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Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains†

Andrew P. Abbott, Glen Capper, David L. Davies,* Helen L. Munro, Raymond K. Rasheed and Vasuki Tambyrajah

Department of Chemistry, University of Leicester, Leicester, UK LE1 7RH. E-mail: dld3@le.ac.uk

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A range of novel, moisture-stable, Lewis-acidic ionic liquids has been prepared by mixing appropriate molar ratios of MCl_2 (M = Zn and/or Sn) and quaternary ammonium salts of formula $[Me_3NC_2H_4Y]Cl$ (Y = OH, Cl, OC(O)Me, OC(O)Ph); the influence of substituent Y and metal M on the physical properties of the melts has been investigated.

Ionic liquids, or room temperature molten salts, have attracted increasing interest over recent years, particularly in the area of green chemistry, due to their advantageous properties including negligible vapour pressure and wide liquid range.[1–3] Work has focussed on liquids formed from dialkylimidazolium halides which are readily prepared from 1-methylimidazole and a slight excess of the desired haloalkane.[4] Addition of a suitable molar ratio of aluminium chloride to these salts gives rise to ionic liquids containing complex metal anions which have been used in a number of applications such as electroplating, electrochemical devices and catalysts for organic synthesis.[1,4–6] The main disadvantage of imidazolium-based liquids is their relatively high cost for bulk applications, whilst chloroaluminate ionic liquids have the additional problem of their low tolerance to moisture, necessitating the use of glove box and Schlenk techniques to prepare and investigate their properties. The former problem may be overcome by using cheaper ammonium salts whereas the latter may be solved by replacing aluminium with less reactive metals.

Recently, Freeman and coworkers have characterised ionic liquids formed from $FeCl_2$ or $FeCl_3$ and 1-butyl-3-methylimidazolium chloride.[7] However, other examples of ionic liquids made from metal chlorides other than aluminium are less well characterised and are mainly cited in conference proceedings[8] or in the patent literature.[9,10] Here we report the synthesis and characterisation of new moisture-stable, Lewis-acidic ionic liquids made from metal chlorides and quaternary ammonium salts that are commercially available or simple to synthesise. These offer the potential to tailor the physical properties *e.g.* melting point, viscosity and conductivity, and to tune the Lewis acidity by choosing a different metal or indeed combinations of metals.

To investigate the parameters necessary for a salt to be liquid at or near room temperature we have heated a range of ammonium salts with zinc chloride in a 1 : 2 molar ratio and the results are shown in Table 1.‡ Using salts of symmetrical cations, H_4NCl and Me_4NCl, no liquid is formed below 200 °C whereas with the longer chain NEt_4Cl the freezing point was *ca.* 90 °C. It has been established in the imidazolium systems that reducing the symmetry of the cation leads to a lower freezing point for the ionic liquid, thus, we have examined cations of the general formula Me_3NR^+. Using Me_3NEt^+ gives a freezing range of 53–55 °C, *i.e.* a reduction of *ca.* 35 or 140 °C compared with Et_4N^+ and Me_4N^+ respectively. However, we have found that functionalised ethyl chains, $Me_3NC_2H_4Y^+$, give even lower freezing points; *e.g.* if Y = OH or Cl, room temperature liquids are observed with freezing points of 23–25 °C. Even when the substituent is significantly larger, *e.g.* Y = OC(O)Me or OC(O)Ph, the salts formed have lower freezing points than for Me_3NEt^+. These results suggest that both lower symmetry and the presence of a functional group reduce the freezing points of the salts formed, though the exact role of the functional substituent is not yet clear. In all cases the liquids formed are viscous and hygroscopic but moisture-stable so can be easily prepared and stored without the need for specialist equipment.

Since choline chloride, $[Me_3NC_2H_4OH]Cl$, gave the lowest freezing point we have characterised this system in more detail. Heating mixtures of choline chloride and zinc chloride in molar ratios between 1 : 1 and 1 : 3 gave rise to clear colourless liquids, with the freezing points varying between *ca.* 65 °C (1 : 1), 25 °C (1 : 2) and 45 °C (1 : 3). Unlike analogous aluminium systems,[4,11,12] ratios with a molar excess of choline chloride, *i.e.* basic melts, do not form ambient temperature liquids in these systems. This would imply that complex zinc anions, in which the charge can be delocalised, are necessary in the formation of these ionic liquids. Further characterisation of the 1:2 liquid is described below.

