COMMUNICATION

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

Zhengfei Chen,[a] Tamar L. Greaves,[b] Gregory G. Warr[c] and Rob Atkin*[a]

The melting point of a deep eutectic solvent formed from a ternary mixture of ethylammonium bromide (EABr), butylammonium bromide (BABr) and urea is 10 °C, which is almost 40 °C lower than the melting points of binary DESs formed from either EABr:urea or BABr:urea mixtures. This reveals a new route to prepare room temperature DESs *via* mixing different cations.

Deep eutectic solvents (DES) are formed by mixing two or more components at their eutectic point, which is the composition with the lowest freezing point.[1] DESs are often formed from mixtures of quaternary ammonium halides and a molecular hydrogen bond donor (HBD), such as urea.[2]

The archetypal DES is formed from choline chloride (ChCl, mp = 301 °C) and urea (mp = 133 °C) at a molar ratio of 1 : 2 salt : HBD.[1] In an effort to understand the marked reduction in freezing point in ChCl : urea (1 : 2) compared to the parent materials, interactions between the ions with each other and the HBD has been extensively studied computationally.[3] In addition to the expected Cl···HN hydrogen bonds, urea also hydrogen bonds with the choline cation (*e.g.* OH···O=C and OH···NH), resulting in both Ch–urea and Cl–urea clusters.[3] This may explain why the eutectic point occurs at 1 : 2 ChCl : urea.

The properties of DESs are often compared with ionic liquids,[4,5] which are pure salts that have been molecularly designed to have low freezing points.[6] Many DESs have properties commonly associated with ionic liquids such as non-flammability, low volatility, high thermal stability and high ionic conductivity.[7] Unlike most ionic liquids, DESs are easily prepared from relatively low cost starting materials, and can also be biocompatible and/or of

low toxicity.[1,8,9] The properties and current applications of DESs (mostly based on ChCl) have been comprehensively reviewed.[2,10]

Studies of DESs' applications are frequently related to their use as electrolytes.[11–15] However, the ionic conductivities of DESs are relatively low, especially those with urea as the HBD. For example, the conductivity of 1 : 2 ChCl : urea at 40 °C is only 0.2 mS cm^{-1}.[16] Low conductivity is chiefly due to the intrinsically high viscosities of DESs, and these factors limit their practical application and wider uptake. Here we demonstrate a simple way to reduce DES melting points and viscosity using an equimolar mixture of ammonium cations with different alkyl chain lengths.

Differential scanning calorimetry (DSC) was used to assess the effect of adding the urea HBD to the salts EABr, BABr, and EABr:BABr mixtures.‡ Fig. 1A presents DSC traces without added urea. The endotherms at 205 °C for BABr and 162 °C for EABr show the melting points of the pure salts. EABr has an additional endothermic peak at 95 °C, but the sample remained solid, revealing a solid–solid phase transition and indicating a protic organic ionic plastic crystal.[17] The melting point of 1 : 1 EABr : BABr is 80 °C, much lower than either pure salt, and the endotherm is broader. Similar effects have been noted for mixtures of ionic liquids,[18] and attributed to the different sized cations frustrating ion packing.[19] Fig. 1B shows the effect of adding an

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

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

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

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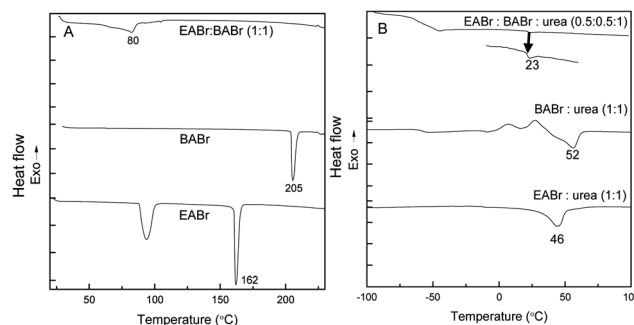

Fig. 1 DSC curves of (A) EABr, BABr and 1 : 1 EABr : BABr molar ratio and (B) 1 : 1 EABr : urea, 1 : 1 BABr : urea and 0.5 : 0.5 : 1 EABr : BABr : urea. A magnified region (indicated by the arrow) shows the melting point of the ternary mixture.

equal number of moles of urea to each salt. The melting points of 1:1 EABr:urea and 1:1 BABr:urea are depressed to 46 °C and 52 °C, respectively, which are much lower than the pure salts, but still well above room temperature. On the other hand, the melting point of the 0.5:0.5:1 EABr:BABr:urea ternary mixture is lowered to approximately room temperature (23 °C).

