Supporting file for

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

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Experimental details

Materials. Alkylamines (ethylamine (66-72% in H_2O) and butylamine (99.5%)) were purchased from Sigma Aldrich. Concentrated hydrobromic acid (HBr) (48% in H_2O) 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.
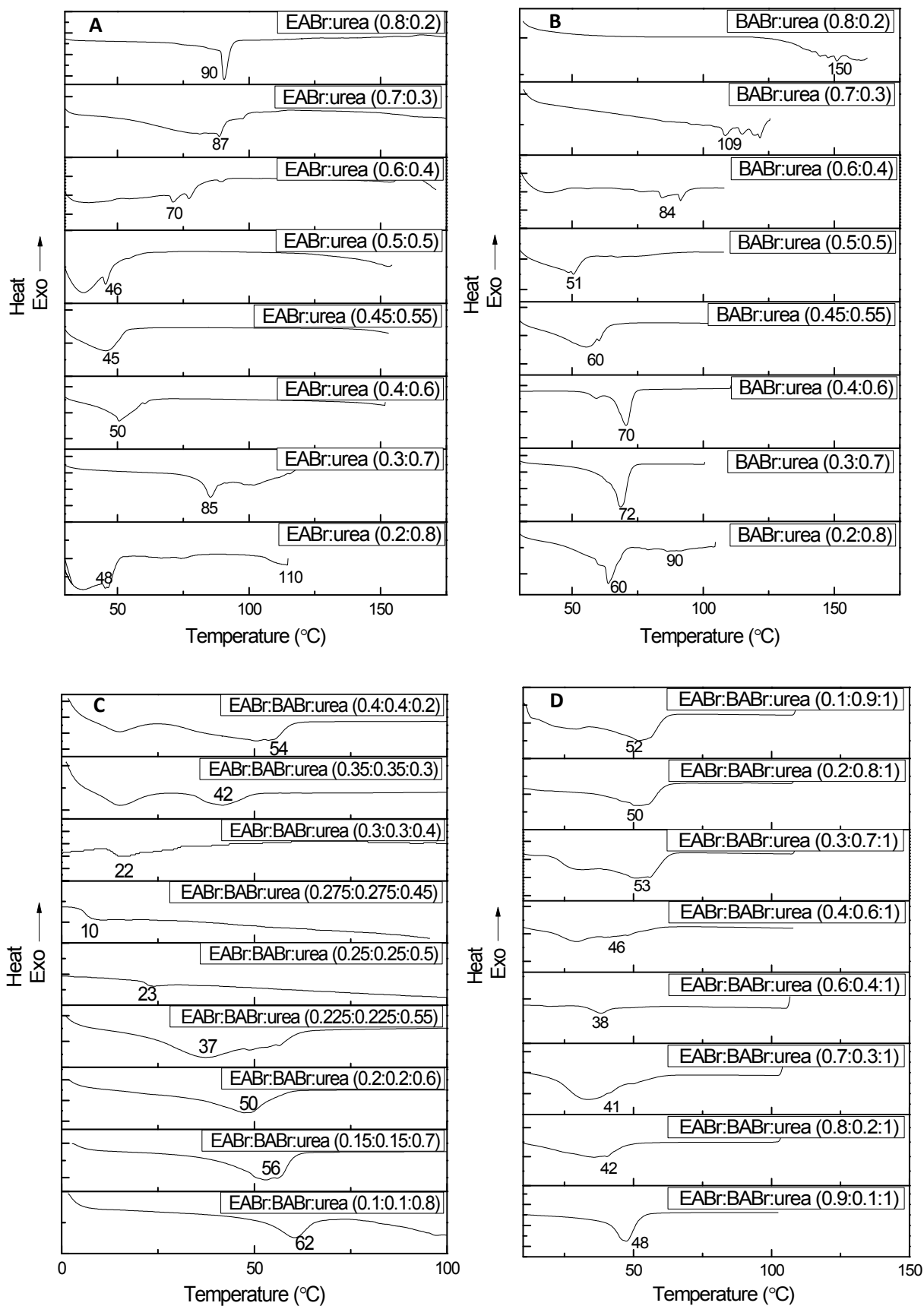
Figure S1. DSC traces for all samples that shown in Figure 2 in the main text. A: EABr:urea system; B: BABr:urea system; C: EABr:BABr:urea system and D: samples for Figure 2 inset. Samples were run at 10 °C/min. Both samples of EABr:urea (0.2:0.8) and BABr : urea (0.2:0.8) show two endothermic peaks, due to the phase separation at higher urea concentration.
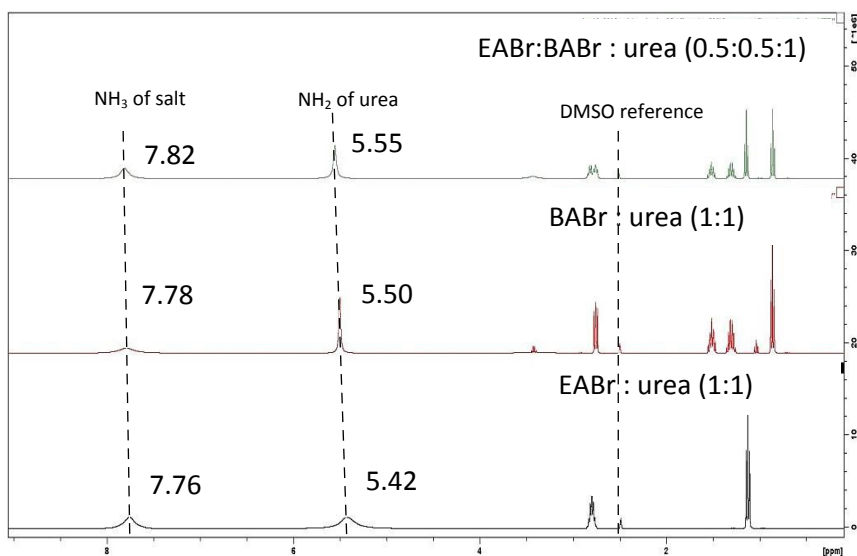
Figure S2. ^{1}H NMR spectra of EABr:urea (1:1), BABr:urea (1:1) and EABr:BABr:urea (0.5:0.5:1) showing the shift of NH$_3$ and NH$_2$ peaks toward higher chemical shifts.
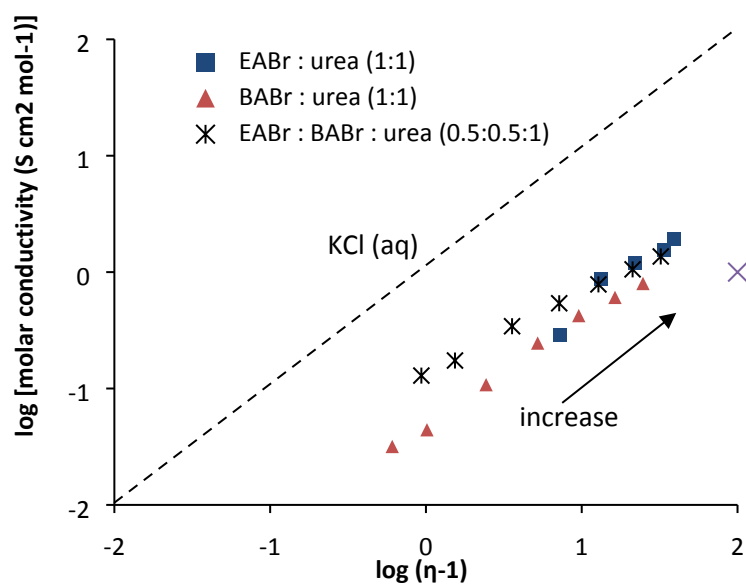

