Ionic Liquid Analogues Formed from Hydrated Metal Salts

Andrew P. Abbott,* Glen Capper, David L. Davies, and Raymond K. Rasheed[a]

Abstract: A dark green, viscous liquid can be formed by mixing choline chloride with chromium(III) chloride hexahydrate and the physical properties are characteristic of an ionic liquid. The eutectic composition is found to be 1:2 choline chloride/chromium chloride. The viscosity and conductivity are measured as a function of temperature and composition and explained in terms of the ion size and liquid void volume. The electrochemical response of the ionic liquid is also characterised and it is shown that chromium can be electrodeposited efficiently to yield a crack-free deposit. This approach could circumvent the use of chromic acid for chromium electroplating, which would be a major environmental benefit. This method of using hydrated metal salts to form ionic liquids is shown to be valid for a variety of other salt mixtures with choline chloride.

Keywords: chromium · electrochemistry · green chemistry · ionic liquids

Introduction

Ambient temperature ionic liquids have received extensive interest for both electrochemical and synthetic applications.[1–11] The studies to date can broadly be divided into two types of ionic liquids; those based on chlorometallate anions, such as $Al_2Cl_7^-$, and those based on non-metal-containing anions, such as BF_4^- and $(CF_3SO_2)_2N^-$. Most of the initial work focused on imidazolium or pyridinium salts with aluminium chloride. Osteryoung[1] showed that *n*-butylpyridinium salts with $AlCl_3$ gave liquids over a wide range of composition at ambient temperatures. Similar results were also found using dialkylimidazolium chloroaluminate melts.[2] The properties of these ionic liquids are controlled by various chloroaluminate anions, whose relative concentrations change considerably with the melt composition. The density, viscosity and electrical conductivity of these systems have been characterised by Hussey et al.[3] The electrochemistry of aluminium and a range of transition-metal salts have been studied in a variety of chloroaluminate melts and this has found application for batteries and the electrodeposition of aluminium and its alloys.[4–7] The chemical and electrochemical properties of $AlCl_3$-containing melts have recently been reviewed in a number of articles.[8–11]

It has recently been shown that ionic liquids can be formed by using zinc chloride with pyridinium,[12] dimethylethylphenylammonium[13] and imidazolium salts.[14–16] These have higher melting points than the corresponding chloroaluminate melts, but are still fluid at ambient temperatures. In recent work[17] we have also shown that choline (2-hydroxyethyltrimethylammonium) chloride also forms ionic liquids with metal halides, for example, with $ZnCl_2$ and $SnCl_2$. Not only are these ionic liquids easy to prepare, but in contrast to the $AlCl_3$-containing liquids, they are water and air insensitive; in addition their low cost enables their use in large-scale applications such as metal finishing.[18] Analogous to $AlCl_3$, $ZnCl_2$ forms complex anions with Cl^- and the change in properties of the ionic liquids with composition and temperature can be predominantly ascribed to the equilibria given in Equations (1) and (2).[19]

$$ZnCl_3^- + ZnCl_2 \rightleftharpoons Zn_2Cl_5^- \tag{1}$$

$$Zn_2Cl_5^- + ZnCl_2 \rightleftharpoons Zn_3Cl_7^- \tag{2}$$

Other metal salts, such as $SnCl_2$ and $FeCl_3$, could also be used to form room-temperature ionic liquids.[17,19] However, the limited range of anhydrous metal salts that form ionic liquids with choline chloride, restricts the use of such media for a variety of important electrochemical processes. The current work reports the inclusion of other metals into ionic liquids as hydrate salts and focuses on the system formed between choline chloride and hydrated chromium chloride with the specific application of electrodepositing chromium.