Fig. 2 presents melting points for EAB–urea, BABr–urea and 1:1 EABr:BABr–urea mixtures as a function of urea mole fraction. These were determined from DSC traces for each system, which are presented in the ESI† (Fig. S1). Melting points for BABr:urea are higher than those of EABr:urea at all compositions, which is attributed to stronger interactions between alkyl chains. For urea mole fractions above 0.55 the freezing point of EABr:BABr:urea is approximately the same as BABr:urea, but below 0.55 the freezing point of EABr:BABr:urea is significantly lower. The eutectic points are at 1:1.2 for BABr:urea, 1:1 for EABr:urea and 0.6:0.6:1 for EABr:BABr:urea.

Fig. 2 (inset) shows the effect of cation composition on the melting point for the ternary EABr:BABr:urea mixtures, where the ratio of the total number of moles of cation ($EA^+ + BA^+$) to urea is fixed at 1:1. The melting point minimum occurs when equal numbers of EA^+ and BA^+ ions are present; when the ion ratios are slightly unbalanced the melting point is ~20 °C higher. The reason for this marked depression in melting temperature when equal numbers of cations and anions are present, and the nature of their interaction with urea, is currently the topic of further study using neutron diffraction experiments with empirical potential structure refinement fitting, and will be reported in a forthcoming article.

For simplicity of comparison, subsequent experiments use 1:1 EABr:urea, 1:1 BABr:urea and 0.5:0.5:1 EABr:BABr:urea mixtures, where the total number of moles of salt and urea are equal.

The ^1H NMR spectra of the alkylammonium bromide:urea DESs are presented in the ESI† (Fig. S2). Chemical shifts for alkyl chain protons are the same for the three mixtures. However, protons of the cation ammonium group and the urea amine groups shift towards low field in the order 1:1 EABr:urea, to 1:1 BABr:urea, to 0.5:0.5:1 EABr:BABr:urea. As low field shifts are a consequence of stronger H-bonds,[20,21] this reveals the strength of hydrogen bonding between $-NH_3$ and $-NH_2$ with bromide increases in the order 1:1 EABr:urea < 1:1 BABr:urea < 0.5:0.5:1 EABr:BABr:urea. The fact that the strongest hydrogen bonds are found for the ternary mixture, which has the lowest melting point, is at first glance surprising. However, the melting point is determined by the sum of the cohesive interactions in the liquid, which means increased hydrogen bond strength in the ternary mixture must be more offset by decreased strength of other cohesive interactions (e.g. electrostatic, van der Waals, etc.) where mixed cations are used. In ionic liquids, weaker electrostatic interactions enable ions to adopt orientations that are more favourable for hydrogen bonding.[22] A similar effect could account for stronger hydrogen bonding yet lower melting points in the ternary system compared to the binary system.

The viscosities, η, of 1:1 EABr:urea, 1:1 BABr:urea and 0.5:0.5:1 EABr:BABr:urea between 25 °C and 80 °C are shown in Fig. 3. The experiments were performed from high temperature to low, and the data represents average values from three repeats. Data is not presented for 1:1 EABr:urea below 40 °C because it solidified. Results are shown down to room temperature for 1:1 BABr:urea which remains in a supercooled liquid state below its freezing point (for a variable time period). The viscosities of all three liquids are high, similar to glycerol,[23] over the temperature range probed. The viscosity of 0.5:0.5:1 EABr:BABr:urea lies between that of 1:1 EABr:urea and 1:1 BABr:urea, in accordance with results for mixtures of molecular liquids[24] and ionic liquids, but critically it is a thermodynamically stable liquid at 25 °C whereas the binary mixtures are not.[25]

Fig. 4 shows that the ionic conductivity (σ) of 0.5:0.5:1 EABr:BABr:urea is between that of 1:1 EABr:urea, and 1:1 BABr:urea over the entire liquid range. In accordance with these viscosity results, the conductivity of the ternary mixture
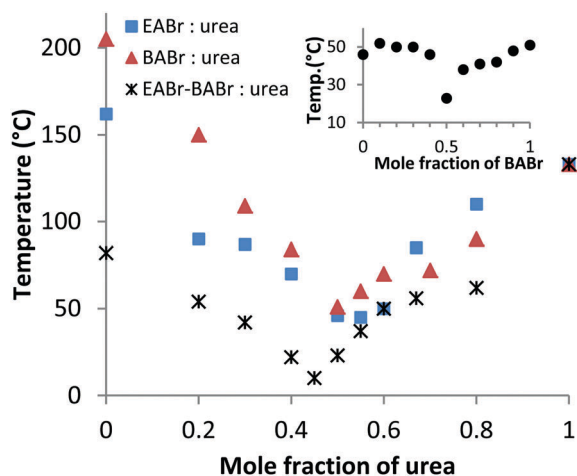

