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Eutectic-Based Ionic Liquids with Metal-Containing Anions and Cations

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Abstract: Eutectic mixtures of zinc chloride and donor molecules such as urea and acetamide are described and it is proposed that these constitute a new class of ionic liquids. FAB-MS analysis shows that the liquids are made up of metal-containing anions and cations in which the donor is coordinated to the cation. Data on the viscosity, conductivity, density, phase behaviour and surface tension are presented and these are shown to be significantly different to other related ionic liquids that incorporate quaternary ammonium salts. The conductivity and viscosity are comparable with other ionic liquids and the data fit well to the Hole theory model recently proposed.

Keywords: eutectic solvents · ionic liquids · physical properties · zinc

Introduction

Ionic liquids are one of the most widely studied topics in the condensed phase at present. They were initially of interest for the reduction of aluminium for both battery and plating applications.[1,2] The ionic liquids studied were eutectics between $AlCl_3$ and quaternary ammonium salts and these were found to contain complex anions such as $AlCl_4^-$ and $Al_2Cl_7^-$. In the last 10 years a plethora of papers has appeared where the complex anions have been replaced by discrete, closed-shell anions such as BF_4^-, PF_6^- and $(CF_3SO_2)_2N^-$ and a number of good reviews have been published in this area.[3–6] These salts have tended to have lower viscosities, higher conductivities and wider potential windows. These liquids have been proffered as suitable for a wide variety of applications ranging from fuel desulphurization[7] to metal processing.[8] However, very few have come to practical fruition as yet although several are at pilot scale. This is partly due to the complexity of synthesis and purification.

In an endeavour to produce simpler liquids with applications in metal finishing that is, large volume applications, several groups[9–11] have revisited the eutectic based ionic liquids and shown that the ideas used for aluminium eutectics are valid for other metals for example, Zn and Sn. The ideas can be expanded to use hydrated metal salts[12] and even hydrogen-bond donors[13,14] (HBD) to complex the halide ion of the quaternary ammonium salt. This leads to a large number of different permutations and to differentiate them we have devised a simple classification system. Eutectic based ionic liquids can be expressed in terms of the following general formula $R^1R^2R^3R^4N^+ X^- \cdot Y^-$.

Type 1 Eutectic $Y = MCl_x$, M = Zn, Sn, Fe, Al, Ga

Type 2 Eutectic $Y = MCl_x \cdot y\,H_2O$, M = Cr, Co, Cu, Ni, Fe

Type 3 Eutectic $Y = R^5Z$, $Z = CONH_2$, COOH, OH

One difficulty associated with ionic liquids is the large size of the ionic species and the small size of the voids in the liquid. This affects the viscosity and conductivity of the liquids, however, there is a limit to the amount the ionic radius can be reduced as it impacts on the freezing point of the liquids. In the current work we show that it is possible to make ionic liquids without the use of quaternary ammonium or phosphonium salts. Eutectics can be formed between metal salts and simple organic alcohols or amides, these have both metal-containing anions and cations and the physical properties are consistent with other ionic liquids.

Results and Discussion

To date most work on ionic systems that are liquid at ambient temperature has used an organic cation based principally around ammonium, phosphonium and sulphonium moieties.

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Inorganic cations do not tend to form ambient temperature ionic liquids due to their high charge density. Previous work has shown that mixtures of urea with alkali metal halides form eutectics with melting points of $<150\,°C$, however, it is only the iodide and nitrate salts which approach ambient temperatures.[16,17] The interest of the current study is to incorporate transition metal salts such as those used already in type I eutectics. The expected result is that these types of salts would not normally ionise in non-aqueous media. We have studied a wide variety of metal salts and found that they do indeed form ambient temperature eutectics (see above) but for the purposes of this study we will only report the results for $ZnCl_2$.