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Results and Discussion

Table 1 shows the freezing point of choline chloride mixtures with $CrCl_3{\cdot}6H_2O$. As with the anhydrous $ZnCl_2$ and $SnCl_2$ cases reported previously,[17] the eutectic composition occurs at a composition of 1:2 choline chloride/$CrCl_3{\cdot}6H_2O$. At this composition it is a dark green viscous liquid at ambient temperature. The liquid cannot be formed by adding anhydrous $CrCl_3$ to choline chloride with six equivalents of water, and the anhydrous salt is also insoluble in the ionic liquid formed from the hydrated salt. This shows that the waters of hydration are vital in controlling the co-ordination chemistry around the chromium centre and the liquid is not simply a concentrated aqueous solution. It could be argued that a system containing water molecules is not strictly an ionic liquid, but since all of the physical properties are comparable to the anhydrous analogues (see below) and the water molecules behave as ligands rather than solvent molecules, it seems appropriate to classify them as fluids analogous to ionic liquids.

Table 1. Freezing temperatures of choline chloride/$CrCl_3{\cdot}6H_2O$ mixtures as a function of composition.

ChCl/ $CrCl_3{\cdot}6H_2O$	Freezing point [K]	ChCl/ $CrCl_3{\cdot}6H_2O$	Freezing point [K]
1:1	300.2	1:1.5	290.3
1:2	286.9	1:2.5	292.6
1:3	321.5		

The physical properties change markedly with temperature and composition, and above 65–70 °C the colour of the liquid changes to purple showing that the coordination sphere around the chromium centre is changing. Thermogravimetry shows that the waters of hydration are released in two steps; the first starts at about 85 °C, which equates to approximately three water molecules, and the second at about 180 °C, corresponding to the other three water molecules. A gradual weight loss is observed above 270 °C, probably due to the decomposition of the choline cation and no further mass loss is observed between 500 and 1000 °C. Thermogravimetry of $CrCl_3{\cdot}6H_2O$ shows that three waters of hydration are released at 71 °C, that is, slightly lower than in the ionic liquid, suggesting that the quaternary ammonium salt affects the coordination sphere around the chromium centre.

The chemistry of $CrCl_3{\cdot}6H_2O$ is extremely complex and a variety of species could be present in the ionic liquid. In aqueous solutions the main equilibria include those in Equation (3), and the dominant species are dependent upon the solution environment.[21]

$$[Cr(H_2O)_6]Cl_3\ [0] \rightleftharpoons [Cr(H_2O)_5Cl]Cl_2 \cdot H_2O\ [I] \rightleftharpoons [Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O\ [II] \rightleftharpoons [Cr(H_2O)_3Cl_3] \cdot 3H_2O\ [III] \tag{3}$$

Elving and Zemel showed that the UV-visible spectrum of the chromium species is affected by the number of chloride and water ligands bound to the metal. For each complex two bands are observed; the first in the range 407 to 475 nm and the second in the range 575 to 665 nm. In each range the lower value corresponds to the hexaaqua complex [0] and the upper value to the trichloro species [III]. The addition of each chloride ligand shifts the lower wavelength band by about 20 to 25 nm and the upper band by 30 nm.[21] In a neutral aqueous solution species [I] and [II] dominate and species [III] is only observed when the solution contains 12 M HCl. In the 2:1 $CrCl_3{\cdot}6H_2O$/choline chloride mixture, two bands are also seen, one at 470 nm and the other at 669 nm. This suggests that in the ionic liquid the trichloro species is present. A pronounced shoulder is observed at 700 nm suggesting a species with four chlorides is formed in the high chloride environment [Eq. (4)]:

$$CrCl_3 \cdot 3H_2O + Cl^- \rightleftharpoons [CrCl_4 \cdot 2H_2O]^- + H_2O \tag{4}$$

Electrospray MS of the eutectic mixture shows some evidence for $[CrCl_4]^-$ (*m*/*z*: 192/194*/196) in the ionic liquid (the waters of hydration are bound too weakly to be observed and $[Cr(H_2O)_3Cl_3]$ is neutral and therefore not detected) although no evidence is observed in FAB MS. In the mixtures of choline chloride with $ZnCl_2$ and $SnCl_2$, di- and trimetal-containing anions with bridging chloride ligands were observed.[19] No evidence was obtained for dichromium containing complexes; however, these may be very weak complexes and hence not detectable by using FAB-MS. No evidence is observed for the dianion $[CrCl_5(H_2O)]^{2-}$. In addition, no major chromium-containing ions were seen in the positive ion spectra. Hence we conclude that the main chromium complex in the ionic liquid is $[Cr(H_2O)_3Cl_3]$.

