Physicochemical properties of highly conductive urea–EtMeImCl melts†

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Urea–EtMeImCl mixtures have melting points from 333 to 363 K at 10–80 mol% urea, and, at temperatures >343 K, these melts show the highest conductivity reported to date for urea-based binary melts.

Research based on ionic liquid (or molten salt) solvents that exhibit attractive physical and chemical properties, such as chemical inertness, negligible vapor pressure, high thermal stability, and resistance to oxidation and reduction, have created many technological opportunities. For example, high-temperature ionic liquids (HTILs) have made it possible to produce Ti and Si directly from their oxides.[1] Likewise, the increased interest in room-temperature ionic liquids (RTILs) has opened new pages in the study of materials science and energy technology.[2] However, ionic liquid solvents, whether high- or low-melting, have certain drawbacks. For example, HTILs are often difficult to handle, especially when their melting temperatures are >573 K, and, without exception, RTILs are very expensive to prepare and purify compared to the conventional molecular solvents that they are supposed to replace in certain applications.

In a precise sense, urea-based mixtures[3–6] are not ionic liquids, but the combination of a salt and anhydrous urea. Depending on the salts that are used to prepare these mixtures, it is possible to obtain melts that are liquid below room temperature, *e.g.*, $t_m \leq 298$ K, or melts that become liquid in the temperature interval between 298 K and the decomposition point of urea. These melts often possess physicochemical and solvent properties that are comparable to low-melting organic salt-based ionic liquids, but their most attractive feature is their low cost of production. One serious drawback to these urea–salt melts (USMs), particularly with regard to electrochemical applications, is their low electrical conductivity. In this article, we describe recent results with a USM prepared by combining urea with the dialkylimidazolium salt, 1-ethyl-3-methylimidazolium chloride (EtMeImCl).[7] This mixture exhibits much higher conductivity than the other binary urea-based melts that have been described to date.

The urea used in this investigation (ACS reagent, 99–100%) was pretreated by drying under vacuum (1×10^{-3} Torr at 373 K). The preparation and purification of EtMeImCl have been described in a previous article.[7] All of the mixtures were prepared in a dry argon-filled glove box equipped with an inert gas purification system (VAC, O_2 and $H_2O < 1$ ppm) and were agitated in capped glass bottles at 373 K for 24 h before use. The resulting USMs were clear and colorless.

Fig. 1 shows the melting points of urea–1-ethyl-3-methylimidazolium chloride binary mixtures as a function of the mole fraction of urea. When the mixture composition is between 10 and 80 percent mole fraction (mol%) urea, the melting points are between 333 and 363 K. The melting point diagram exhibits two eutectic points at 25.0 and 72.5 mol% urea. The physical properties of the melts at 25.0 and 75.0 mol% urea are summarized in Table 1 along with those reported for other urea-based binary melts and selected RTILs. What is most notable about these melts is that they are substantially more conductive than the other urea–salt base mixtures that have been reported to date, including the popular urea–choline chloride melts.[5] In fact, they exhibit conductivities that are comparable to those of traditional non-chloroaluminate RTILs such as $EtMeImTf_2N$. The high electrical conductivities (≥ 10 mS cm^{-1}), low viscosities (≤ 50 cP), and low melting points (≤ 373 K) of these urea–EtMeImCl melts suggest that they would be useful solvents for chemistry and electrochemistry.

The interactions among $EtMeIm^+$, Cl^-, and urea in the 25.0 and 75.0 mol% urea–EtMeImCl melts were investigated by the use of FTIR and NMR. FTIR spectra covering the hydrogen-stretching region for solid urea[11] and solid EtMeImCl[12] were identical to those previously reported (see ESI Fig. S1 (top)†). The urea spectrum is characterized by prominent bands at approximately 3350 and 3450 cm^{-1} that are attributed to symmetrical and asymmetrical N–H stretches and a weak band at $\sim$3260 cm^{-1}. The spectrum of solid EtMeImCl exhibits a broad cluster of absorption bands centered at $\sim$3050 cm^{-1}. This band, albeit somewhat shifted in energy, is also seen in Lewis basic $AlCl_3$–EtMeImCl and was designated by Dieter *et al.*[13] as the Cl^- interaction band.

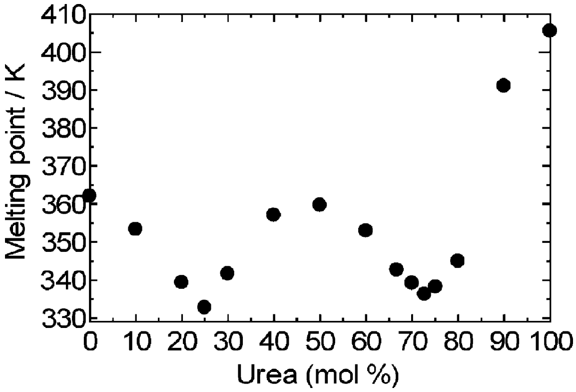

Fig. 1 Melting points of urea–EtMeImCl melts.