Figure S3. Walden plot of EABr : urea, BABr : urea and EABr-BABr : urea mixtures as a function of temperature.
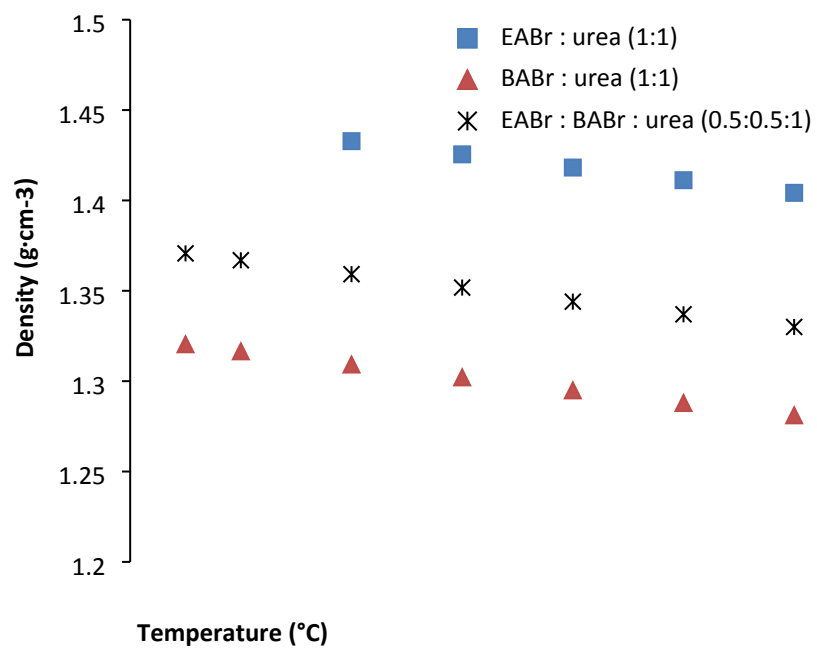
Figure S4. Densities of EABr : urea, BABr : urea and EABr : BABr : urea mixtures as function of temperature.