Figure 1 shows the viscosity of ChCl/$CrCl_3{\cdot}6H_2O$ mixtures as a function of temperature and composition. It is noticeable that the viscosity of these ionic liquids is considerably lower than the ChCl/$ZnCl_2$ ionic liquids reported previously,[19] suggesting that the waters of hydration play a significant role in solvation. The viscosity of the medium is reduced as the mole fraction of $CrCl_3{\cdot}6H_2O$ is increased, and the minimum viscosity is not observed at the eutectic composition.

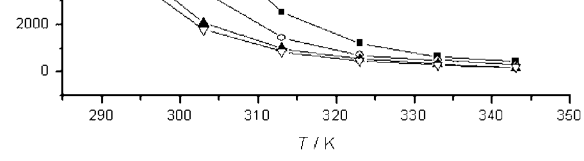

Figure 1. Viscosity of ChCl/$CrCl_3{\cdot}6H_2O$ mixtures as a function of temperature and composition

The change in viscosity (η) with temperature is given by Equation (5):

$$\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT} \tag{5}$$

in which η_0 is a constant and E_η is the energy for activation of viscous flow.[22] Table 2 shows that all the data in Figure 1 fit well to Equation (5); the values obtained for E_η are also given in Table 2.

Table 2. Activation energies for viscous flow (E_η) and conductivity (E_A) as a function of liquid composition. Coefficients of correlation (r) for the fits to Equations (5)[a] and (8)[b] are also given.

ChCl/ $CrCl_3\cdot 6H_2O$	E_η [kJ mol^{-1}]	r[a]	E_A [kJ mol^{-1}]	$-r$[b]
1:1	58.5	0.997	43.7	0.999
1:1.5	55.5	0.994	50.5	0.995
1:2	54.2	0.998	41.2	0.996
1:2.5	52.4	0.996	40.6	0.992
1:3	–	–	37.8	0.999

It has been shown empirically that E_η values are related to the melting point of liquids (T_m) by Equation (6).[22]

$$E_{\eta=}3.74\,RT_m \tag{6}$$

This has been found to be valid for a range of molecular liquids and high-temperature molten salts.[22] This would suggest an E_η value of approximately 9 kJ mol^{-1} for the $ChCl/CrCl_3\cdot 6H_2O$ mixtures, which is significantly smaller than that shown in Table 2. The values for the chromium-containing liquid are, however, similar to other room-temperature ionic liquids. Branco et al.[23] reported the viscosity of a range of imidazolium salts and using these data the energy for activation of viscous flow was found to range from 37.2 (C_4mimBF_4) to 59.7 kJ mol^{-1} ((C_5O_2mimCl). Figure 2 shows the plot of E_η verus RT for the data in Figure 1 and that extracted from the Branco study.[23] A roughly linear trend is observed with a constant of proportionality of 20.7. This suggests that the empirical relationship observed in Equation (6) for molecular liquids and high-temperature molten salts, is not valid for ambient-temperature ionic liquids and may result from the large size of the solvent ions found in the latter.

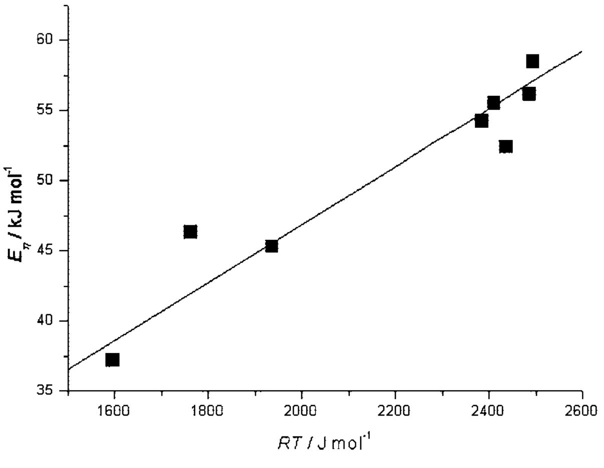

Figure 2. Energy for activation of viscous flow as a function of ionic liquid freezing point.

