Inorg. Chem. **2004**, *43*, 3447–3452

Inorganic Chemistry
Article

Ionic Liquids Based upon Metal Halide/Substituted Quaternary Ammonium Salt Mixtures

Andrew P. Abbott,* Glen Capper, David L. Davies, and Raymond Rasheed

Chemistry Department, University of Leicester, Leicester LE1 7RH, U.K.

Received January 16, 2004

The synthesis of ionic liquids based upon functionalized quaternary ammonium salts and metal salts of zinc, tin, or iron is demonstrated. The freezing point of these ionic liquids was studied as a function of the quaternary ammonium cation. The complex anions were identified and quantified using mass spectrometry and potentiometry. It is shown that the primary zinc anion is $Zn_2Cl_5^-$ with $Zn_3Cl_7^-$ becoming more abundant in more Lewis basic solutions. Similar results were observed for ionic liquids containing $SnCl_2$. The surface tension was also measured and was used to explain the high viscosity of the ionic liquids in terms of the large ion:hole size ratio and the small probability of finding a hole of suitable dimensions adjacent to a given ion to permit movement. The phase behavior of a variety of quaternary ammonium halides/$ZnCl_2$ mixtures is characterized and it is shown that the depression of freezing point is related to the increase in size of the component ions.

Introduction

In recent years ambient-temperature ionic liquids have been studied extensively for both catalytic and electrochemical applications.[1−3] They are of interest because they have negligible vapor pressure, large liquid temperature ranges, wide potential windows, and high ionic conductivities, and in some cases they are Lewis acid catalysts. Early investigations focused on imidazolium or pyridinium cations with chloroaluminate anions although increasing amounts of work have been carried out using inert anions such as BF_4^- and PF_6^-. Osteryoung[4] showed that *n*-butylpyridinium salts gave liquids over a wide range of composition with $AlCl_3$, and similar results were found using *n*-alkylimidazolium chloroaluminate melts.[5] The chemistry of these ionic liquids is controlled by the chloroaluminate anions; the relative proportions of each anion change considerably with melt composition.[6] These melts have been used for metal deposition, for aluminum batteries, and as media in which to carry out a variety of reactions.[7,8]

The water sensitivity of chloroaluminate melts coupled with the cost of imidazolium salts has hindered the widespread application of these ionic liquids. Relatively few examples have been reported of ionic liquids based on metal salts other than aluminum. It has recently been shown that ionic liquids can be formed using zinc chlorides with pyridinium,[9] dimethylethylphenylammonium,[10] and imidazolium salts.[11−14] These have higher melting points than the corresponding chloroaluminate melts but are still fluid at ambient temperatures. It was also shown that ferric[15] and stannous salts[16,17] form ionic liquids with 1-butyl-3-methylimidazolium chloride. We have recently reported that ionic liquids can be formed using zinc or tin chlorides with substituted quaternary ammonium salts such as choline chloride.[18] Not only are these ionic liquids easy to prepare

---

* Author to whom correspondence should be addressed. E-mail: andrew.abbott@le.ac.uk.

(1) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667. Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A.-C.; Plaquevent, J.-C. *Tetrahedron: Asymmetry* **2003**, *14*, 3081.
(2) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH Verlag: Weinheim, Germany, 2003.
(3) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.
(4) Osteryoung, R. A. *Molten Salt Chemistry*; Mamantov, G., Marassi, D., Eds.; Reidel Publishing: Dordrecht, Holland, 1987.
(5) Osteryoung, R. A.; Robinson, J. *J. Am. Chem. Soc.* **1979**, *101*, 323.
(6) Carpio, R. A.; King, L. A.; Lindstrom, R. E.; Nardi, J. C.; Hussey, C. L. *J. Electrochem. Soc.* **1979**, *126*, 1644.
(7) Wier, T. P. U. S. Patent 2,446,350, 1948.
(8) Zhao, Y.; Vandernoot, T. J. *Electrochim. Acta* **1997**, *42*, 3.
(9) Koura, N.; Endo, T.; Idemoto, Y. *J. Non-Cryst. Solids* **1996**, *205*, 650.
(10) Simanavicius, L.; Stakenas, A.; Starkis, A. *Electrochim. Acta* **1997**, *42*, 1581.
(11) Lin, Y.; Sun, I. *Electrochim. Acta* **1999**, *44*, 2771.
(12) Chen, P.; Lin, M.; Sun, I. *J. Electrochem. Soc.* **2000**, *147*, 3350.
(13) Chen, P.; Sun, I. *Electrochim. Acta* **2001**, *46*, 1169.
(14) Dupont, J.; Suarez, P. A. Z.; Umpierre, A. P.; de Souza, R. F. *Catal. Lett.* **2001**, *73*, 211.
(15) Sitze, M. S.; Schreiter, E. R.; Patterson, E. V.; Freeman, R. G. *Inorg. Chem.* **2001**, *40*, 2298.
(16) Wasserscheid, P.; Waffenschmidt, H. *J. Mol. Catal. A: Chem.* **2002**, *182*, 419.
(17) Parshall, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 8716.

