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Physicochemical Properties of Highly Conductive Urea-EtMeImCl Melts

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Experimental

Measurement of physicochemical properties.-Density measurements were carried out with a 10 mL Pyrex glass pycnometer. Viscosities were determined with a modified Cannon-Fenske Number 200 viscometer (Fischer Scientific). The construction of the pycnometer and viscometer as well as the detailed experimental procedures that were used for these measurements are presented in previous articles.¹ The pycnometer and the viscometer were calibrated with dry propylene glycol and 66.7 mol % AlCl₃–EtMeImCl room-temperature ionic liquid. The data reported herein are the average values of at least three measurements. The melting points of the urea–EtMeImCl melt were measured with a Barnstead|Thermolyne Mel-Temp[®] Model 1101D.

Specific conductance measurements were carried out in an airtight Pyrex[®] glass conductivity cell equipped with platinum flag electrodes. The resistance of the conductivity cell was determined as a function of frequency with a Stanford Research Systems Model SR720 LCR meter operated at a drive potential of 0.10V. The conductivity cell was calibrated with 0.002, 0.01, 0.05, 0.10, and 0.20 mol L⁻¹ solutions of KCl and 66.7 mol % AlCl₃–EtMeImCl room-temperature ionic liquid, according to IUPAC recommendations.² Each of the reported specific conductance values was the average of at least 5 measurements.

FT-IR and NMR measurements.-FT-IR data were obtained by the use of a Perkin-Elmer Paragon 500 FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded by using a Bruker Avance DRX-500 spectrometer operated at 363 K.³ The chemical shifts were externally referenced to DMSO-d₆ in a concentric capillary placed in a 5 mm diameter tube.

Electrochemical experiments.-Electrochemical experiments were conducted with an EG&G PARC Model 263A potentiostat/galvanostat. This instrument was controlled with a desktop computer utilizing EG&G PARC Model 270 software. All electrochemical experiments were carried out in three-electrode cells. Electronic resistance compensation was employed during voltammetric experiments. The working electrodes were a Pt disk electrode (Bioanalytical Systems, MF-2013, 0.020 cm²) and a glassy carbon (GC) disk electrode (Bioanalytical Systems, MF-2012, 0.0707 cm²). A 0.05-cm diameter straight platinum wire and coil of the same platinum wire (Alfa Aesar, 99.95 %), both immersed

in a neat melt with the same composition as the bulk melt, were used as quasi-reference and counter electrodes, respectively. These two electrodes were separated from the bulk melts by a porosity E glass frit (ACE glass). All electrochemical experiments were carried out with the cell isolated in a dry argon-filled glove box equipped with an inert gas purification system (Vacuum Atmosphere Company, NEXUS system with O_2 and $H_2O < 1$ ppm).

Characterization of the electrodeposits.-Characterization of the Ag samples electrodeposited in the urea-EtMeImCl melt was conducted with a Perkin-Elmer Optima 2100 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). The surface morphology of the resulting samples was studied with a Nikon Epiphot 300 optical microscope at 400-fold magnification.

Additional discussion

¹³C NMR experiments.-Figures S2 and S3 show ¹³C NMR spectra of the urea–EtMeImCl melts as a function of urea composition. Major shifts in the spectra were observed for the signals corresponding to the carbon atoms at the *c* and *h* sites. The shift at the *c* site is very similar to that seen in the ¹H NMR spectra (See main text.). Although we could not investigate the interactions related to the urea carbonyl group in the melt by FTIR spectroscopy experiments because the carbonyl stretching bands overlapped the bands for EtMeImCl, the ¹³C NMR experiment revealed that the signal for the *h* site (carbonyl carbon) shifts slightly toward higher magnetic field as the fraction of EtMeImCl in the melt increases. In fact, it is well-known that the carbonyl group of the urea strongly interacts with added salts,⁴ and similar interactions likely exist in the urea–EtMeImCl melt as well.

References

 J. R. Sanders, E. H. Ward, and C. L. Hussey, *J. Electrochem. Soc.*, 1986, 133, 325 and 1526; T. Tsuda, C. L. Hussey, H. Luo, and S. Dai, *J. Electrochem. Soc.*, 2006, 153, D171.
E. Juhasz and K. N. Marsh, *Pure Appl. Chem.*, 1981, 53, 1841.

3. **1-Ethyl-3-methylimidazolium chloride**: ¹H NMR (500 MHz, DMSO-d₆) δ 9.47 (s, 1H), 7.70 (s, 1H), 7.57 (s, 1H), 3.67 (quartet, 2H, J = 7.2 Hz), 3.38 (s, 3H), 0.62 (t, 3H, J = 7.2 Hz); ¹³C NMR (125 MHz, DMSO-d₆) δ 135.7, 122.2, 120.8, 43.0, 34.9, 13.9.

4. H. Liang, H. Li, Z. Wang, F. Wu, L. Chen, and X. Huang, *J. Phys. Chem. B*, 2001, **105**, 9966; A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, and V. Tambyrajah, *Chem. Commun.*, 2003, 70 and electronic supplementary information.



Figure S1. FT-IR spectra of (top) (—)solid urea and (---) solid EtMeImCl and (bottom) (—) 25.0 mol % and (---) 75.0 mol % urea–EtMeImCl solid salts. The powder samples were analyzed as KBr pellets. (•) asymmetrical and (\circ) symmetrical NH₂ stretching vibrations for urea.



Figure S2. ¹³C NMR of urea–EtMeImCl ($0 \le \text{urea} \le 80 \text{ mol }\%$) melts at 363 K.



Figure S3. Enlarged ¹³C NMR of urea–EtMeImCl ($0 \le \text{urea} \le 80 \text{ mol }\%$) melts at 363 K.



Figure S4. Cyclic staircase voltammograms recorded at a platinum disk electrode in 75.0 mol % urea–EtMeImCl melt. (inset) Plot of the ratios of the cathodic to anodic peak current densities as a function of scan rate. The temperature was 343 K, the step size was 2 mV, and the scan rates were 25, 50, 100, 200, 300, 400, 500, and 750 mV s⁻¹.