The eutectic mixture has a very high refractive index (1.5470), which is larger than that of most molecular solvents and comparable to many of the imidazolium-based ionic liquids and high-temperature molten salts.[24–26] The density is also extremely large (1.54 g cm^{-3} at 60 °C) and is greater than other imidazolium-based ionic liquids and suggests a small void volume in the liquid. The surface tension (77.68 ± 0.05 mN m^{-1} at 40 °C) is higher than water and is comparable to high temperature molten salts, for example, KBr $\gamma = 77.3$ mN m^{-1} at 900 °C.[26]

In high-temperature molten salts hole theory has been used to explain the mobility of ions. It can be shown that in a molten salt the radius of the average sized void (r) is related to the surface tension of the liquid (γ) by the expression given in Equation (7):[22]

$$4\pi\langle r^2\rangle = 3.5\frac{kT}{\gamma} \tag{7}$$

in which k is the Boltzmann constant and T the absolute temperature. Hence, in the ionic liquid containing chromium chloride the average void radius is 1.24 Å, while the radius of the choline ion is 3.29 Å. By contrast, for KBr at 900 °C the average void radius is 2.1 Å, whereas the cation radius is 1.3 Å.[22] This explains the significant disparity between the viscosity of molten salts and ionic liquids, namely, the ratio of ionic radius to void radius is considerably larger for ionic liquids than molten salts making ionic motion considerably easier in the latter case. We therefore suggest that the large spread of E_η values could be due to the inordinately large solvent/hole ratio, which appears to be characteristic of room-temperature ionic liquids. This is, however, difficult to prove at present, because of the lack of consistent viscosity and E_η data available.

Figure 3 shows the conductivity of choline chloride/chromium chloride mixtures as a function of temperature and composition. The data show liquids that have conductivities that are an order of magnitude larger than the $ZnCl_2/ChCl$ system and comparable to imidazolium salts. This is probably related to the viscosity of the ionic liquids, since the $ZnCl_2/ChCl$ system is an order of magnitude more viscous and the imidazolium salts have similar viscosities to those shown in Figure 1. Analogous to the viscosity data, conductivity (σ) of ionic liquids have been fitted to Equation (8).[22]

$$\ln \sigma = \ln \sigma_0 - \frac{E_A}{RT} \tag{8}$$

The activation energy for conduction (E_A) is listed in Table 2 as a function of composition. As with the E_η values, they are significantly larger than high-temperature molten salts (typically group I halides have values of 5 to 20 kJ mol^{-1}).[26]

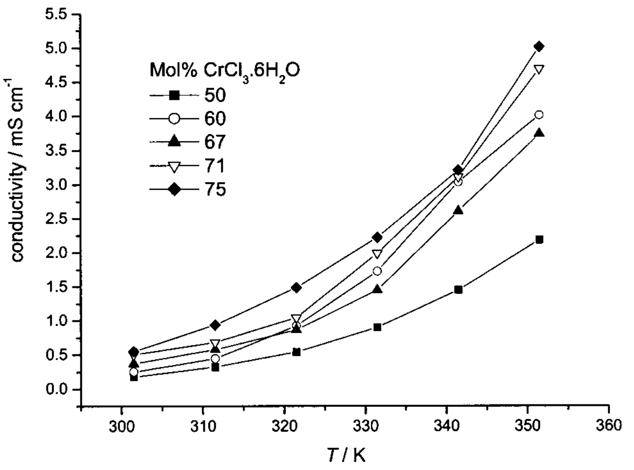

Figure 3. Conductivity of ChCl/CrCl$_3$·6H$_2$O mixtures as a function of temperature and composition.

