Do Group 1 metal salts form deep eutectic solvents?

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Abstract

Mixtures of metal salts such as $ZnCl_2$, $AlCl_3$ and $CrCl_3 \cdot 6H_2O$ form eutectic mixtures with complexing agents, such as urea, liquids. The aim of this research was to see if alkali metal salts also formed eutectics in the same way. It is shown that only a limited number of sodium salts form homogeneous liquids at ambient temperatures and then only with glycerol. None of these mixtures showed eutectic behaviour but the liquids showed the physical properties similar to the group of mixtures classified as deep eutectic solvents. This study focussed on four sodium salts: NaBr, NaOAc, $NaOAc \cdot 3H_2O$ and $Na_2B_4O_7 \cdot 10H_2O$. The ionic conductivity and viscosity of these salts with glycerol were studied, and it was found that unlike previous studies of quaternary ammonium salts with glycerol, where the salt decreased the viscosity, most of the sodium salts increased the viscosity. This suggests that sodium salts have a structure making effect on glycerol. This phenomenon is probably due to the high charge density of Na^+, which coordinates to the glycerol. ^1H and ^{23}Na NMR diffusion and relaxation methods have been used to understand the molecular dynamics in the glycerol-salt mixtures, and probe the effect of water on some of these systems. The results reveal a complex dynamic behaviour of the different species within these liquids. Generally, the translational dynamics of the ^1H species, probed by means of PFG NMR diffusion coefficients, is in line with the viscosity of these liquids. However, ^1H and ^{23}Na T_1 relaxation measurements suggest that the Na-containing species also play a crucial role in the structure of the liquids.

Introduction

Deep Eutectic Solvents (DES) are mixtures of Lewis and Brönsted acids and bases. The most commonly studied systems are those composed of quaternary ammonium salts and hydrogen bond donors such as amides, alcohols or acids.[1,2] The depression of freezing point for some mixtures can be up to 200 $^{\circ}$C. Many applications of these compounds have already been studied including their use as: catalysts, solvents, extraction media and media to carry out electrochemical processes. A comprehensive review on the properties and applications of DESs has recently been published.[3]

A variety of metal salts e.g. $ZnCl_2$ and $AlCl_3$ and metal salt hydrates e.g. $CrCl_3 \cdot 6H_2O$ have been shown to form eutectic mixtures with compounds such as urea.[45] Most form ionic species due to disproportionation of the metal salt:

e.g. $2AlCl_3 + urea \rightarrow [AlCl_2.urea]^+ + AlCl_4^-$
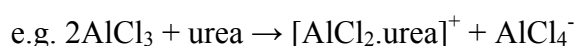
These liquids have been studied for metal deposition applications.[6] Gambino *et al.*[7] have shown that mixtures of alkali metal halides with urea can form eutectic mixtures with typical melting points greater than 120 $^{\circ}$C; however, the systems were not suitable for the applications tested. Mjalli *et al.*[8] applied the same methodology to mixtures of potassium carbonate and glycerol, or ethylene glycol, and found that a 1:4 respective molar mixture of potassium carbonate and glycerol formed a colourless liquid at room temperature, with the potential application as a CO_2 capture medium.[8]

Ideally, a DES based on a concentrated mixture of NaCl and glycerol would be the most economically viable DES.[9] Unfortunately, NaCl has a relatively low solubility in glycerol (83 g kg^{-1} of glycerol), which is not sufficiently concentrated enough to be compared against DES and ILs.[10] DESs exhibit rather complex behaviour; in particular, the presence of several molecular and ionic species makes these systems very interesting to study. Diffusion often does not obey the classical Stokes Einstein model and it was suggested other factors such as the amount of free volume in the liquid and size of "hole", are important factor in controlling the motion of these species.[11] Initial studies on DESs have been carried out to understand the dynamics of molecular and ionic species and see how these relate to macroscopic properties such as viscosity and electric conductivity.[12] Recent diffusion studies on aqueous choline chloride-based DES were able to show that some of these liquids are inhomogeneous at a macroscopic level and it was observed that the addition of water significantly changes the molecular and ionic interactions between the different species.[13] For example, in some cases,

the hydroxyl protons of the hydrogen bond donor behave differently from its parent molecule when water is added to the system.

