Do Group 1 metal salts form deep eutectic solvents?

A. P. Abbott,*[a] C. D'Agostino,*[b] S. J. Davis,[a] L. F. Gladden[b] and M. D. Mantle[b]

[a] Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK.

[b] Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, UK.

Supplementary data

Density

The density of an IL system is heavily dependent on the structure, charge density and functional groups of the ions, and have been reported to have densities ranging from 1.12 g cm^{-3} for $[(n\text{-}C_8H_{17})(C_4H_9)_3N][(CF_3SO_2)_2N]$ to 2.40 g cm^{-3} for a 1:2 molar ratio of a $[(CH_3)_3S]Br/AlBr_3$ eutectic system.[1,2] IL densities are generally insensitive to changes in temperature, and the presence of impurities. [3,4] The densities of DES are also dependant on the nature of the species present, with DES based on ChCl and a range of HBD typically displaying densities of 1.10 – 1.40 g cm^{-3}. [5,6] Type IV DES are generally denser with densities ranging from 1.40 g cm^{-3}to 1.80 g cm^{-3} because of the larger masses of the metals in the salts.[21] Figure S1 shows how the densities of a series of salt: glycerol mixtures varies as a function of salt content, and demonstrates for all of the sodium salts investigated, an increase in density. Sodium salt: glycerol mixtures appear to have densities similar to many of the ChCl: HBD DESs previously reported by the Abbott group, with a 3.55 M NaBr: glycerol mixture provided the highest density of 1.48 ± 0.02 g cm^{-3} due to the high mass of bromine.[26]

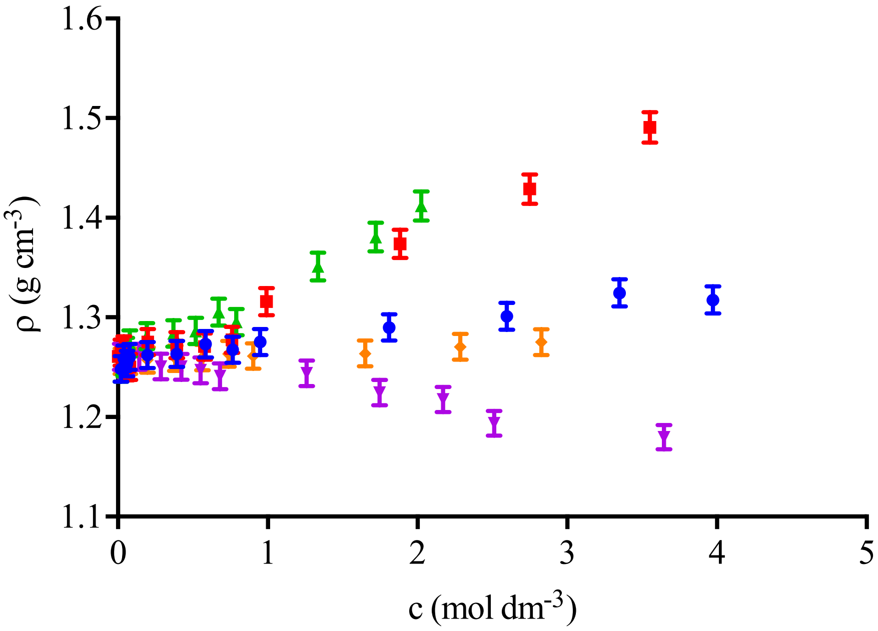

Figure S1: Density measurements for a series of salt: glycerol mixture as a function of salt concentration: (blue) NaOAc, (red) NaBr, (green) $Na_2B_4O_7.10H_2O$*, (purple) ChCl and (yellow)* $NaOAc.3H_2O$*, measured at 298 K*

Abbott *et al.* found that for DESs based on ChCl and ethylene glycol, or 1,4 butanediol, showed an increase in density as a function of ChCl content, whereas when ChCl was mixed with glycerol, system density was found to decrease with ChCl content.[7] This phenomenon was explained by the fact that diol based HBD formed linear aggregates of hydrogen-bonded molecules, whereas the addition of ChCl to glycerol, breaks up the 3D structure of intermolecular hydrogen bonds through complexation to the chloride anion of the salt. The significant breakdown in the glycerol structure suggests the surface tension of the ChCl: glycerol system decreases, accommodating an expansion in free volume, which leads to a decrease in density.