10.1021/ic049931s CCC: $27.50

and water and air insensitive but their low cost enables their use in large-scale applications. We have recently outlined their use for zinc[19] and zinc alloy deposition,[20] batteries,[19] and Diels−Alder and Fisher indole catalysis.[21,22]

Analogous to chloroaluminate ionic liquids, one of the major factors controlling the chemistry and electrochemistry of these zinc- or tin-containing ionic liquids is the form of the complex anion. In this work we outline the chemical and electrochemical properties of ionic liquids formed by $ZnCl_2$, $SnCl_2$, and $FeCl_3$ with a variety of quaternary ammonium salts including characterization of the complex anions present.

Experimental Section

Choline chloride (ChCl) (99%), (2-chloroethyl)trimethylammonium chloride (98%), (2-bromoethyl)trimethylammonium bromide (98%), (3-bromopropyl)trimethylammonium bromide (98%), triethylmethylammonium bromide (99%), triethylhexylammonium bromide (99%), (*S*)-(−)-(3-chloro-2-hydroxypropyl)trimethylammonium chloride (and the (*R*)-(+)- enantiomers) (both 99%), and acetylcholine chloride (98%) and anhydrous metal salts, $ZnCl_2$ (98%), $ZnBr_2$ (98+%), $SnCl_2$ (98%), and $FeCl_3$ (98%), were all obtained from Aldrich and were dried under vacuum before use. Benzoylcholine chloride (99%) and hexyltrimethylammonium bromide (98%) were obtained from Lancaster. Propyltrimethylammonium chloride, ethyltrimethylammonium chloride, and (2-fluoroethyl)trimethylammonium bromide were synthesized by the following procedure:

The appropriate haloalkane (30 mmol) was frozen with liquid N_2 in a Schlenk tube. The tube was then evacuated, an excess of gaseous Me_3N passed into the tube, and the sample refrozen in liquid N_2. The mixture was transferred to a dry ice bath and allowed to thaw to room temperature. Any unreacted Me_3N was evaporated and any unreacted haloalkane removed under vacuum leaving a white solid (yield > 60%), which was characterized by NMR and mass spectroscopy. A similar procedure using $NMe(CH_2CH_2OH)_2$ in place of Me_3N was used to produce $[PhCH_2NMe(CH_2CH_2OH)_2]Cl$ and $[NMe_2(CH_2CH_2OH)_2]I$.

Preparation of Ionic Liquids. A mixture of the metal halide and quaternary ammonium salt in the desired molar ratio (from 4:1 to 1:4) was heated to between 80 and 120 °C with gentle stirring until a clear colorless liquid formed (in the case of $FeCl_3$ a dark brown liquid was obtained).

Measurements. The freezing point for each ionic liquid was determined by the lack of viscous flow of the meniscus. The viscosity was determined using a Brookfield DV-E viscometer fitted with a thermostated jacket. A Krüss K11 tensiometer equipped with a thermostated jacket was used for the surface tension experiments. The equilibrium geometry and volumes of the ions were calculated using a Hartree−Fock method utilizing an STO-3G model provided by commercially available software.[23] Negative ion FAB mass spectrometry was run both with and without NBA present to identify the anionic species present. The presence of NBA did not affect the results obtained.

Table 1. Freezing Points for 1:2 QAS/Metal Halide Ionic Liquids

R_1	R_2	R_3	R_4	anion	metal halide	T_f/°C
Me	Me	Me	C_2H_4OH	Cl^-	$ZnBr_2$	38
Me	Me	Me	C_2H_4OH	Cl^-	$FeCl_3$	65
Me	Me	Me	C_2H_4OH	Cl^-	$SnCl_2$	37
Me	Me	Me	$C_2H_4OC(O)Me$	Cl^-	$ZnBr_2$	48
Me	Me	Me	$C_2H_4OC(O)Me$	Cl^-	$SnCl_2$	20
Me	Me	Me	C_2H_4Cl	Cl^-	$SnCl_2$	63
Me	Me	benz	C_2H_4OH	Cl^-	$SnCl_2$	17
Me	Me	benz	C_2H_4OH	Cl^-	$FeCl_3$	21

Voltammetry. Cyclic voltammetry was carried out using an Autolab/PGSTAT12 potentiostat interfaced with a computer equipped with GPES software. A three-electrode system consisting of a platinum micro working electrode (5×10^{-4} cm radius), a platinum counter electrode, and a reference electrode in the form of a wire was used. The working electrode was polished with 0.3 and 1.0 μm alumina paste prior to all measurements. All voltammograms were taken at 60 °C using a scan rate of 20 mV s^{-1}.