Phase behaviour and speciation: Figure 1 shows the phase behaviour of urea: $ZnCl_2$ mixtures as a function of composition. It is observed that the composition with the lowest freezing temperature, T_f (the eutectic composition) occurs at a urea/$ZnCl_2$ ratio of 3.5:1. The freezing points of $ZnCl_2$ and urea are 293 and 134 °C, respectively. It was thought initially that these types of liquids are merely a hybrid between type I and III eutectics described above but these eutectics only form for a limited number of metal salts and an even narrower range of donors. While urea forms ambient temperature eutectics with $SnCl_2$ and $FeCl_3$ it does not form with $AlCl_3$. A number of other donors were also studied but it was found that only a limited number of amides and dialcohols were effective at forming room temperature liquids. Amongst these were acetamide, ethylene glycol and 1,6-hexanediol and these are the examples that will be described in this work. Surprisingly the carboxylic acids do not form ambient temperature eutectic liquids with $ZnCl_2$ as they do with quaternary ammonium salts. This suggests that the complex is not formed through a hydrogen bond, but more probably through an oxygen bond between the donor and the metal centre. Table 1 shows the eutectic composition and freezing points of the $ZnCl_2$ mixtures studied. These eutectics mixtures are distinctly different from type I and III eutectics and hence we propose to classify them as a type IV eutectic.

Table 1. Phase behaviour of $ZnCl_2$ eutectics with various amide and diol donors.

Donor	Eutectic donor/$ZnCl_2$	T_f [°C]	T_f* [°C]
urea	3.5	9	134
acetamide	4	−16	78
ethylene glycol	4	−30	13
hexanediol	3	−23	43

Previous work, focused on mixtures of $ZnCl_2$ with quaternary ammonium salts such as choline chloride (ChCl), showed that the eutectic composition of ChCl/$ZnCl_2$ occurred at a molar ratio of 1: 2, with a T_f of 23 °C.[9] In comparison the urea/$ZnCl_2$ eutectic has a T_f of 9 °C. This is as expected, as the freezing point of a deep eutectic solvent is partially determined by the melting points of the pure constituent parts, T_f* (cf. urea m.p. 134 °C and ChCl m.p. 303 °C). Figure 1 shows the depression of freezing point (with respect to an ideal mixture of the two components at the eutectic ratio) is 150 °C. The depression of freezing point is lower than the corresponding ChCl/$ZnCl_2$ system (272 °C). The depression of freezing point is related to the interaction between the two components and it would be expected that the interaction of Cl^- with $ZnCl_2$ would be stronger than the corresponding interaction with urea. The upper limit at which these liquids can be studied depends upon the stability of the donor molecule. The mixtures do not decompose but rather they lose the organic component at temperatures close to the boiling point of the pure component.

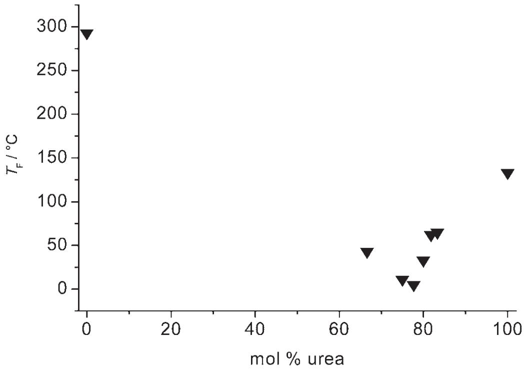

Figure 1. Phase diagram urea/$ZnCl_2$ system as a function of composition.

In order to understand the difference between types I, III and IV, the identity of the ionic species in the solution must be determined. It has previously been shown that ionic species can be identified using FAB mass spectrometry.[9] The ChCl/$ZnCl_2$ liquid showed the presence of a number of complex zinc anions, including, $[ZnCl_3]^-$, $[Zn_2Cl_5]^-$, $[Zn_3Cl_7]^-$ and a number of higher clusters at very low intensities. The only cationic species was found to be $[Ch]^+$.