For ionic fluids, the conductivity is generally governed by the mobility of the charge carriers. Hence a plot of σ versus η^{-1} should be linear for a given charge carrier. The case of chromium chloride is somewhat complex because of the various ligand permutations that are possible [Eq. (9)].

$$\begin{aligned}&\mathrm{ChCl} + [\mathrm{Cr(H_2O)_4Cl_2}]\mathrm{Cl}\cdot 2\,\mathrm{H_2O} \rightleftharpoons [\mathrm{Cr(H_2O)_3Cl_3}]\cdot 3\,\mathrm{H_2O}\\&+\mathrm{ChCl} \rightleftharpoons \mathrm{Ch^+}[\mathrm{Cr(H_2O)_2Cl_4}]^-\cdot 4\,\mathrm{H_2O}\end{aligned} \tag{9}$$

Figure 4 shows a strong linear correlation between conductivity and the reciprocal of viscosity, which shows that the ionic mobility is controlling the conductivity of the liquid. It also shows that since the slope is approximately constant at all compositions, the charge-carrying species is dominated by one species. The UV-visible data suggests that $[\mathrm{Cr(H_2O)_3Cl_3}]\cdot 3\,\mathrm{H_2O}$ is the major chromium containing species and hence the charge carriers are presumably Ch$^+$ and Cl$^-$.

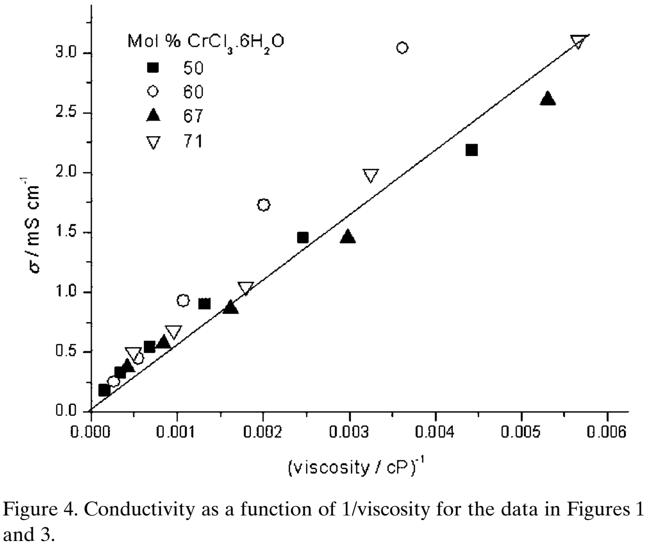

Figure 4. Conductivity as a function of 1/viscosity for the data in Figures 1 and 3.

The clear application of an ionic liquid containing chromium is for the study of chromium electrodeposition. Figure 5 shows the cyclic voltammogram for the 1:2 ChCl/CrCl$_3$·6H$_2$O system at 60 °C on a Pt microelectrode at a sweep rate of 20 mV s^{-1}. The reduction process that is initiated at approximately 0 V is most probably due to the reduction of Cr^{3+} to Cr^{2+}. At fast sweep rates (>100 mV s^{-1}) the process appears to be quasi-reversible, but at 20 mV s^{-1} the reduction current decreases markedly when $E < -0.5$ V; this is indicative of electrode passivation. This could either be due to the precipitation of a Cr$^{\mathrm{II}}$ species or the reaction of a Cr$^{\mathrm{II}}$ species to give an insoluble product on the electrode surface. The instability of Cr$^{\mathrm{II}}$ species, even considering that the solvent is ionic, suggests that the latter is the most likely explanation for the passivation process. Assuming that the current (i) for the process prior to passivation is diffusion limited, the diffusion coefficient (D) for the reduction reaction in Equation (10) is given by Equation (11)[27] in which F is the Faraday constant, c is the concentration and r the radius of the electrode.

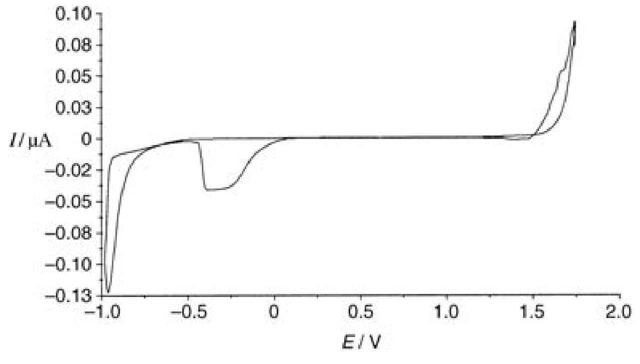

Figure 5. Cyclic voltammogram for the 1:2 ChCl/CrCl$_3$·6H$_2$O system at 60 °C on a Pt microelectrode at a sweep rate of 20 mV s^{-1}.