Results and Discussion

Phase Behavior. We have previously reported the preparation of a range of novel, moisture-stable, Lewis-acidic ionic liquids by heating mixtures of 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, or OC(O)Ph).[18] Here we examine the nature of the anionic species present and extend the range of metals and cations. Numerous other anhydrous metal salts were tested (LiCl, $BeCl_2$, NaCl, $MgCl_2$, $AlCl_3$, KCl, $CaCl_2$, $TiCl_4$, VCl_3, $CrCl_3$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $GaCl_3$, YCl_3, $ZrCl_4$, $MoCl_5$, AgCl, $CdCl_2$, $InCl_3$, $SnCl_4$, $SbCl_3$, $HfCl_4$, WCl_4, $AuCl_3$, $HgCl_2$, $PbCl_2$, $BiCl_3$), but none gave materials that were liquid below 100 °C when mixed with choline chloride in a 2:1 ratio (and most were solid above 200 °C). This includes aluminum, which is surprising since chloroaluminate ionic liquids form with a variety of aromatic ammonium salts as well as imidazolium and pyridinium halides. Since benzyltrimethylammonium chloride forms a liquid that freezes below 0 °C and replacing the phenyl group with CH_2OH causes a change in the freezing point of over 200 °C, this reinforces the previous idea that aluminum-containing ionic liquids are stabilized through charge-transfer interactions between the chloroaluminate anion and aromatic portion of the cation.[24] In support of this, $AlCl_3$ was found to form an ionic liquid with $[BzN(Me_2)C_2H_4OH]Cl$ in a 2:1 ratio with a T_f of 88−90 °C and also with benzoylcholine chloride but not with choline chloride or acetylcholine chloride.

In addition to the previously reported $SnCl_2$ and $ZnCl_2$[18] it was found that $FeCl_3$ and $ZnBr_2$ also form materials that freeze below 100 °C when mixed together with choline chloride in a 2:1 ratio. The freezing points of these mixtures are given in Table 1. It is thought that the ability of a metal salt to form a low melting point ionic liquid will be related

---

(18) Abbott, A. P.; Capper, G.; Davies, D. L.; Munro, H.; Rasheed, R. K.; Tambyrajah, V. *Chem. Commun.* **2001**, 2010.

(19) Abbott, A. P.; Capper, G.; Davies, D. L.; Munro, H.; Rasheed, R. K.; Tambyrajah, V. *Ionic Liquids as Green Solvents: Progress and Prospects*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2003; p 439.

(20) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. *Trans. Inst. Met. Finish.* **2001**, *79*, 204.

(21) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. *Green Chem.* **2002**, *4*, 24.

(22) Morales, R. C.; Tambyrajah, V.; Jenkins, P. R.; Davies, D. L.; Abbott, A. P. *Chem. Commun.* **2004**, 158.

(23) *Spartan Pro*; Wave function Inc.: Irvine, CA, 2000.

(24) Abbott, A. P.; Eardley, C. A.; Farley, N. R. S.; Pratt, A. *Trans. Inst. Met. Finish.* **1999**, *77*, 26.

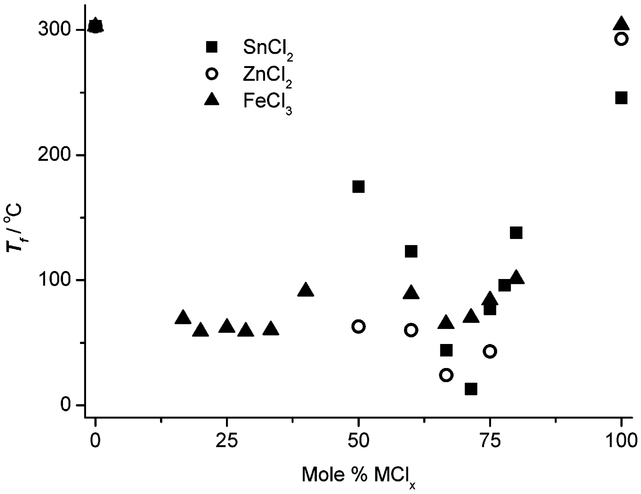

Figure 1. Freezing point for the $ZnCl_2$/ChCl and $SnCl_2$/ChCl systems as a function of composition.

to its own melting point. Hence aluminum chloride (mp = 190 °C) has shown to be useful with a wide range of quaternary ammonium salts. Relatively low melting points are also possessed by the salts used in this study: $ZnCl_2$ (283 °C); $ZnBr_2$ (394 °C); $SnCl_2$ (246 °C); $FeCl_3$ (306 °C). These metal salts also form singly charged complex anions when mixed with halide salts. All of the metal salts listed above that did not form ionic liquids have melting points considerably in excess of 400 °C and most do not form singly charged halometalate complex anions.