Analogous measurements with 3.5 urea/1 $ZnCl_2$ also gave peaks at *m/z*: 171, 307 and 442, indicating the presence of the $[ZnCl_3]^-$, $[Zn_2Cl_5]^-$ and $[Zn_3Cl_7]^-$, ions that were also present in the ChCl/$ZnCl_2$ eutectic. However, unlike the ChCl based liquid, the +ve FAB mass spectrum also showed evidence of the presence of Zn containing cations. Signals that were characteristic of a Zn isotope-splitting pattern were observed at 159, 219 and 279. These were determined to be due to the presence of the following $[ZnCl]^+$ based cations, $[ZnCl(urea)]^+$, $[ZnCl(urea)_2]^+$ and $[ZnCl(urea)_3]^+$. This is the first example of a eutectic based ionic liquid being formed with a metallic cation, a factor that is very significant for deposition studies as it means that metal-containing cations will be present in the double layer at cathodic potentials. Analogous experiments with the other donor molecules gave similar results. The −ve FAB mass spectra showed the same zinc containing anions for all of the donor molecules. The cationic spectrum also showed zinc splitting patterns at 158, 217 and 276, these have been determined to be $[ZnCl(acetamide)]^+$, $[ZnCl(acetamide)_2]^+$ and $[ZnCl(acetamide)_3]^+$. For the ethylene glycol system the cationic species were found to be $[ZnCl(\text{ethylene glycol})]^+$ and $[ZnCl(\text{ethylene glycol})_2]^+$. For the hexanediol system, in addition to the expected zinc species, a splitting pattern indicative of a cationic dizinc species $[Zn_2Cl_3(\text{1,6-hexanediol})_2]^+$ was also observed.

Viscosity: Figure 2 shows the viscosity of the eutectic mixture of urea/$ZnCl_2$ as a function of temperature. The viscosity at 25 °C was found to be 11.34 Pa s; this is significantly below that of the $ZnCl_2$/ChCl liquids previously noted in the literature, which were found to have a viscosity of 85.0 Pa s at 25 °C.[9] This reduction in viscosity means improved mass transport and should lead to a decrease in electrical resistance. The change in viscosity, η with temperature can be described by the following equation:[18]

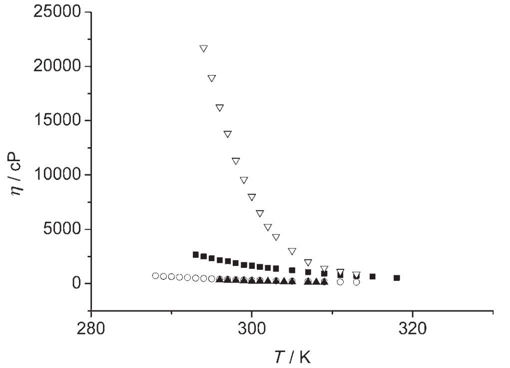

Figure 2. Viscosities of a series of eutectic donor/$ZnCl_2$ liquids as a function of temperature. ■: 1,6-hexanediol/$ZnCl_2$, ○: ethylene glycol/$ZnCl_2$, ▲: acetamide/$ZnCl_2$, ▽: urea/$ZnCl_2$.

$$\ln\eta = \ln\eta_0 + \frac{E_\eta}{RT} \qquad (1)$$

where η_0 is a constant and E_η is the energy for activation of viscous flow.

Applying Equation (1) to the data in Figure 2 the E_η were calculated and are shown in Table 2. Previous studies have shown that the E_η values for ionic liquids are considerably larger than conventional liquids and high temperature molten salts.[14] This is due to the large ion to hole radius ratio in ionic solvents. Figure 2 also shows that the donor has a significant effect upon the viscosity. A stark difference is observed between urea and acetamide even though the two molecules are similar in size. The difference between the two liquids must arise from the ability of urea to form hydrogen bonds through its two NH_2 functionalities whereas acetamide only has one. This is manifested through a difference in liquid density and surface tension (see below).

