Supporting file for

Mixing cations with different alkyl chain lengths markedly depresses the freezing point in deep eutectic solvents formed from alkylammonium bromide salts and urea

Zhengfei Chen, Tamar L. Greaves, Gregory G. Warr and Rob Atkin*

Priority Research Centre for Advanced Fluids and Interfaces, Newcastle Institute for Energy and Resources, The University of Newcastle, Callaghan, NSW 2308, Australia. Email: rob.atkin@newcastle.edu.au.

School of Science, College of Science, Engineering and Health, RMIT University, GPO Box 2476, Melbourne, Victoria 3001, Australia.

School of Chemistry, The University of Sydney, Sydney, NSW 2006 Australia.

Experimental details

Materials. Alkylamines (ethylamine (66-72% in H₂O) and butylamine (99.5%)) were purchased from Sigma Aldrich. Concentrated hydrobromic acid (HBr) (48% in H₂O) was purchased from Fluka. Urea powder was purchased from Sigma Aldrich. All materials were used without further purification.

General sample preparation. Alkylammonium bromide salts were prepared via a 1:1 molar acid-base reaction in an ice-chilled environment. Concentrated hydrobromic acid (HBr) was slowly added to a diluted, aqueous solution of alkylamine (~ 40%) and then stirred for several hours. The majority of water was removed using a rotational evaporator at 50 °C to yield a colourless solid. The alkylammonium bromide salts (ethylammonium bromide (EABr), or butylammonium bromide (BABr)) were further dried in an oven at 110 °C for at least 2 hours.

Mixtures of EABr, BABr or EABr-BABr with urea were prepared by mixing the alkylammonium salts and urea at different salt : urea molar ratios in a sealed glass vial at 80 °C until a homogeneous clear solution was formed. For higher salt content, higher temperatures were used but for a very short period due to the reactions between salt and urea at elevated temperatures. The water contents were always below 0.6 wt% for the investigated mixtures, determined by Karl Fischer titration (Metrohm 870 KF Titrino Plus). The purity of each system at the eutectic point was examined using ¹H-NMR-Spectroscopy (c.f. ESI, Figure S3).
Melting point determination. Differential scanning calorimetry (DSC) was performed using a DSC-60A (Shimadzu) system under a nitrogen atmosphere. An indium standard was used to calibrate the DSC temperature (0.3 °C). The DES solid samples were run in an aluminium pan in a sealed furnace from room temperature to 250 °C at a rate of 10 °C /min. The liquid samples were cooled to -80 °C before heating at 10 °C /min up to 250 °C. The melting temperature, $T_m$, was determined from the exothermic peak of the DSC traces.

Density and viscosity measurements. The density and viscosity of the deep eutectic solvents were measured simultaneously on a density meter coupled with a microviscometer (Anton Paar DMA4100M) from 25 °C to 80 °C in a sealed environment. The EABr : urea (1:1) solidified quickly below its melting point (46 °C) therefore its density and viscosity could not be determined.

Ionic conductivity. Ionic conductivity measurements were carried out with an Eutech Instruments Con 510 conductivity meter. The instrument was calibrated with a 0.01 M potassium chloride (KCl) solution before each measurement. A glass vial containing the DES was sealed with parafilm after the electrode was inserted to prevent water absorption. Temperature was controlled using a water bath with an accuracy of ±0.5 °C. The heating rate for all samples was less than 1 °C / min.
Figure S1. DSC traces for all samples that shown in Figure 2 in the main text. A: EABr:urea system; B: BABr:urea system; C: EABr:BABr:urea system and D: samples for Figure 2 inset. Samples were run at 10 °C/min. Both samples of EABr:urea (0.2:0.8) and BABr:urea (0.2:0.8) show two endothermic peaks, due to the phase separation at higher urea concentration.
Figure S2. $^1$H NMR spectra of EABr:urea (1:1), BABr:urea (1:1) and EABr:BABr:urea (0.5:0.5:1) showing the shift of NH$_3$ and NH$_2$ peaks toward higher chemical shifts.

Figure S3. Walden plot of EABr : urea, BABr : urea and EABr-BABr : urea mixtures as a function of temperature.
Figure S4. Densities of EABr : urea, BABr : urea and EABr : BABr : urea mixtures as function of temperature.