Addition of sodium salts to glycerol does not have the same effect as the addition of QASs, and suggests sodium salts have a kosmotropic effect of glycerol, which is due to the system volume not increasing by a significant amount, yet a large increase in the system mass occurs. The limited increase in system volume is likely to be caused by *electrostriction*: where the strong electrical forces on charge dense ions exert pressure on solvent molecules, which limit system expansion.[8] QASs are charge diffuse and the disruptive hydrogen bonding interactions between glycerol and ions dominate over electrostriction forces. Motin *et al.* found NaCl, $CuCl_2$, $CuSO_4$ and $MgSO_4$ to have a kosmotropic effect on water and water: urea mixtures, whereas NH_4Cl was found to have a chaotropic effect on the same solvent systems.[9] Research by Trusler *et al.* also found that a range of group I and group II salts, and mixtures thereof, increased the density of water as a function of salt concentration.[10]

Surface Tension and Free Volume

The density measurements shown in Figure S1 demonstrate that all of the salts tested have a strong influence upon the structure of glycerol. Further structural information can be taken from calculating the system *free volume* assuming a hard sphere model.[10] From the density measurements in Figure S1, the molar volume (V_m) can be calculated with respect to density (ρ) as shown in equation S1.

$$V_m = \frac{M_r}{\rho} \tag{S.1}$$

The relative molecular mass (M_r) of the mixture is calculated from the sum of partial relative molecular masses (M_{Salt}) of the components, where X_{Salt} is the mole fraction of the species concerned, as shown in equation S.2.

$$M_r = x_{Salt}M_{Salt} + x_{Glycerol}M_{Glycerol} \tag{S.2}$$

The volume occupied by the components (V_{Comp}) can be treated as the sum of the molecular volumes (V_{Salt}) per mole of the system, where N_A is Avogadro's constant, as shown in equation S.3. Molecular volumes were calculated using commercially available software.[11]

$$V_{Comp} = (x_{Salt}V_{Salt} + x_{Glycerol}V_{Glycerol})N_A \tag{S.3}$$

The relative difference between the V_m and V_{Comp} of a system can be treated its free volume (V_{Free}), as demonstrated by equation S.4.

$$V_{free} = \frac{(V_m - V_{Comp})}{V_m} \tag{S.4}$$

V_{free} is known to have a strong influence on the transport properties of liquids and the Cohen-Turnbull equation, as shown in equation S.5 where: A and γ are constants, and V^*_{free} is the minimum required void size, which links free volume with the self-diffusion coefficients (D) of species. [12] Combination of the Cohen-Turnbull equation with the Stokes-Einstein equation, as shown in equation S.6 relates viscosity to free volume, and combination with the Nernst-Einstein equation, as shown in equation S.7 relates ionic conductivity to free volume, and has been shown to be valid for ionic liquids.[13]

$$D = A\sqrt{T}e^{\left(-\frac{\gamma V^*_{Free}}{V_{Free}}\right)} \tag{S.5}$$

$$\eta = C_1\sqrt{T}e^{\left(\frac{\gamma V_{Free}^{*}}{V_{Free}}\right)} \tag{S.6}$$

$$\kappa = \frac{C_2}{\sqrt{T}}e^{\left(-\frac{\gamma V_{Free}^{*}}{V_{Free}}\right)} \tag{S.7}$$

Figure S2 outlines the theoretical volumes used to calculate V_{comp} in equation S.3. Volumes were calculated by optimising the component molecular structure using a Hartree-Fock (HF) computational method coupled with a 3-21G basis set, followed by fitting a van der Waals (VDW) density surface. From the volumes calculated, hard sphere geometry was assumed and a corresponding hard sphere radius was calculated.