The zinc- or tin-containing ionic liquids described above are clear and colorless liquids. They are hygroscopic but moisture stable and insensitive to air. Any water absorbed during storage can be removed by direct heating with no adverse effect on the ionic liquids. The liquids can be frozen and thawed without change to their physical properties. Thus, they can be prepared and stored without the need for specialist Schlenk techniques or dryboxes. Ionic liquids formed between QAS's (quaternary ammonium salts) and iron(III) chloride can also be prepared in ambient conditions but will hydrolyze slowly in the presence of moisture. It is also interesting to note that ionic liquids can be formed with mixed halide salts e.g. ChCl/$ZnBr_2$ (1:2). These do tend to have slightly higher freezing points than those containing one type of halide; however, the depression of freezing point with respect to the pure metal salt is considerably lower.

Figure 1 shows the freezing point of choline chloride mixtures with zinc chloride, tin(II) chloride, and iron(III) chloride. Mixtures with excess ammonium salt, i.e. Lewis basic mixtures, do not form liquids at ambient temperatures with $SnCl_2$ and $ZnCl_2$ but did with $FeCl_3$. In the Lewis basic melts the predominant species will presumably be $SnCl_3^-$ and $ZnCl_3^-$ (see below), and these will have a relatively high charge-to-size ratio and hence a high freezing temperature. Conversely $FeCl_4^-$ behaves in a manner similar to $AlCl_4^-$ and eutectic points are observed in Lewis acidic and Lewis basic compositions. Surprisingly no homogeneous phase could be formed in an equimolar mixture of ChCl and $FeCl_3$, and the reason for this observation is unknown. The freezing point increases considerably as the composition deviates from that of the eutectic mixture. For the zinc chloride/choline chloride mixtures the eutectic is observed at a 2:1 composition, whereas for the tin chloride/choline chloride mixtures it is observed at 2.5:1. Presumably, small changes in concentration of each of the complex anions change the ion−ion interactions markedly, and this in turn changes the freezing point. For example, $ZnCl_3^-$ ions are smaller and have a higher charge density than $Zn_2Cl_5^-$ anions so are likely to have stronger electrostatic interactions with the cation thus increasing the freezing point. Hence, as the mole fraction of $ZnCl_2$ increases from 50%, the amount of $Zn_2Cl_5^-$ relative to $ZnCl_3^-$ should increase and the freezing point decreases. Above a mole fraction of 66% $ZnCl_2$ the freezing point increases again. We assume that this is due to a higher concentration of $Zn_3Cl_7^-$ anions and that its greater molecular mass becomes a significant factor.

The eutectic composition for the $SnCl_2$/ChCl system occurs at 2.5:1. This is presumably because $SnCl_2$ is less Lewis acidic than $ZnCl_2$ and hence more $SnCl_2$ is require to push the equilibrium for the reaction

$$SnCl_2 + SnCl_3^- \approx Sn_2Cl_5^-$$

to the optimum $Sn_2Cl_5^-$ composition.

Ionic Species. FAB-mass spectra were obtained for the liquids at 2:1 metal chlorides/ChCl composition. The spectrum for the zinc-containing ionic liquid shows the presence of three main chlorozincate anions, $ZnCl_3^-$ (*m*/*z* 171), $Zn_2Cl_5^-$ (*m*/*z* 307), and $Zn_3Cl_7^-$ (*m*/*z* 443). Higher clusters are also detectable but occur at very low intensities. FAB-MS for the tin-based ionic liquid shows the presence of $SnCl_3^-$ (*m*/*z* 225) and $Sn_2Cl_5^-$ (*m*/*z* 412). For the iron system the only anionic species detected was $FeCl_4^-$ (*m*/*z* 197). For the tin and iron systems no $Sn_3Cl_7^-$ or $Fe_2Cl_7^-$ clusters could be detected, but this could because they are too unstable to be observed using FAB-MS.

It was also confirmed that the liquid formed by mixing $ZnBr_2$ with ChCl gave complex anions of the form $Zn_2Br_4Cl^-$. In an analogous way, mixed-metal ions are observed for zinc/tin melts [$ZnSnCl_5^-$] (*m*/*z* 361) and zinc/iron [$ZnFeCl_6^-$] (*m*/*z* 330).