Conductivity: Figure 3 shows the conductivity of the urea/$ZnCl_2$ eutectic liquid as a function of temperature. The conductivity is considerably higher than that observed in the ChCl/$ZnCl_2$ system.[9] An analogous expression to equation 1 has been shown to valid for the variation of conductivity, κ, with temperature, namely:[18]

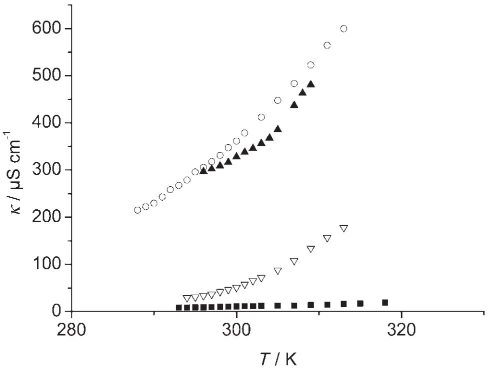

Figure 3. Plot of conductivity as a function of temperature for the donor/$ZnCl_2$ systems. ■: 1,6-hexanediol, ○: ethylene glycol, ▲: acetamide, ▽: urea.

$$\ln\kappa = \ln\kappa_0 + \frac{E_\Lambda}{RT} \qquad (2)$$

At 315 K the conductivities were found to be 180 and 60 $\mu S\,cm^{-1}$ for the $ZnCl_2$/3.5 urea and 2 $ZnCl_2$/choline chloride based systems, respectively.[9] The values obtained using acetamide were approximately three times those obtained using urea and this is in line with the differences in viscosity for the two liquids shown in Figure 2. This difference in properties, as previously noted, is likely to be due to a difference in liquid density, which arises from differing degrees of hydrogen bonding in the two systems. The most surprising result to arise from the conductivity data is the value obtained for 1,6-hexanediol. From the viscosity data it would be expected to be more conducting than the more viscous urea-based liquid, however, this is found not to be the case. The low conductivity of this liquid could be due to the larger metal clusters as indicated by FAB MS or it could also arise from a lower degree of ion dissociation. In the case of ChCl/$ZnCl_2$ eutectics then the following equilibrium:

$$ZnCl_2 + ChCl \rightleftharpoons Ch^+ + ZnCl_3^- \qquad (3)$$

is known to lie to the right since Cl^- is a strong Lewis Base

Table 2. E_η and E_Λ for the donor/$ZnCl_2$ mixture. Density ρ and hole dimensions were obtained at 25 °C.

Donor/$ZnCl_2$	E_η [kJ mol^{-1}]	E_Λ [kJ mol^{-1}]	ρ [g cm^{-3}]	R_h [Å]	R_+ [Å]	$R_{+/-}/R_h$
3.5 urea/$ZnCl_2$	135	−77	1.63	1.26	3.56	2.83
4 acetamide/$ZnCl_2$	62	−28	1.36	1.47	3.57	2.43
4 ethylene glycol/$ZnCl_2$	50	−31	1.45	1.41	3.07	2.17
1,6-hexanediol/$ZnCl_2$	49	−25	1.38	1.52	3.62	2.38

and $ZnCl_2$ is a strong Lewis acid. However, for the systems in the present study the position of the equilibrium:

$$2\,ZnCl_2 \rightleftharpoons ZnCl^+ + ZnCl_3^- \tag{4}$$

will depend upon the degree to which the amide or alcohol can stabilise the cation. If the system is not totally ionic the conductivity will be lower than expected. FAB mass spectrometry unfortunately gives no information on neutral molecules present in a system.

Density and surface tension: Table 2 shows the density measurements for the four donor/$ZnCl_2$ liquids. The difference in density between the acetamide/$ZnCl_2$ and urea/$ZnCl_2$ eutectic mixtures suggests that there is a difference in packing between the two liquids. It has been previously been proposed that ionic liquids contain empty vacancies, or holes, the size of which will determine the liquid's density. The acetamide/$ZnCl_2$ deep eutectic solvent has a density of 1.36 $g\,cm^{-3}$ whereas the urea/$ZnCl_2$ system has a density of 1.63 $g\,cm^{-3}$. The densities of these two liquids are higher than those of the pure organic components (acetamide: 1.16 and urea: 1.32 $g\,cm^{-3}$) but the density ratio of the two liquids is similar to that of the two solids. The increased density of the urea/$ZnCl_2$ system suggests a reduction in the average hole radius in the system and therefore a decrease in mass transport properties and an increase in viscosity.