$$\mathrm{Cr^{3+}} + \mathrm{e^-} \rightleftharpoons \mathrm{Cr^{2+}} \tag{10}$$

$$D = i/4nFcr \tag{11}$$

This yields a diffusion coefficient of 8.2×10^{-12} m^2 s^{-1} which is somewhat higher than that predicted by the Stokes–Einstein equation (2.4×10^{-12} m^2 s^{-1}); however, Equation (11) does make the assumption that the process is diffusion limited, which may be less valid given the high concentration of the chromium salt (4.4 mol dm^{-3}). Notwithstanding, the electrochemical process is clearly due to the reduction of the Cr$^{\mathrm{III}}$ complex.

Probably the most interesting observation is that no reduction current for the decomposition of water is observed. This suggests that the water molecules are highly coordinated and, since the medium acts as a poor base, the protons on the water are less acidic than in an aqueous solution.

At larger negative over-potentials a nucleation loop characteristic of deposition is observed. This suggests that whatever is partially passivating the electrode surface is still conducting enough to allow its subsequent reduction to the metallic form. The deposition process is apparently irreversible; this is surprising since the deposition of aluminum in an ionic liquid is reversible.[28]

Electrodeposition of chromium is usually carried out from aqueous solutions based either on CrO_3/H_2SO_4 or trivalent chromium salts/complexing agents.[29] Both of these solutions have their limitations primarily due to the competing hydrogen evolution process, which limits the current efficiency and leads to hydrogen embrittlement of the substrate, but also because of the highly cracked deposit that is produced.[29] The high toxicity of Cr^{VI} is also an issue in its use.

Bulk deposition from the 1:2 $ChCl/CrCl_3{\cdot}6\,H_2O$ system at 60 °C for 2 h onto a nickel electrode at a current density of 0.345 $mAcm^{-2}$ resulted in an amorphous pale blue/grey deposit of 27 µm thickness. Negligible gas evolution was observed confirming that the waters of hydration are less electrochemically active than bulk water. The current efficiency for the process was found to be in excess of 90 %. Exact quantification was not possible due to the incorporation of a small, but undetermined, amount of chloride in the film. Hard chrome plating based on aqueous chromic acid results in an inherently inefficient process; only 10–20 % of the energy supplied is utilised for electrodeposition.[29] Also, the deposition of the metal from Cr^{VI} naturally necessitates twice as much current as the corresponding Cr^{III} complex. Power consumption is an important factor in the practical operation and the very high efficiency of the ionic-liquid-based processes could have a greatly beneficial impact on the industrial sustainability of chrome plating. Also, the absence of hydrogen production during plating will eliminate the potential for hydrogen embrittlement, a significant factor for component failure.

Figure 6 shows the scanning electron micrograph of the deposit formed from the bulk electrolysis of the chromium-containing ionic liquid, and it can clearly be seen that it is not micro-cracked as is typical of the deposits formed from aqueous chromic acid solutions. A defect-free coating is important, as it is these micro-cracks that can lead to pitting corrosion in the substrate material. EDAX analysis showed that the deposit was predominantly chromium with a small amount of residual chloride. The hardness of the film was 242 Vickers, which is less than the chrome hydride formed by the chromic acid process (typically 800 to 900 Vickers) but greater than pure chromium (typically 220 Vickers). This shows that chromium(III)-containing ionic liquids could be a suitable alternative to hexavalent chrome baths for the deposition of crack-free chromium coatings.