During the formation of 1:2 choline chloride/zinc chloride the expected reaction is shown in eq 1, while equilibria 2 and 3 also effect the actual zinc species present.

$$2ZnCl_2 + Ch^+Cl^- \approx Zn_2Cl_5^- + Ch^+ \tag{1}$$

$$2Zn_2Cl_5^- \approx ZnCl_3^- + Zn_3Cl_7^- \tag{2}$$

$$Zn_2Cl_5^- \approx ZnCl_2 + ZnCl_3^- \tag{3}$$

To further investigate the anionic equilibria in the choline chloride/zinc chloride mixtures we have carried out potentiometry as a function of composition. Heerman and D'Olislager[25] measured the potential of the cell

---

(25) Heerman, L.; D'Olislager, W. *Inorg. Chem.* **1985**, *24*, 4704.

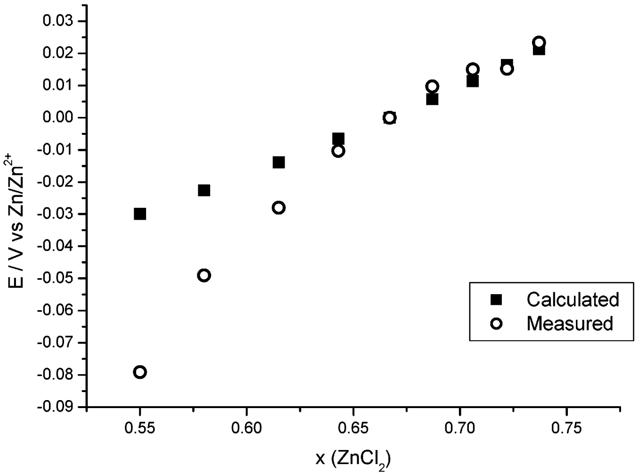

Figure 2. Potential of the cell Zn|ZnCl$_2$ (0.667), ChCl (0.333)||ZnCl$_2$ (x), ChCl (1 −x)|Zn at 60 °C for various values of x.

$$\text{Al}|\text{BuPyCl, AlCl}_3(\text{ref})||\text{AlCl}_3(x)\text{, BuPyCl}(1-x)|\text{Al} \qquad (4)$$

and fitted the data to the Nernst equation over the region $x = 0.6-0.67$. They found that the equilibrium constant for eq 5 was 2.93×10^{-3} at 60 °C; i.e., $Al_2Cl_7^-$ is the most abundant species in solution.

$$2Al_2Cl_7^- \approx AlCl_4^- + Al_3Cl_{10}^- \qquad (5)$$

Figure 2 shows the potential for the analogous choline chloride/zinc chloride cell (6) at 60 °C for various values of mole fraction, x.

$$\text{Zn}|\text{ZnCl}_2\text{ (0.667), ChCl (0.333)}||\text{ZnCl}_2(x)\text{, ChCl }(1-x)|\text{Zn} \qquad (6)$$

Using a method analogous to that described by Heerman and D'Olislager,[25] the equilibrium constant for eq 2 was found to be 2.0×10^{-5}. The value is lower than that for the analogous aluminum case, which would be expected on Lewis acidity arguments. Figure 2 also shows the data calculated from the Nernst equation for reaction 2. A good fit is observed in more Lewis acidic melts, but significant deviations occur below 1.6:1 ZnCl$_2$/ChCl. This is presumably because reaction 3 becomes more important as the solution becomes less Lewis acidic. Figure 3 shows the composition of chlorozincate species as a function of ZnCl$_2$ content calculated by the method of Heerman and D'Olislager (limited to the region of Figure 2 where eq 2 gives an accurate fit to the experimental data). The major species is $Zn_2Cl_5^-$ with an increasing contribution from $ZnCl_3^-$ as the amount of ChCl is increased. The concentration of $Zn_3Cl_7^-$ is small but significant across the range of composition studied. Hence properties such as catalytic activity, solution viscosity, ionic conductivity, and electrochemical properties will depend on solution composition.

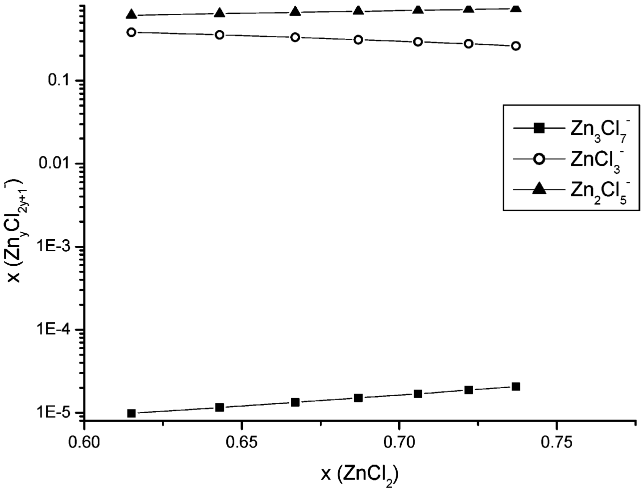

Figure 3. Mole fraction of chlorozincate anions in a choline chloride/zinc chloride ionic liquid as a function of composition at 60 °C.