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Table 1 Physical properties of urea–EtMeImCl melts

USMs/ RTILs	T/K	ρ^a/ g cm^{-3}	η^b/ cP	κ^c/ mS cm^{-1}	Ref.
25.0 mol% urea–EtMeImCl	343	1.136	97.69	11.20	
	348	—	—	13.58	
	353	1.128	59.32	16.24	
	358	—	—	20.63	
	363	1.121	31.94	23.77	
75.0 mol% urea–EtMeImCl	343	1.196	47.31	13.17	
	348	—	—	15.83	
	353	1.190	28.68	18.80	
	358	—	—	21.68	
	363	1.182	18.33	24.70	
78.3 mol% urea–$LiTf_2N^d$	323	—	—	1.2^e	4
76.7 mol% urea–$LiTf_2N^d$	333	—	—	2.24^e	6
66.7 mol% urea–ChCl^f	353	—	—	*ca.* 7.6^e	5
50.0 mol% $AlCl_3$–EtMeImCl	343	1.258	6.654	52.45^e	8
EtMeImF$(HF)_{2.3}$	343	1.098	2.55	173.0	9
EtMeImTf_2N	343	—	—	15.21^e	10

^{a} Density. ^{b} Viscosity. ^{c} Conductivity. ^{d} $LiN(SO_2CF_3)_2$. ^{e} Estimated from references. ^{f} Choline chloride.

These workers also ascribe bands appearing at 3120–3200 cm^{-1} to the hydrogen stretches at the *c*, *e* and *f* sites on the EtMeIm$^+$ ring (*cf.* Fig. 2). They noted that the addition of solvents such as dichloromethane and benzene to this ionic liquid leads to a decrease in the overall intensity of the Cl^- interaction band because hydrogen bonding between the hydrogen atoms on the EtMeIm$^+$ ring and Cl^- is disrupted by the addition of these solvents. This is also the case in urea–EtMeImCl mixtures. In solid solutions containing 25.0 mol% urea, the intensity of the Cl^- interaction band is decreased from that seen for solid EtMeImCl and virtually disappears from the solid solution containing 75.0 mol% urea (see ESI Fig. S1 (bottom)†). Similar behavior has also been noted in fluorohydrogenate RTILs.[14] Interactions between the Cl^- and urea are also evident. For example, the two prominent N–H stretching vibrations seen at 3350 and 3450 cm^{-1} in the solid urea sample are shifted to 3307 and 3430 cm^{-1}, respectively, in the 25.0 mol% urea–EtMeImCl solid solution (See ESI Fig. S1 (bottom)†), suggesting that Cl^- also interacts with the urea NH_2 groups.

Fig. 2 shows ^1H NMR spectra of various urea–EtMeImCl melts as a function of composition (The results from ^{13}C NMR experiments are given in the ESI†). As expected, based on the results of the FTIR experiments, the hydrogen atoms at the *c*, *e*, and *f* sites on the EtMeIm$^+$ cation are most obviously affected by the melt composition, shifting to higher magnetic field strength as the urea composition increases and the concentration of Cl^- decreases. A much smaller shift is seen for the urea protons at the *g* site. This behavior is similar to that observed when non-electrolytes such as acetonitrile or benzene are added to the Lewis basic $AlCl_3$–EtMeImCl RTIL,[13] and it indicates that the addition of these solvents decreases the interactions between Cl^- and the hydrogen atoms on the imidazolium ring. Obviously, the addition of urea to EtMeImCl also decreases these interactions. A similar phenomenon is reported to take place in fluorohydrogenate RTILs.[14] The reduced interactions between Cl^- and the hydrogen atoms on the imidazolium ring may explain in part the unexpectedly high conductivity of urea–EtMeImCl melts.

The electrochemical stability of the urea–EtMeImCl melts was estimated by using staircase voltammetry. The potential scan was initiated from the rest potential, which is indicated by the origin of the directional arrows in Fig. 3. As shown in Fig. 3(a) and (b), the electrochemical window at a glassy carbon (GC) electrode is *ca.* 2.75 V in the 25.0 mol% urea melt and 2.98 V in the 75.0 mol% melt. (This window was estimated by measuring the cathodic and anodic limiting potentials at which a current density of ±0.3 mA cm^{-2} was observed.) However, if an electrode with a smaller hydrogen overpotential is employed, *e.g.*, platinum, the electrochemical window is decreased, and the reduction current increases as the urea content of the melt is increased. In fact, a number of research groups have reported that hydrogen evolution results from the electrochemical reduction of urea in urea-based melts,[15] according to the reaction:

$$H_2N\text{–}CO\text{–}NH_2 + e^- \rightleftarrows 1/2H_2\,(g) + H_2N\text{–}CO\text{–}NH^-$$