Fig. 2 Melting points of EAB–urea, BABr–urea and 1:1 EABr:BABr–urea mixtures as a function of urea mole fraction. The inset shows the melting point of EABr:BABr:urea mixtures versus cation composition where (EABr + BABr):urea = 1:1.
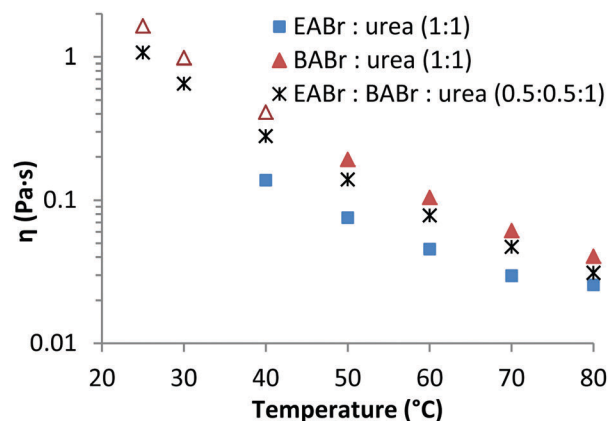

Fig. 3 Viscosities of 1:1 EABr:urea, 1:1 BABr:urea and 0.5:0.5:1 EABr:BABr:urea mixtures as a function of temperature. The open triangles for 1:1 BABr:urea indicate temperatures where the liquid was supercooled.
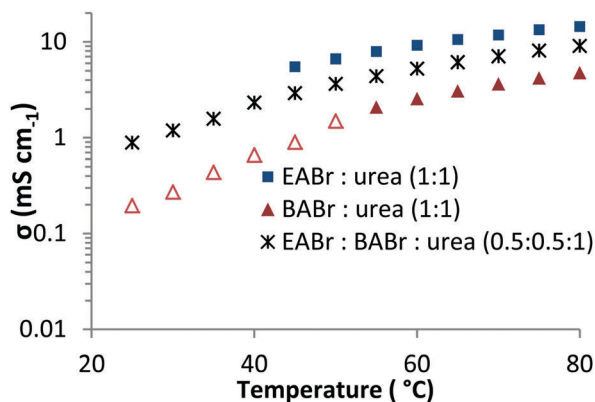
Fig. 4 Ionic conductivities of 1:1 EABr:urea, 1:1 BABr:urea and 0.5:0.5:1 EABr:BABr:urea mixtures as a function of temperature. The open triangles for 1:1 BABr:urea indicate temperatures where the liquid was supercooled.

lies between that of the two binary mixtures. At 25 °C the conductivity of 0.5:0.5:1 EABr:BABr:urea is 0.88 mS cm^{-1}, which is more than three time higher than the supercooled 1:1 BABr:urea DES, and at this temperature 1:1 EABr:urea is solid.

At 0.88 mS cm^{-1}, the conductivity of the ternary mixture is more than 4 times higher than 1:2 choline chloride:urea and other urea based DESs at the same temperature,[16] and also significantly higher than for other choline-based DESs formed from less viscous HBDs.[10] Most DESs are formed from 1:2 salt:HBD mixtures, whereas in the ternary mixture the (EABr + BABr):urea is 1:1, i.e. the effective salt concentration is about 2 times higher, which leads to higher conductivity.

Like similar DESs, Walden plots (see ESI,† Fig. S3) for 1:1 EABr:urea, 1:1 BABr:urea and 0.5:0.5:1 EABr:BABr:urea fall well below the ideal 0.01 M KCl line. (The densities as a function of temperature for the three liquids are also shown in the ESI,† Fig. S4.)

In conclusion, the eutectic temperature of EABr:BABr:urea is 10 °C, which is more than 40 °C lower than those of EABr:urea and BABr:urea. The EABr:BABr:urea eutectic composition is 0.6:0.6:1, which means the salt:urea is 1.2:1. This means the salt concentration is EABr:BABr:urea is much higher than common DESs like 1:2 choline chloride:urea, leading to significantly higher ionic conductivity. While the primary alkyl ammonium bromide salts examined here are less electrochemically stable than quaternary cations like choline, the approach of mixing cations could also be applied to electrochemically robust ions,

thereby increasing the range of parent salts that can be liquefied. This is the topic of continued investigation.

Notes and references

‡ The melting points of the salt–urea mixtures were determined by DSC at 10 °C min^{-1}. It should be noted there may be some discrepancy in values if other techniques are used due to the slow kinetics in these mixtures.

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