Previous studies have fitted the viscosities of deep eutectic solvents and ionic liquids to the Hole theory model.[19] The vacancies generated in a liquid when it melts are of a random size and position and are in constant motion. The theory states that an ion can only move through an ionic liquid if it is adjacent to a hole of equal or greater size. Ionic liquids have inherently high viscosity because the average size of an ion is about 0.4 nm whereas the average hole radius is only about 0.2 nm. Therefore, only a very small fraction of the ions in an ionic liquid are in motion at any one time due to the lack of suitably sized voids. The average hole size, r, in a liquid is given by:[18]

$$4\pi \langle r^2 \rangle = 3.5\,\frac{kT}{\gamma} \tag{5}$$

where γ is the surface tension of the liquid and k is the Boltzmann constant. Figure 4 shows the measured surface tensions of the four donor/$ZnCl_2$ systems as a function of temperature and it can be seen that the liquids with the highest viscosity have the largest surface tension and density. The average hole sizes for the acetamide and urea based liquids are 1.47 and 1.26 Å, respectively. The anionic species are the same in both liquids and the cationic compositions only differ by the replacement of urea with acetamide. The main ionic species are therefore $[ZnCl\,(acetamide)_2]^+$ (r = 3.57 Å), $[ZnCl(urea)_2]^+$ (r = 3.57 Å), and $[ZnCl_3]^-$ (r = 2.86 Å).[15]

If we consider viscosity as a measure of the ease with which species move through a liquid, it would be expected that liquids containing similar sized species with similar densities would have similar viscosities. The $[Ch^+]$ cation is smaller than the cations found in the donor/$ZnCl_2$ systems and accounts for the slightly higher viscosities observed in the latter (cf. ChCl/HBDs $\eta = 0.05$–5 Pa s).[14] In fact there is an order of magnitude difference between the viscosities of the urea- and acetamide-based liquids. In order to understand the difference in transport properties of the deep eutectic solvents their surface tensions were measured.

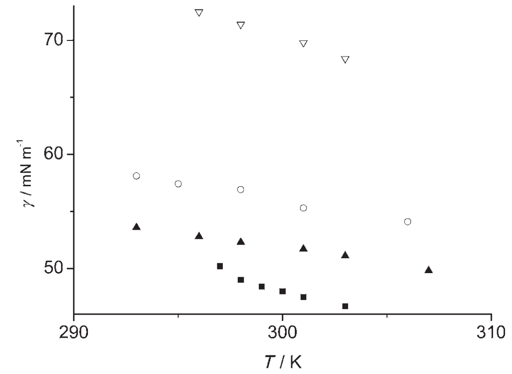

Figure 4. Surface tensions of a series of donor/$ZnCl_2$ eutectic liquids as a function of temperature. ■: 1,6-hexanediol, ○: ethylene glycol, ▲: acetamide, ▽: urea.

The surface tension of the urea/$ZnCl_2$ eutectic liquid was found to be 72 $mN\,m^{-1}$ at 25 °C. The acetamide-based mixtures on the other hand had a smaller surface tension at around 53 $mN\,m^{-1}$. The ethylene glycol/$ZnCl_2$ and 1,6-hexanediol/$ZnCl_2$ liquids have surface tensions, at 25 °C, of 56.9 and 49 $mN\,m^{-1}$, respectively. Although these values are larger than those generally found for molecular liquids, they are similar to those found previously for high temperature molten salts, for example, KBr $\gamma = 77.3$ $mN\,m^{-1}$ at 900 °C,[20] ionic liquids, for example, [BMIM][BF_4] $\gamma = 38.4$ $mN\,m^{-1}$ at 63 °C,[21] and deep eutectic solvents, for example, malonic acid/ChCl $\gamma = 65.8$ $mN\,m^{-1}$ at 25 °C.[14]