A ^1H NMR spectrum of the neat ionic liquid was recorded and shows resonances at δ 2.97, 3.34 and 3.94 assigned to the methyl groups, N–CH_2 protons, and the CH_2OH protons, respectively, of the choline cation. All signals were broad and poorly resolved, even at 80 °C, due to the viscosity of the melt. The FAB mass spectrum shows the presence of complex zinc chloride ions $[ZnCl_3]^-$, $[Zn_2Cl_5]^-$ and $[Zn_3Cl_7]^-$. Higher clusters are also detectable but occurred at very low intensities. Similar species have been observed in aluminium chloride-based ionic liquids.[13]

The ionic liquid has a conductivity of 36 μS cm^{-1} at 40 °C and this increases exponentially with temperature, due to a decrease in the viscosity and hence an increase in the mobility of the ions in the melt.† The conductivity is similar to that found in alkylpyridinium-based ionic liquids[14] and is sufficient for them to be suitable media for electrochemical applications such

Table 1 Freezing points for the materials formed from heating a quaternary ammonium chloride and MCl_2 (M = Zn, Sn) in a 1 : 2 molar ratio

	Cation	M	Freezing point/°C
1	NH_4	Zn	> 200
2	Me_4N	Zn	> 200
3	Et_4N	Zn	90–92
4	Me_3NEt	Zn	53–55
5	$Me_3NCH_2CH_2OH$	Zn	23–25
6	$Me_3NCH_2CH_2Cl$	Zn	23–25
7	$Me_3NCH_2CH_2OC(O)Me$	Zn	30–32
8	$Me_3NCH_2CH_2OC(O)Ph$	Zn	46–48
9	$Me_3NCH_2CH_2OH$	Sn	43–45
10	$Me_3NCH_2CH_2Cl$	Sn	69–71
11	$Me_3NCH_2CH_2OC(O)Me$	Sn	13–15
12	$Me_3NCH_2CH_2OH$	Zn/Sn[a]	21–23

[a] The ratio $[Me_3NCH_2CH_2OH]Cl : ZnCl_2 : SnCl_2$ was 1 : 1 : 1.

† Electronic supplementary information (ESI) available: plot of conductivity *vs.* temperature for the ionic liquid formed from zinc chloride and choline chloride (2 : 1). See http://www.rsc.org/suppdata/cc/b1/b106357j/

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as batteries and metal deposition. The liquids provide an electrochemical window of about 2 V positive from the Zn/Zn^{2+} couple. Further details of the conductivity and electrochemical properties are reported elsewhere.[15]

Having established that the cationic component can be varied we have also investigated changing the metal-containing, *i.e.* anionic, component. Heating choline chloride and $SnCl_2$ in a 1 : 2 molar ratio provides a viscous liquid which has a freezing range of 43–45 °C. The negative ion FAB mass spectrum shows the presence of $[SnCl_3]^-$ and $[Sn_2Cl_5]^-$; however, no higher ions are observed in this case. For the tin-containing melts the liquid formed from $[YC_2H_4NMe_3]Cl$ (Y = OC(O)Me) gave the lowest melting point. Heating choline chloride : $ZnCl_2$: $SnCl_2$ in a 1 : 1 : 1 molar ratio gives a liquid with a freezing point of 21–23 °C, *i.e.* similar to the pure zinc-containing melt but significantly lower than the pure tin-containing one. The FAB mass spectrum of this liquid shows the presence of the individual metal-containing ions and the mixed metal ion $[SnZnCl_5]^-$. Mixed metal melts allow the possibility of tuning the catalytic properties of the liquids, as well as opening up possibilities for electrodeposition of metal alloys.

To conclude, we have shown that heating functionalised quaternary ammonium halides $[Me_3NC_2H_4Y]Cl$ and MCl_2 (M = Zn, Sn) gives materials that are conducting, viscous liquids at or around room temperature. The freezing points are dependent upon the symmetry of the cation and upon the nature of the functionalised side chain. The advantages of these new ionic liquids over presently available metal-containing ionic liquids are that they are insensitive to moisture and are much cheaper than imidazolium-based liquids. In addition, their Lewis acidity can be altered by varying the metal chloride(s) used. The use of these liquids as catalysts for the Diels–Alder reaction of acroleins and dienes will be reported elsewhere.

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Notes and references

‡ The general route for the synthesis of the ionic liquids was as follows: quaternary ammonium salt (20 mmol) was mixed with zinc chloride (40 mmol) and heated to *ca*. 150 °C in air with stirring until a clear colourless liquid was obtained. In contrast with the usual $AlCl_3$-based ionic liquids the reaction appears to be endothermic.

Drying the liquids under vacuum at 100 °C overnight has only a small effect on the freezing point, a few degrees, suggesting that immediately after preparation the liquids do not contain much water. The liquids are at least as thermally stable as $AlCl_3$-based liquids, and can be heated to at least 190 °C.

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