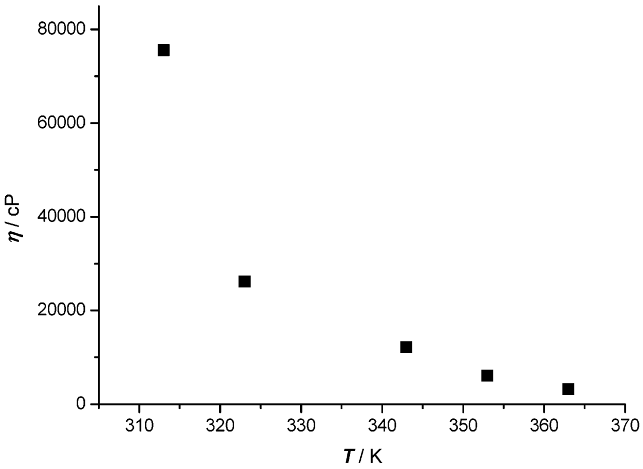

Figure 4. Viscosity of a 2 ZnCl$_2$/1 ChCl mixture as a function of temperature.

Viscosity. Figure 4 shows the viscosity of the 2:1 ZnCl$_2$/ChCl mixture as a function of temperature. The viscosity, η, is considerably higher than analogous chloroaluminate melts.[26] This is due to the difference in volume of the $Zn_2Cl_5^-$ (162 Å^3) and $Al_2Cl_7^-$ (227 Å^3) ions, which means that the latter interacts less with the cation in the liquid. Previous studies in ionic liquids and molten salts have analyzed such viscosity data by the empirical equation[27]

$$\eta = \eta_0 e^{E_\eta/RT} \qquad (7)$$

where η_0 is a constant, T is the absolute temperature, and E_η is the energy for activation of viscous flow. The data from Figure 4 fit eq 7 well ($r = 0.990$) and yield a value for E_η of 55.7 kJ mol^{-1}. This is considerably larger than for conventional molecular liquids[28] but comparable to other room-temperature ionic liquids,[29] and this is thought to be due to the size of the ions with respect to the size of the voids in the liquid.

The radius of the average voids, r, in the ionic liquids can be found using the surface tension of the liquid, γ, by the expression[27]

---

(26) Mantz, R. A.; Trulove, P. C.; Carlin, R. T.; Osteryoung, R. A. *Inorg. Chem.* **1995**, *34,* 3846.

(27) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum Press: New York, 1970; Vol. 1, Chapter 6.

(28) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Solvent Properties and Methods of Purification*, 4th ed.; J. Wiley and Sons: New York, 1986.

(29) Branco, L. C.; Rosa, J. N.; Ramos, J. J. M.; Afonso, C. A. M. *Chem.—Eur. J.* **2002**, *8*, 3671.

Table 2. Freezing Points, T_f, of Various Ionic Liquids of the General Formula $R_1R_2R_3R_4N^+Hal^-/2\ ZnCl_2$ Together with the Melting Point of the Pure Quaternary Ammonium Halide, T_m*, and the Ionic Volume of the Cation

entry	R_1	R_2	R_3	R_4	Hal^-	T_f/°C	T_m*/°C	V_+/Å^3
1	Me	Me	Me	C_2H_4OH	Cl^-	23−25	303	149.2
2	Me	Me	Me	C_2H_4Cl	Cl^-	23−25	255	155.8
3	Me	Me	Me	$C_2H_4OC(O)Me$	Cl^-	30−32	148	212.0
4	Me	Me	Me	$C_2H_4OC(O)Ph$	Cl^-	46−48	205	261.1
5	Me	Me	Me	C_2H_5	Cl^-	53−55	294	138.2
6	Me	Me	Me	C_2H_4F	Br^-	41−43	257	145.3
7	Me	Me	Me	C_2H_4Br	Br^-	49−51	244	162.8
8	Me	Me	Me	C_3H_6Br	Br^-	22−24	210	183.4
9	Me	Me	Me	C_3H_7	Br^-	45−47		158.6
10	Me	Me	Me	C_6H_{13}	Br^-	41−43	176	220.0
11	Me	Me	Me	C_7H_{15}	Br^-	46	115	239.1
12	Me	Me	Me	$C_{10}H_{21}$	Br^-	48		297.9
13	Me	Me	$C_{12}H_{25}$	$C_{12}H_{25}$	Br^-	27	164	563.5
14	Et	Et	Et	CH_3	Br^-	39	307	175.8
15	Et	Et	Et	C_6H_{13}	Br^-	56	115	277.2
16	Me	C_2H_4OH	C_2H_4OH	$C_6H_5CH_2$	Cl^-	50−52	97	262.4
17	Me	Me	C_2H_4OH	C_2H_4OH	I^-	27−29	76	178.4
18	Me	Me	Me	*S*-(−)-$ClCH_2CH(OH)CH_2$	Cl^-	48−50	210	185.9
19	Me	Me	Me	*R*-(+)-$ClCH_2CH(OH)CH_2$	Cl^-	48−50	210	185.9