Table 2 shows the average void radii for the four eutectic donor/$ZnCl_2$ liquids, calculated from the data in Figure 4 and Equation (3) at 25 °C. It is observed that there is a large ratio of ion radius/hole radius for the deep eutectic solvents. This means that there is a limited availability of suitably sized holes within the liquids, restricting ionic motion and accounting for their inherent viscosity. As the acetamide/$ZnCl_2$ liquid has a smaller $R_{+/-}/R_h$ ratio than the urea/$ZnCl_2$ liquid, ion motion is less restricted, which explains the difference in viscosities of the two systems.

The difference in hole size between the acetamide/$ZnCl_2$ and the urea/$ZnCl_2$ liquids can be explained by the degree of hydrogen bonding within the two systems. Primary amines are known to be moderate hydrogen-bond donors whereas methyl groups are very weak hydrogen-bond donors.[22] Acetamide has one primary amine and a weakly hydrogen bond donating methyl group. In the urea/$ZnCl_2$ system each urea has two NH_2 groups that can readily hydrogen bond to ions in the liquid. This leads to an extra dimension of structure in the urea/$ZnCl_2$ system as a hydrogen-bonded network is formed throughout the liquid. This large degree of hydrogen bonding decreases the void size in the liquid, which is demonstrated by the increased density, which in turn leads to a reduction in mass transport and therefore the observed increased viscosity. If the viscosity of a liquid is limited by the availability of suitably sized holes, the activation energy of viscous flow, E_η, should be proportional to $R_{+/-}/R_h$.[14] Figure 5 shows the data from the donor/$ZnCl_2$ liquids, some previously studied ionic liquids, high-temperature molten salt systems and a number of molecular liquids.[14,19] It can be seen that there is a good fit for the donor/$ZnCl_2$ systems, proving that their viscosity is controlled by the $R_{+/-}/R_h$ ratio, that is, the availability of suitably sized holes.

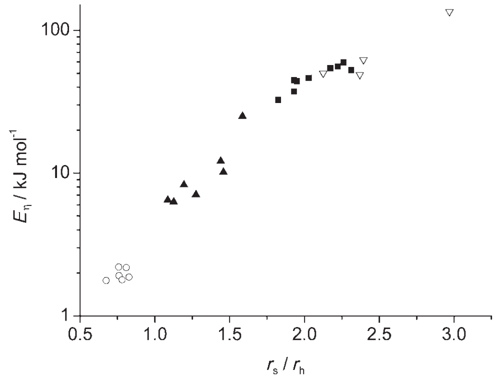

Figure 5. Energy for activation of viscous flow as a function of ion to hole radius ratio. ■: ionic liquids, ○: molten salts, ▲: molecular liquids, ▽: this study.

It can be seen that large E_η values are characteristic of ionic liquids and eutectic solvent systems, which results from the energy required to form and enlarge the voids that control mass transport. The movement of species within these systems is controlled by the ease of migration through voids, which in turn is controlled by the dimensions of the vacant sites. The conductivity data for the systems were analysed to determine whether it is also controlled by the availability of suitably sized vacancies in the liquid.

Table 2 shows the E_Λ of the donor/$ZnCl_2$ systems range between 25–77 kJ mol^{-1}. These values are larger than those found for high temperature molten salts but are comparable with those for HBD/ChCl deep eutectic solvents (cf. E_Λ HBD/ChCl = 29–54 kJ mol^{-1}).[14]

