$_4$]: The same procedure was followed as that described above for [C$_2$OHmim][BF$_4$]: [C$_5$O$_2$mim][Cl] (25.00 g, 0.11 mol) and NaBF$_4$ salt (14.00 g, 0.13 mol) were used, and the product was obtained [C$_5$O$_2$mim][BF$_4$] (29.00 g, 97 %) as a colourless liquid; water content of 2.30 µg (H$_2$O) mL^{-1} (RTIL). ^{1}H NMR (400 MHz, neat, 25 °C): $\delta = 3.31$ (s, 3H), 3.53 (brs, 2H), 3.65 (brs, 2H), 3.89 (brs, 2H), 4.01 (s, 3H), 4.45 (brs, 2H), 7.58 (s, 1H), 7.67 (s, 1H), 8.93 (s, 1H); ^{13}C NMR (100 MHz, neat, 25 °C): $\delta = 35.20$, 49.95, 57.46, 67.83, 69.40, 70.90, 122.41, 122.84, 136.61; IR (film): $\tilde{\nu}_{max} = 653.6$, 757.1, 845.8, 923.9, 1063.2, 1171.7, 1248.3, 1286.5, 1354.0, 1454.1, 1574.6, 1631.1, 1719.0, 2885.4, 2926.5, 3120.5, 3161.2, 3394.3, 3609.7 cm^{-1}; elemental analysis calcd (%) for C$_9$H$_{18}$N$_2$O$_2$BF$_4$ (273.06): C 39.59, H 6.60, N 10.26; found: C 39.40, H 6.46, N 10.31.

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