Electrical conductivity, density and viscosity measurements of relatively dilute alkali metal halides and glycerol have been previously carried out.[14] In this study, very concentrated salt-glycerol systems have been studied and their properties are compared to deep eutectic solvents. NMR diffusion and relaxation studies have been carried out to understand the dynamics of molecular and ionic species in sodium-based DES. ^{1}H PFG NMR diffusion and ^{1}H and [23]Na T_1 relaxation methods were used to understand translational and rotational dynamics of molecular and ionic species, including Na^+ ions and see how microscopic behaviour correlates with the viscous properties of these fluids in order to understand what are the main factors affecting the macroscopic behaviour of these fluids.

Experimental

Glycerol (Fisher Scientific) was heated to 50 ^{o}C and mixed with one of the four salts NaOAc, (Fisher Scientific) NaBr, (Sigma-Aldrich) $Na_2B_4O_7 \cdot 10H_2O$ (Sigma-Aldrich) or $NaOAc \cdot 3H_2O$ (Fisher Scientific) using an overhead stirrer (Stuart Scientific, ss10, 500 rpm) until all the components formed a homogeneous liquid phase. All liquids were stored at 50 ^{o}C. The mixtures salt/glycerol are labelled as NaOAc, NaBr, $Na_2B_4O_7 \cdot 10H_2O$ and $NaOAc \cdot 3H_2O$.

The viscosities of all the ionic solvents were measured using a rotational viscometer (Brookfield DV-II+PRO), fitted with a temperature probe. Samples were heated to 45 ^{o}C and viscosity measurements were taken down to 25 ^{o}C ($\pm$ 1 ^{o}C). Ionic solvents were tested for non-Newtonian fluid behaviour using the above instrument and apparatus over the viscometer rotation speed range 10-200 rpm. Sample viscosity was recorded for 10 minutes for each rotation speed to provide a stable measurement. Where error bars are not obvious they are within the dimensions of the plot symbol.

The electrical conductivities of all the ionic solvents were measured using a conductivity probe (Jenway 4510, cell constant K = 0.96), which was fitted with an integral temperature probe. Conductivity was measured over the temperature range 25-45 ^{o}C ($\pm$ 1 ^{o}C).

Glass transition temperatures were determined using a Differential Scanning Calorimeter (Mettler Toledo, DSC1) controlled by STARe version 12.10 software. The mass of each sample ranged between 5 - 20 mg, and was sealed inside a 40 µl Al pan (Mettler Toledo) with a vent hole pierced into the lid. Samples were cooled to -140 ^{o}C at a rate of 10 ^{o}C min^{-1}, then held at -140 ^{o}C for 10 min and then heated up to 25 ^{o}C at a rate of 5 ^{o}C min^{-1}. All experiments

were carried out under a N_2 atmosphere. The resulting theromgrams showed an endothermic peak corresponding to the glass transition of the samples.

All NMR measurements were conducted on a Bruker DMX 300 spectrometer operating at a frequency of 300.13 MHz. A diffusion diff-30 probe equipped with gradient coils capable to produce a maximum magnetic field gradient in the z-direction of up to 11.76 T m^{-1} was used for both diffusion and relaxation measurements, using ^{1}H and ^{23}Na resonant coils for ^{1}H and ^{23}Na NMR measurements respectively. ^{1}H PFG NMR measurements were conducted using the APGSTE (alternating pulsed gradient stimulated echo) pulse sequence with a homospoil gradient, which has the advantage of minimizing the effect of any possible background gradient present in the sample.