The large E_Λ values for the type IV $ZnCl_2$ systems can also be explained with hole theory. It has been shown that the conductivity of ionic liquids is limited by the availability of suitably sized holes within the system.[23] If it is assumed that for room temperature ionic liquids the holes are at almost infinite dilution and their migration is independent of one another, their conductivity can be calculated from a formula derived from the Stokes–Einstein equation, Equation (6):[23]

$$\kappa = \frac{z^2 F \cdot e}{6\pi\eta}\left(\frac{1}{R_+} + \frac{1}{R_-}\right)\frac{\rho}{M_w} \qquad (6)$$

where z is the charge on the ion, F is the Faraday constant, e is the electronic charge, ρ is the density, M_w is the molecular weight and η is the viscosity of the liquid. If the conductivity of the type IV $ZnCl_2$ is limited by the availability of suitably sized voids, the conductivities calculated from Equation (6) should equal those determined experimentally. Figure 6 shows that a strong correlation is seen between the observed conductivities and those calculated using Equation (6) for the type IV $ZnCl_2$ liquids. Data from for a variety of other ionic liquids is also included in the plot for comparison.[23] Figure 6 proves that conductivity in the type IV $ZnCl_2$ liquids is limited by ion mobility, which is in turn limited by the availability of suitably sized holes. Analogous to the E_η, the large E_Λ values are due to the energy required for formation and expansion of the voids that limit mass transport. We have recently proposed that the difference between an ionic liquid and an ionic solution is that charge transport is limited by hole density in the former whereas ion density controls the latter.[24] From the results shown in Figures 5 and 6 we conclude that the type IV eutectics are indeed a class of ionic liquid rather than simple solutions. Figure 6 also shows that the equilibrium shown in Equation (4) must produce an ion concentration that is significantly in excess of the hole concentration.

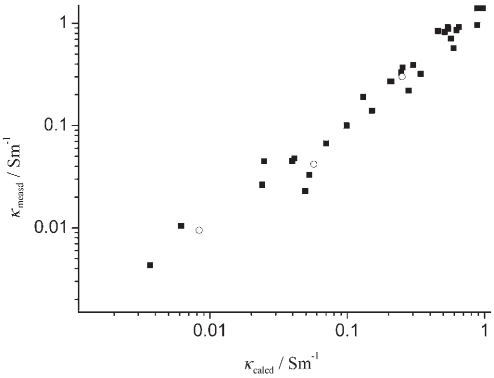

Figure 6. Calculated conductivities versus measured conductivities for donor/$ZnCl_2$ eutectics.[18] ■: ionic liquids, ○: this study.

Electrochemistry: Figure 7 shows a cyclic voltammogram of a Pt microelectrode in a 3.5:1 urea/$ZnCl_2$ deep eutectic solvent. The liquid has a potential window of 2 V, limited by Zn deposition at the cathodic end and chlorine evolution at the anodic end. Figure 7 also shows a cyclic voltammogram of a Pt microelectrode in a 4:1 ethylene glycol/$ZnCl_2$ deep eutectic solvent. The liquid again has the same potential window. There is some evidence of under-potential deposition occurring at −0.180 V in a similar manner to the ChCl/2 $ZnCl_2$ system.[24] The potential window is also similar to the type I analogue despite the significant difference in the

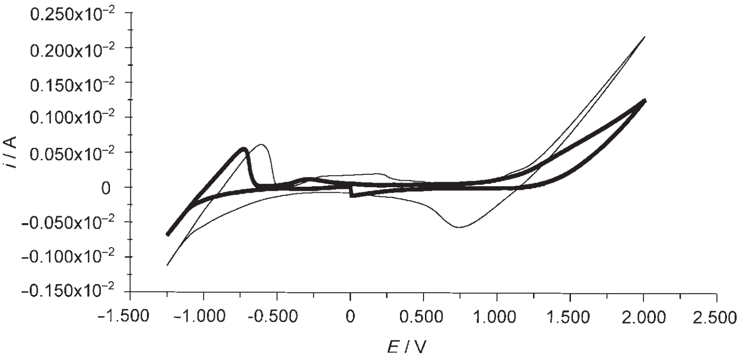

Figure 7. Cyclic voltammograms of a 0.5 mm Pt microelectrode immersed in a 3.5:1 urea/$ZnCl_2$ (-----) and a 1:4 ethylene glycol/$ZnCl_2$ based liquids (——). Scan rate = 20 mV s^{-1}. T = 60 °C.