Table S.1 Table of theoretical hard sphere radii for the components studied

Species	Hard sphere radius (10^{-10} m)	Hard sphere volume (10^{-30} m^{-3})
Na^+	2.66	7.85
Ch^+	6.74	128
Cl^-	4.36	34.6
Br^-	4.66	42.3
OAc^-	5.29	62.0
$B_4O_7^{2-}$	6.35	107
H_2O	3.56	18.9
$C_3H_8O_3$	6.02	91.5

Figure S2 shows the V_{free} values of a series of sodium salt: glycerol mixtures as a function of salt mole fraction, as well as the trend for a ChCl: glycerol system (purple trend). NaOAc, NaBr and NaOAc.3H_2O all show a decrease in V_{free} as a function of salt concentration, which is consistent with respect to observed changes in system density. In contrast, ChCl shows an increase in V_{free}, which is consistent with the decrease observed in system density. Abbott *et al.* also observed an increase in the V_{free} of a ChCl: glycerol mixture when compared with the fluidity of the system, and eluded the increase in V_{free} was a consequence of ChCl breaking down the structure of glycerol.[10] Abbott *et al.* also demonstrated that mixtures of $CrCl_3.6H_2O$ and urea showed an increase in system free volume with increasing $CrCl_3.6H_2O$ content, which coincided with decreases in viscosity and density.[14] The mechanism through which this phenomenon occurs can be related to the structural changes that occur in HBDs, which indicates disruptive hydrogen bonding interactions between the HBD and ions dominate over the ordering effect of electrostriction forces. The decrease in V_{free} observed in Figure S2 further reinforces the concept of NaOAc, NaBr and NaOAc.3H_2O having a kosmotropic effect on glycerol, which may be due to the charge density of the ions promoting electrostriction.

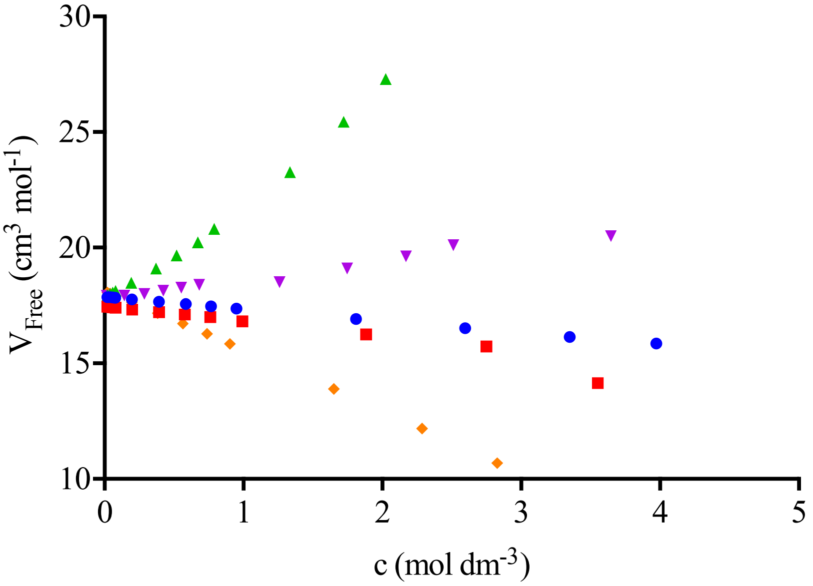

Figure S2 Free volume calculations for a series of salt: glycerol mixture as a function of salt concentration: (blue) NaOAc, (red) NaBr, (green) $Na_2B_4O_7.10H_2O$, (purple) ChCl and (yellow) NaOAc.$3H_2O$, at 298 K

The role of waters of hydration is not clear from the data in Figure S2 as $Na_2B_4O_7.10H_2O$ suggests a structure breaking regime, whereas NaOAc.3H_2O suggests a structure making regime. It may be possible that water plays a different role in both systems but further studies are required to fully understand the role of water in these systems. The systems in Figure S2 are difficult to model as the speciation is still not fully understood, and even though the speciation of many DES have been previously reported by the Abbott group using extended X-ray atomic fine structure (EXAFS), the speciation is dependent on the choice of components, and further research is required.[15]

Viscosity

There are conflicting arguments in the scientific literature regarding the fluid behaviour of ILs and DESs, but component choice has been repeatedly regarded as the deciding factor. [16,17,18] Figure S3 shows how viscosity for a series of approximately 2 M salt: glycerol mixtures varied as a function of viscometer rotation speed (ω). A Newtonian fluid displays a linear relationship between shear stress and shear rate, whereas a non-Newtonian fluid can show a variety of the shear stress-rate relationships. When reviewing dynamic viscosity versus rotation rate plots, a Newtonian fluid is represented by a linear trend of zero gradient, as shown by NaBr, $Na_2B_4O_7.10H_2O$, ChCl, $NaOAc.3H_2O$ systems and pure glycerol in Figure S3. NaOAc showed a positive gradient, which suggests the NaOAc: glycerol system is behaving as a *shear-thickening* fluid.