$$4\pi\langle r^2\rangle = 3.5\frac{kT}{\gamma} \qquad (8)$$

where k is the Boltzmann constant. The eutectic $ZnCl_2$/ChCl mixture was found to have a surface tension of 50.9 dyn cm^{-1} leading to an average void radius of 1.50 Å. Considering that the radius of the choline(+) and $Zn_2Cl_5^-$ ions are 3.29 and 3.38 Å, respectively, it is evident that the high viscosity of these fluids arises from the large difference between the ion size and the average hole radius. The probability, P, of finding an adjacent hole of sufficient radius, r, for the ion to move into is given by[27]

$$P\,\mathrm{d}r = \frac{16}{15\pi^{1/2}}a^{7/2}r^6\mathrm{e}^{-ar^2}\,\mathrm{d}r \qquad (9)$$

where

$$a = \frac{4\pi\gamma}{kT}$$

Thus, the probability of finding a hole adjacent to a choline(+) and $Zn_2Cl_5^-$ ion is 2.0×10^{-5} and 8.9×10^{-6}, respectively. Hence the reason that these ionic liquids are viscous is because the liquid consists of large ions with a small void volume and an insignificant number of holes large enough to allow ion movement.

Effect of Cation on Freezing Point. The freezing points of ionic liquids formed between various QAS's and zinc chloride (1:2 molar ratio) are shown in Table 2. The freezing point of these ionic liquids is governed by the interaction between the anionic and cationic species in the liquid, which are affected by ionic size, symmetry, functionality, and molecular mass. The symmetry of the cation is known to affect the freezing point of ionic liquids.[1] Thus, Me_4N^+ gives a higher freezing point than Me_3NR^+ (R = alkyl) up to a certain chain length; this is illustrated by the ethyltrimethylammonium, propyltrimethylammonium, and hexyltrimethylammonium cations (entries 5, 9, and 10, respectively). The slightly anomalous results for the long-chain quaternary ammonium salts (entries 10−13) could result from so-called fastener effects caused by van der Waals interactions. Similar effects have been observed for other amphiphillic species.[30] Ionic liquids formed with functionalized QAS's have slightly lower freezing points than those formed with their related tetraalkyl QAS's. For example, the presence of OH in choline chloride and Cl in (2-chloroethyl)trimethylammonium chloride (entries 1 and 2) leads to a lowering of freezing point by 20 and 30 °C, respectively, from that of ethyltrimethylammonium chloride (entry 5). Chiral ionic liquids have been formed using chiral quaternary ammonium salts (entries 18 and 19). As expected, there does not appear to be any difference in their physical properties induced by the chiral center.

An important requisite is the ability to predict phase behavior of ionic liquids from simple physical properties. In general, the temperature at which a salt melts is dependent upon the potential energy between the ions. This is difficult to model in the case of the ions studied as the charge distribution, particularly on the cation, is generally noncentrosymmetric. However, in the case of these ionic liquids, we can consider the difference in freezing point between that of the quaternary ammonium salt and that of the complex with the metal salt. The change in interionic potential energy, E_p, and the concomitant change in T_f will be related to the expansion of the ionic lattice resulting from the formation of a complex anion. Since

$$E_p = \frac{q_1q_2}{4\pi\epsilon_0 r} \qquad (10)$$

where q is the charge on the ions, ϵ_0 is the vacuum permittivity, and r is the separation between the two charges, therefore

$$\Delta E_p \propto \frac{r_c - r_s}{r_s} \qquad (11)$$

where r_c and r_s are the charge separation in the complex

---

(30) Shi, Z.; Enoki, T.; Imaeda, K.; Seki, K.; Wu, P.; Inokuch, H.; Saito, G. *J. Phys. Chem.* **1988**, *92*, 5044.