zinc mole fraction and the zinc species in the liquid. The main difference between the type I and IV liquids is the zinc stripping process which is less reversible in the latter. This difference is thought to be due to a difference in ionic species present in the double layer. In the ChCl/$ZnCl_2$ system there will be significantly more Cl^- ligands available (probably in the form of $ZnCl_3^-$) in the double layer to complex the oxidised zinc ion at the interface. Previous work using the 1 ChCl/2 $ZnCl_2$ ionic liquid has demonstrated the possibility of reversibly depositing Zn.[25] Figure 8 shows an SEM image of non-micro cracked crystalline Zn deposited from the acetamide/$ZnCl_2$ eutectic liquid at an applied potential of 5 V with an approximate current density of 10 mA cm^{-2} for 20 min at 50 °C. EDAX analysis shows that this surface is pure Zn with negligible chloride residue. The morphology is more compact and less granular than that reported for the type I eutectics.[24]

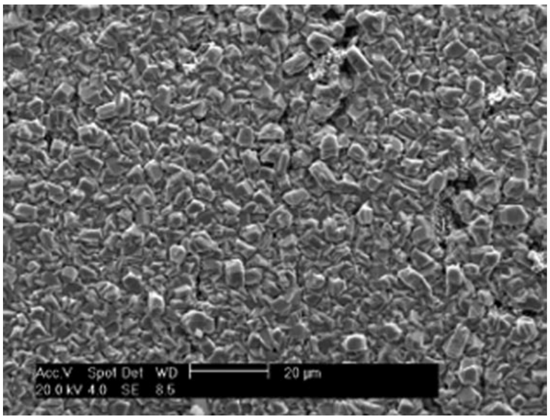

Figure 8. Scanning electron micrograph of zinc deposit on nickel, from acetamide/$ZnCl_2$ (5 V with an approximate current density of 10 mA cm^{-2} for 20 min at 50 °C).

Unlike the type I and III eutectics the type IV eutectics demonstrate low solubility of some metal halides. AgCl and $NiCl_2$ were found to have low solubility's in the type IV $ZnCl_2$ liquids, suggesting that halometallate complexes, for example, $AgCl_2^-$, are not readily formed. However $SnCl_2$ was found to be soluble in the $ZnCl_2$/acetamide presumably because it also auto ionises forming $SnCl^+$ and $SnCl_3^-$. This suggests that there is some potential for some alloy deposition from type IV eutectics.

Conclusion

Novel eutectic based ionic liquids can be formed between $ZnCl_2$ and a range of amides and diols. These have both metal-containing cations and anions. Their physical properties are similar to other ionic liquids and their properties can be described using Hole theory. The inherent viscosity of these systems has been shown to be due to their large ion: hole size ratio, and a relationship has been observed between the activation energy of viscous flow and the ion radius/hole radius ratio. It has been shown that the electrochemistry of the liquids is similar to other zinc-based eutectic and they can be used to effectively deposit dense zinc layers on an electrode surface.

Experimental Section

All materials were obtained from Sigma-Aldrich. The eutectic mixtures were formed by stirring the two components at 100 °C until a homogeneous colourless liquid was formed. The liquids were cooled at a rate of 1 °C min^{-1} and the freezing point was taken as the temperature at which the first solid began to form. The viscosity was determined using a Brookfield DV-E viscometer fitted with a thermostated jacket. The conductivity and its temperature dependence were determined using a Jenway 4071 conductivity meter with temperature and conductivity probes (probe cell constant = 1.01 cm^{-1}). A Kruss K11 tensiometer equipped with a thermostatted jacket, was used for the surface tension and density experiments. 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 working electrode (0.05 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 µm 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}. Electrodepositions were carried out at 5 V with an approximate current density of 10 mA cm^{-2} for 20 min at 50 °C. The equilibrium geometry and volumes of the ions and hydrogen bond donors were calculated using a Hartree–Fock method utilizing an STO-3G model provided by commercially available software.[15]

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