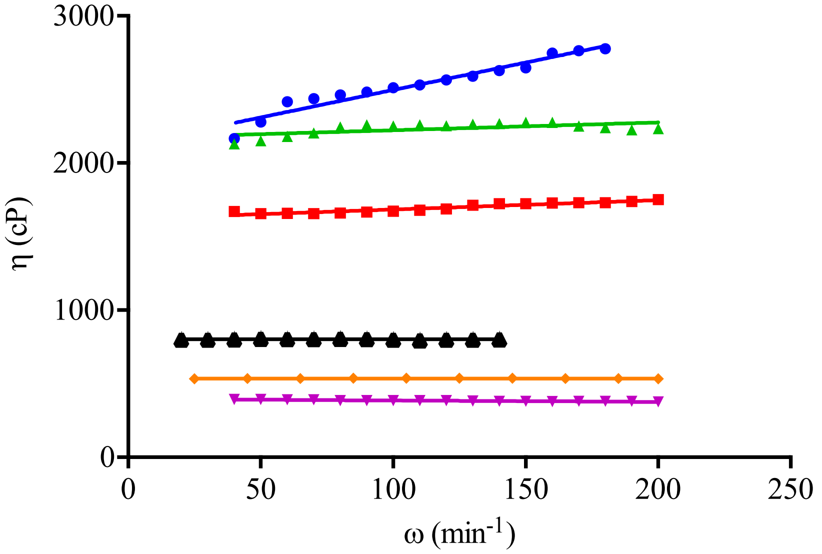

Figure S3 Viscosity for a series of salt: glycerol mixture as a function of viscometer rotation speed: (blue) 1.80 M NaOAc, (red) 1.88 M NaBr, (green) 2.02 M $Na_2B_4O_7.10H_2O$, (purple) 2.17 M ChCl, (yellow) 2.28 M $NaOAc.3H_2O$ and (black) pure glycerol, at 298 K

Shear-thickening fluid behaviour is typical of many colloidal suspensions, and is a result of a system crystallising under stress and behaving more like a solid.[19] ILs generally show shear thinning fluid characteristics at high shear rates, which has been attributed to the onset of stacking of polar and apolar layers that breaks down the hydrogen-bonded network, thus accommodating easier shear deformation.[54] Although, Jacquemin *et al.* found diisopropyl-ethylammonium based protic ionic liquids showed shear-thickening behaviour at shear rates greater than 4000 s^{-1}, but gave no indication as to why the phenomenon occurred. [20] Abbott *et al.* found eutectic mixture of ChCl and urea showed non-Newtonian fluid properties in the pure state, but upon the addition of 2.5 % water was found to behave as a Newtonian fluid.[21] The pronounced effect of water on the fluid behaviour of the ChCl: urea mixture, was linked to the hydrogen bond donating parameter (α) of the system being lower compared to other ChCl: HBD systems and pure water, which suggested water was preferentially solvating the chloride anion.[78] Studies into the solvent parameters of sodium salt: glycerol mixtures have not been investigated, and studies in this area may be needed to explain the uncharacteristic fluid behaviour in the NaOAc: glycerol system.

Arrhenius found that changes in solvent viscosity induced by the addition of salts were related through equation S8, where c is the salt concentration, and A is the *salt constant* at a given temperature.[22] At concentrations greater than 0.1 M the systems investigated in Figure 3 (main article) follow this model with typical R^2 values greater than 99 % however, at concentrations below 0.1 M significant deviations occur, which is well known for this model.[23]

$$\eta = A^c \qquad \text{S.8}$$

Dole and Jones expanded the Arrhenius model and found that the viscosity of a salt solution showed the dependence on ion concentration illustrated in equation S.9, where (η/η_o) is the viscosity of the solution relative to the viscosity of the solvent, also known as relative viscosity (η_r), A and B are system specific constants.[24] The A constant in equation S3 is independent of concentration and is a result of ion-ion interaction, whereas the B constant is related to the solute effect on the solvent.[74] Negative B values indicate the solute is behaving as a chaotrope, and a positive B values suggests the solute is behaving as a kosmotrope.[74]

$$\eta_r = \frac{\eta}{\eta^o} = 1 + A\sqrt{c} + Bc \qquad \text{S.9}$$

Equation S.9 can be rearranged to the simpler form shown in equation S.10, which allows a linear plot of $(\eta_r - 1)/\sqrt{c}$ as a function of $\sqrt{c}$ to be drawn, where A is the y-intercept and B is the slope of the plot.[73]