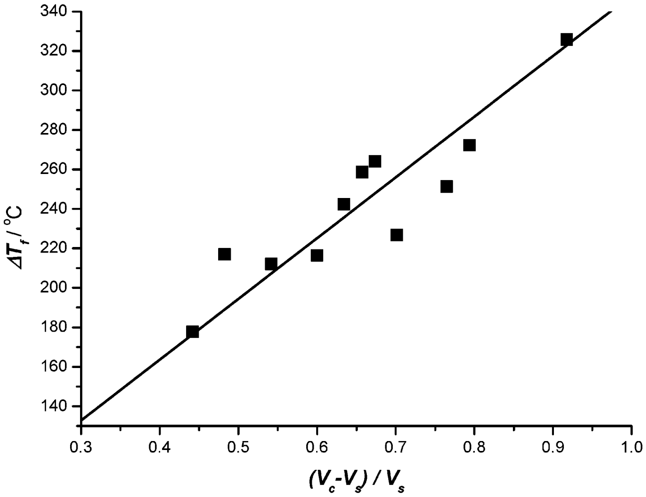

Figure 5. Plot of freezing point depression versus the normalized change in ionic volume for the ionic liquids listed in Table 1. V_c and V_s are the ion volumes of the zinc chloride containing salts and the parent quaternary ammonium halide, respectively. The solid line is the least-squares fit to the data.

mixture and simple quaternary ammonium halide salt, respectively (assuming that the complex anion is predominantly of the form $M_2X_5^-$). The depression of freezing point, ΔT_f, is taken as the difference between the measured freezing point at the eutectic composition, T_f, and the freezing temperature of the pure quaternary ammonium halide. Table 2 lists T_f values for a variety of quaternary ammonium salt mixtures with $ZnCl_2$. Figure 5 shows a plot of freezing point depression as a function of the normalized change in charge separation (eq 11).[31] It can be seen that a good correlation is obtained for $ZnCl_2$-based ionic liquids. This is a significant result as it allows phase behavior to be predicted from simple ionic size considerations and it shows that symmetry has negligible effect on the *depression* of freezing point, but it does change the absolute freezing point. Angell[32] recently used a similar approach to show that a glass transition temperature of a range of ionic liquids is related to the molar volume of the ions.

In general the smaller quaternary ammonium cations cause a larger depression in freezing point, but since the halide salts of the smaller cations also have a higher freezing point, the net result is all of the mixtures have a reasonably similar freezing points (20−60 °C). Hence the cation is observed to have little effect on the absolute freezing point of the ionic liquids.

Electrochemical Stability. The use of metal-containing ionic liquids for electrochemical applications depends on the potential window over which the liquid is stable. The potential windows of 1:2 choline chloride/MX_n (MX_n = $ZnCl_2$, $SnCl_2$, $FeCl_3$) are listed in Table 3. For each ionic liquid the potential window is limited at high potentials by chlorine gas evolution and low potentials by $Fe^{3+} \approx Fe^{2+}$, tin deposition, and zinc deposition for the iron, tin, and zinc melts, respectively. Since $Zn^{2+} \approx Zn^0$ has the lowest position of the three in the electrochemical series, the zinc melt has the largest potential window (approximately 2 V). The tin and iron melts have potential windows of approximately 1.5 and 0.5 V, respectively. The potential windows for all three ionic liquids are surprisingly close to the difference in the standard cell potentials for the corresponding half-cell reactions in aqueous solutions (Table 3). This suggests that while the reduction potential for $Zn_2Cl_5^-$ will be shifted with respect to Zn^{2+}, the oxidation of Cl^- to Cl_2 will be affected by the same amount. The potential window for the $ZnCl_2$ melt is approximately 900 mV less than the aluminum melts; however, the lack of reactivity with water makes them much easier to handle and makes them suitable for large scale processes such as metal deposition.[19,20]

Table 3. Potential Windows for the 2:1 Mixtures of $ZnCl_2$, $SnCl_2$, and $FeCl_3$ Mixtures with ChCl

metal salt	anodic limit/V	cathodic limit/V	ref potential	potential window/V	$E°_M - E°_{Cl}$/V
$ZnCl_2$	1.90	0.00	Zn wire	1.90	2.12
$SnCl_2$	1.60	0.00	Sn wire	1.60	1.50
$FeCl_3$	0.60	0.00	Pt wire	0.60	0.59

Conclusions

Ionic liquids can be formed using a variety of nonsymmetrical quaternary ammonium halides with halides of Sn(II), Zn(II), and Fe(III). The phase diagram of the chloride salts with choline chloride showed that Lewis basic ionic liquids could not be formed with tin and zinc, and this was related to the high charge density of the MCl_3^- anion. Singly charged halide-bridged complex anions are formed in the liquid, analogous to the aluminum chloride case, and these have been identified and in one case quantified. It was found that $Zn_2Cl_5^-$ was the most prevalent species, and the concentration of this species varied significantly with the composition of the ionic liquid. The depression of freezing point for a variety of quaternary ammonium cation complexes with $ZnCl_2$ was found to be related to the change in size of the component ions.

Acknowledgment. The authors acknowledge the funding of this work by the EPSRC (Grant GR/R59199) and Scionix Ltd.

IC049931S

---

(31) The volumes of Cl^- and $Zn_2Cl_5^-$ were 24.8 and 162 Å^3, respectively.
(32) Xu, W.; Angell, C. A. *Science* **2003**, *203*, 422.