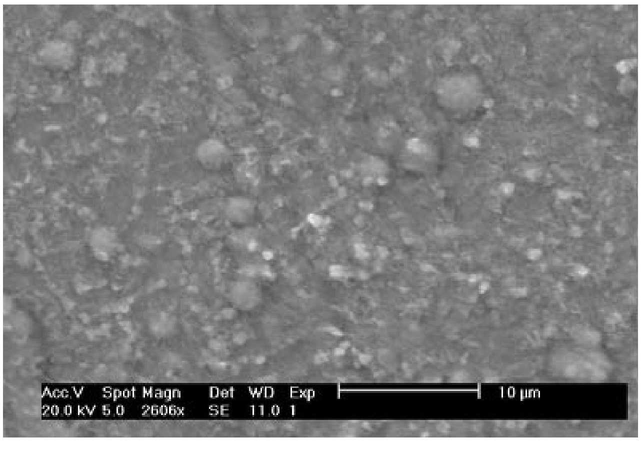

Figure 6. SEM image of the deposit formed following the electrolysis of the 1:2 $ChCl/CrCl_3{\cdot}6\,H_2O$ system at 60 °C for 2 hours onto a nickel electrode at a current density of 0.345 $mA\,cm^{-2}$ (bar = 10 µm).

The mixture of hydrated metal salts with substituted quaternary ammonium salts is by no means limited to $CrCl_3{\cdot}6\,H_2O$. A wide variety of hydrated salt mixtures with choline chloride have been found to form these ionic liquids, including $CaCl_2{\cdot}6\,H_2O$, $LaCl_3{\cdot}6\,H_2O$, $CoCl_2{\cdot}6\,H_2O$, $LiNO_3{\cdot}4\,H_2O$ and $Zn(NO_3)_2{\cdot}4\,H_2O$.[30] This represents a novel method of incorporating other metals into ionic-liquid-like fluids.

Conclusion

It has been shown that ionic liquids can be formed between choline chloride and a variety of hydrated metal salts. A wide variety of metals can be included into ionic liquids by this method and they are shown to have improved transport properties over anhydrous metal salt systems. Specifically the choline chloride/$CrCl_3{\cdot}6\,H_2O$ system has been characterised as a function of composition and temperature and is found to have properties similar to imidazolium-based ionic liquids. The temperature effects on the viscosity and conductivity of these liquids are explained in terms of the ion/hole ratio. The electrodeposition of thick, adherent, crack-free chromium films is demonstrated from this ionic liquid, and it is shown that the waters of hydration are highly coordinated in the liquid and are not significantly electroactive within the potential window of the liquid. This could offer an efficient and environmentally more acceptable process by which to electrodeposit chromium than the current chromic acid based solutions.

Experimental Section

Choline chloride [ChCl] (Aldrich, 99 %) was dried under vacuum prior to use and chromium(III) chloride hexahydrate (Fluka, 98 + %) was used as received to prepare the ionic liquid. Choline chloride and chromium(III) chloride hexahydrate in a molar ratio of 1:2 were combined and heated at approximately 70 °C until a green liquid was obtained, (approximately 30 minutes for 0.03 moles of 1:2 mixture). With prolonged heating the liquid turned purple due to the loss of water molecules from the coordination sphere around the chromium ion. This process was, however, reversible on cooling the mixture.

The viscosity was determined using a Brookfield DV-E viscometer fitted with a thermostated jacket. The conductivity and its temperature dependence were determined by using a Jenway 4071 conductivity meter with temperature and conductivity probes (probe cell constant = 1.01 cm^{-1}). Refractive index measurements were made with a Bellingham and Stanley refractometer, which was calibrated using dichloromethane and toluene as reference standards. A Kruss K11 tensiometer equipped with a thermostatted 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.[20] Thermogravimetric analysis was carried out using Perkin–Elmer Pyris 6 TGA at a heating rate of 5 °C min^{-1}.

Voltammetry and chronoamperometry were carried out using an Autolab PGSTAT12 potentiostat controlled with GPES software. A three-electrode system consisting of a platinum microelectrode ($5x10^{-4}$ cm radius), a platinum counter electrode and a chromium wire reference electrode were used. The working electrode was polished with 0.3 µm alumina paste, rinsed and dried prior to all measurements. Electrochemical measurements were performed at 60°C and a scan rate of 20 $mV s^{-1}$ was used in voltammetric experiments.

The effect of current density on chromium deposit morphology was determined by using a Hull Cell. Two nickel plates were abraded with glass paper (P600), degreased with hexane and dried. Bulk electrolysis experiments were performed by using a Thurlby Thander power supply. Following electrolysis the cathode was washed with deionised water and dried. Surface analysis was carried out by means of scanning electron microscopy (SEM) and energy dispersive analysis by X-rays (EDAX).

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