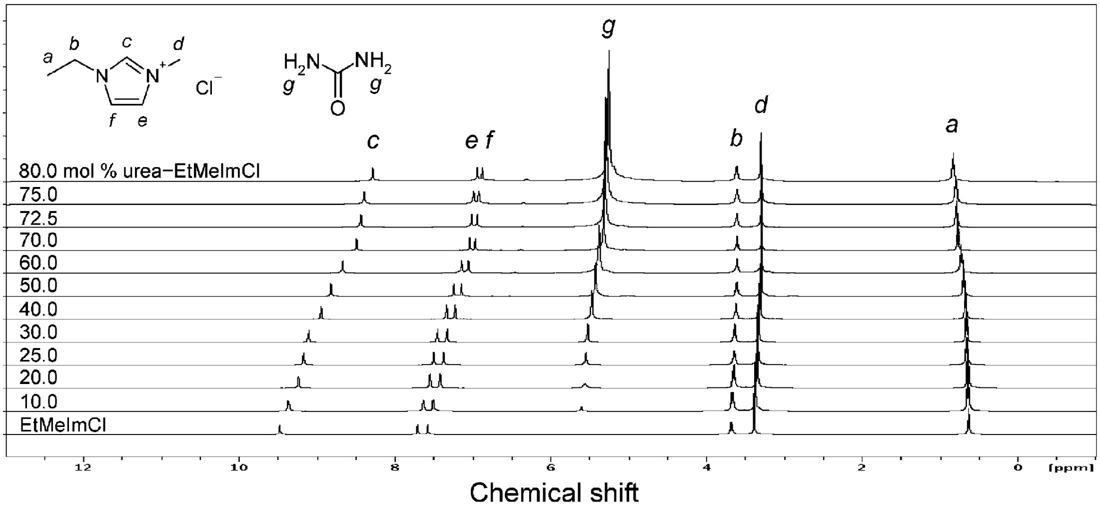

Fig. 2 ^1H NMR of urea–EtMeImCl (0 ≤ urea ≤ 80 mol%) melts at 363 K.

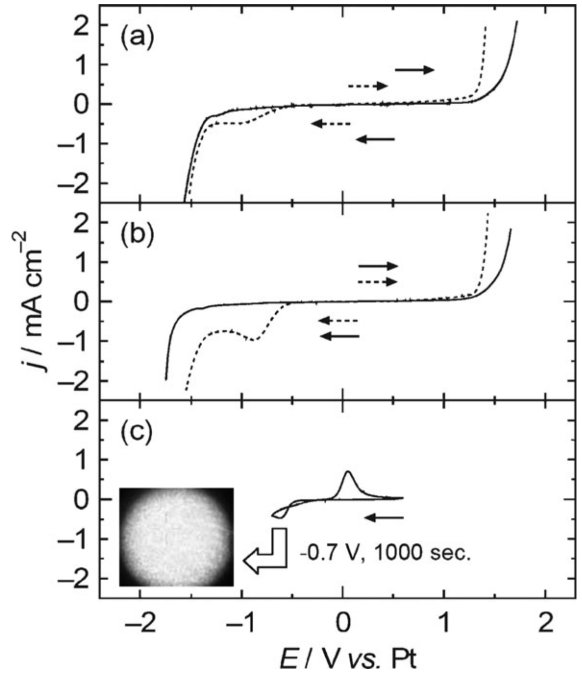

Fig. 3 Linear sweep voltammograms recorded at a Pt (--) and a GC (—) electrode in (a) 25.0 and (b) 75.0 mol% urea–EtMeImCl melts; (c) a cyclic voltammogram recorded at a GC electrode in 25.0 mol% urea–EtMeImCl melt with 10.3 mmol L^{-1} AgCl; (inset) an optical micrograph of the sample electrodeposited at −0.7 V for 1000 s. The temperature was 343 K, and the scan rates were 50 mV s^{-1}.

The reduction of urea in urea–EtMeImCl melts was examined as a function of scan rate (See ESI Fig. S4†).[16] The results are similar to those reported for the reduction of urea in urea–acetamide–NaBr mixtures; however, the much smaller anodic to cathodic peak separation found during this investigation suggests that this reaction is more facile in the urea–EtMeImCl system than in the former melt. The decrease in the anodic to cathodic peak current density ratio, $j_{pa}/|j_{pc}|$, with increasing scan rate as shown in the inset of this figure suggests that the reaction shown above is complicated by a coupled homogeneous reversible chemical reaction,[16] but we were unable to identify this reaction.

Fig. 3(c) shows a cyclic staircase voltammogram recorded at a glassy carbon electrode in 75.0 mol% urea–EtMeImCl containing 10.3 mmol L^{-1} AgCl. A single reduction wave with an associated oxidation wave attributed to the expected reduction of Ag^{+} and oxidation of deposited Ag is present. The cross-over loop in this voltammogram is typical of a nucleation rate-controlled deposition process. As shown in the inset of Fig. 3(c), controlled-potential electrolysis at −0.7 V yielded a good quality Ag deposit. This result implies that the urea–EtMeImCl melt can be used as an electrolyte for plating and other electrochemical technologies as has been demonstrated for some other urea–based melts.[3–6,15]

In conclusion, we describe in this article a novel urea–EtMeImCl melt system with a relatively low melting point and higher conductivity than the other binary urea-based melts reported to date. The melts described herein are easy to prepare and are less expensive than the corresponding dialkylimidazolium-based ionic liquids, such as EtMeImBF$_4$, *n*-BuMeImPF$_6$ or EtMeImTf$_2$N, and they may serve as an effective substitute for these RTILs in many applications.

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