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \qquad \text{S.10}$$

Figure S4 shows the Dole-Jones plots for a series of salt: glycerol mixtures as a function of the square root of salt concentration up to 1 M. The sodium salts investigated all showed an increase in the $(\eta_r - 1)/\sqrt{c}$ term, whereas the ChCl system showed a decrease, indicating positive and negative B constants respectively. The sodium salts investigated all demonstrated negative A values, whereas the ChCl: glycerol system showed an A value very close to zero. A and B values for all of the systems investigated have been listed in Table S2.

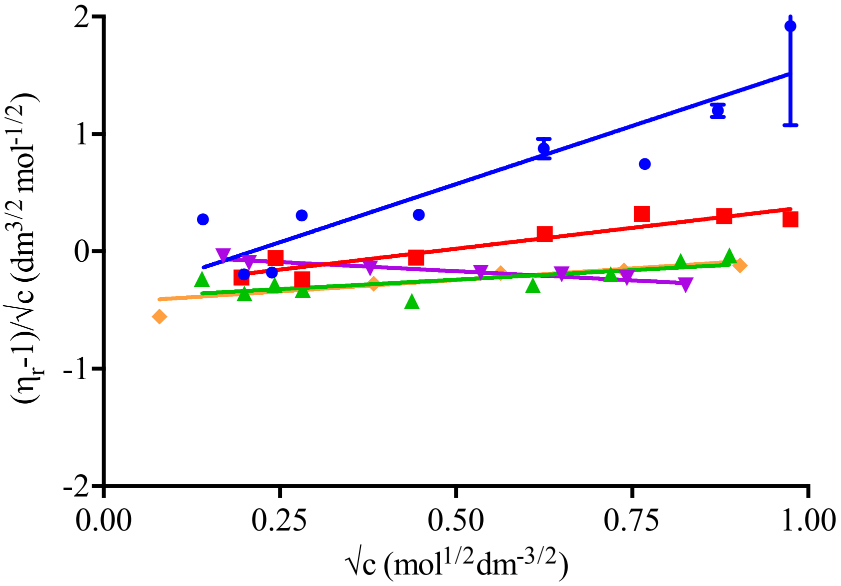

Figure S4 Dole-Jones plots for a series of salt: glycerol mixture as a function of salt concentration: (blue) NaOAc, (red) NaBr, (green) $Na_2B_4O_7.10H_2O$, (purple) ChCl and (yellow) $NaOAc.3H_2O$, at 298 K

Table S.2 Dole-Jones A and B parameters for the systems investigated in Figure S4

Salt	*A* ($mol^{1/2}\ dm^{-3/2}$)	*B*
NaOAc	-0.42 ± 0.20	1.98 ± 0.33
NaBr	-0.33 ± 0.067	0.71 ± 0.11
$Na_2B_4O_7.10H_2O$	-0.40 ± 0.064	0.32 ± 0.12
ChCl	-0.013 ± 0.019	-0.31 ± 0.034
$NaOAc.3H_2O$	-0.44 ± 0.086	0.39 ± 0.15

The values obtained for the *B* parameter give an insight into ion-solvent interactions and suggests the sodium salts investigated are acting as kosmotropes and reinforce the structure of glycerol, which in turn raises E_η of glycerol leading to an increase in the viscosity of the system. The negative *B* parameter for the ChCl: glycerol system indicates a structure breaking effect on glycerol and implies ChCl acts as a chaotrope. Research by Dole and Jones showed the *A* parameter was negative for all strong electrolytes and zero for non-electrolytes, which agrees with the values displayed by all of the systems investigated. The *A* parameter can be calculated from equilibrium theory, which has been demonstrated by Falkenhagen, but additional investigations into the *A* parameter are required to further understand its qualitative significance.[25]

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