The NMR signal attenuation, $E(g)/E_0$ is related to the experimental variables and the diffusion coefficient D according to:

$$\frac{E(g)}{E_0} = \exp\left[-D\gamma_H^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right)\right] \tag{1}$$

where $E(g)$ and E_0 are the NMR signal in the presence and absence of the gradient pulse, respectively; γ_H is the gyromagnetic ratio of the nucleus being studied (i.e., ^{1}H in our case), g is the strength of the gradient pulse of duration δ, and Δ is the observation time. The observation time for diffusion was fixed to $\Delta = 100$ ms with values of δ in the range $1 - 4$ ms. The magnitude of g was linearly varied and up to sixteen points were acquired for each diffusion measurement. Maximum gradient values of up to 11.50 T m^{-1} were necessary to reach the required signal attenuation due to the very low diffusivity observed for some of the species present in these samples. The diffusion coefficients D can be calculated by fitting Equation (1) to the experimental data.

^{1}H and ^{23}Na T_1 relaxation measurements were performed using the inversion recovery pulse sequence using a list of sixteen variable delay times. The T_1 relaxation time constant was obtained by fitting the experimental data to the equation:

$$S(t) = S_0\left[1 - 2\exp\left(-\frac{t}{T_1}\right)\right] \tag{2}$$

where S_0 is the NMR signal at equilibrium (i.e., initial time) and $S(t)$ is the NMR signal recorded after a delay time t. NMR measurements were conducted a variable temperature in the range 25-65 °C and the temperature was controlled by a BVT 3000 control unit.

Results and discussion

Component Selection

Figure 1 shows a selection of group 1 and group 2 metal salts mixed with either: urea, xylitol (an example of a complex sugar alcohol) and glycerol. All of the mixtures in **Figure 1** were heated to 100 °C for 2 hours with intermittent shaking, and all systems were tested at a 1:4 salt to glycerol molar ratio, except for NaCl and KCl, which were tested at a ratio of 1:8. Of the metal salts mixed with urea in **Figure 1** only $Na_2B_4O_7 \cdot 10H_2O$ and $MgCl_2 \cdot 6H_2O$ showed signs of partial liquid formation, whereas all of the other salts tested remained as two separate solid phases. Marginally better miscibility was achieved when urea was substituted for xylitol, but none of the systems investigated completely formed liquids. When xylitol was substituted for glycerol, all of the systems investigated formed colourless liquids at 100 °C, which remained liquid upon cooling to room temperature. In no cases was the freezing point of the mixture below that of pure glycerol and so it can be concluded that salts of groups 1 and 2 do not form eutectic mixtures in the same way as salts such as zinc chloride and aluminium chloride.[4, 5]

Considering the research from Gambino *et al.*,[7] many of the systems tested in **Figure 1** may have fully formed if heated to over 150 °C, but further heating would have resulted in decomposition of urea. Also, in cases where a colourless liquid formed at 100 °C, the system formed a hard glass at room temperature, which means thermo-physical measurements at room temperature would be impractical. From the results shown in **Figure 1**, mixtures of: NaBr, NaOAc, NaOAc·3H₂O or $Na_2B_4O_7 \cdot 10H_2O$ with glycerol were investigated further and their thermo-physical properties were studied as a function of salt concentration.
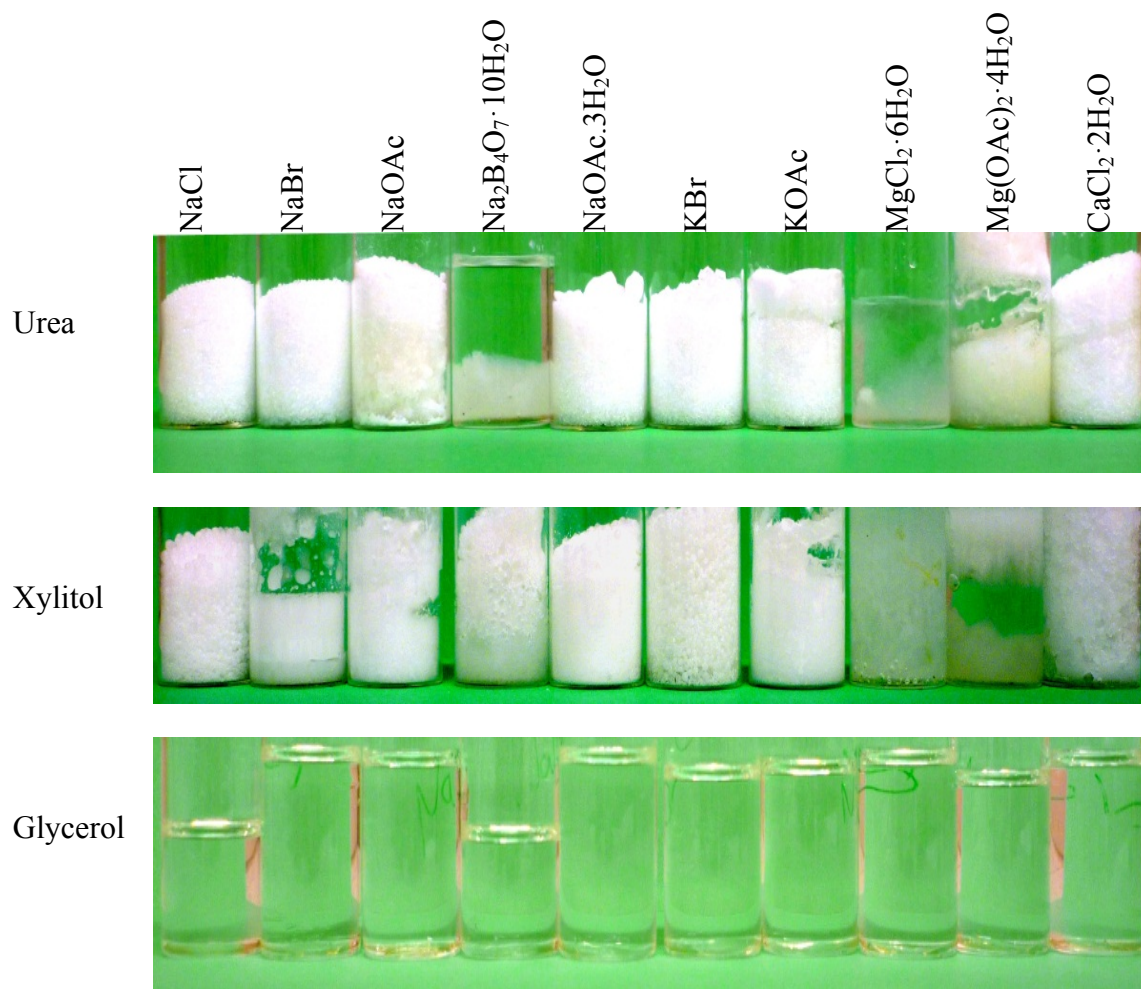
Figure 1. A selection of group 1 and group 2 metal salts mixed with either: urea, xylitol or glycerol. All systems tested were a 1 salt: 4 HBD molar ratio or to, except for NaCl and KCl, which were tested at a ratio of 1:8.

Phase Behaviour

Figure 2 shows the glass transition temperature for a range of sodium salts mixed with glycerol in the concentration range 20 mM to 4 M. All measurements were made using differential scanning calorimetry (DSC). True melting points were not observed, which is common in ILs and some DES as solidification kinetics are slow, and tend to only form glasses. [15] Mixtures of NaOAc, NaBr, $Na_2B_4O_7 \cdot 10H_2O$ or $NaOAc \cdot 3H_2O$ with glycerol all showed a linear increase in T_g with increasing salt concentration, and did not show the characteristic depression, which is observed with DES, which is shown by the purple trend (ChCl) in **Figure 2**. Aqueous solutions of NaCl are known to show a depression in melting

temperature with a eutectic composition of 23.3 wt% which equates to 6.7 mol% or a concentration of approximately 4 M.[16] The 3.55 M NaBr solution in glycerol equates to 22.5 mol% suggesting a eutectic composition might be observable at much lower salt concentrations but because true melting points are not observed (only T_g) eutectic formation may not be observable. Zaidi *et al*. developed an electrolyte based on sodium nitrate and N-methylacetamide and found a 1:9 respective molar ratio lead to a system with a melting point below that of the components, suggesting eutectic systems are possible with sodium salts, and an alternative method of determining melting points may be necessary.[17]
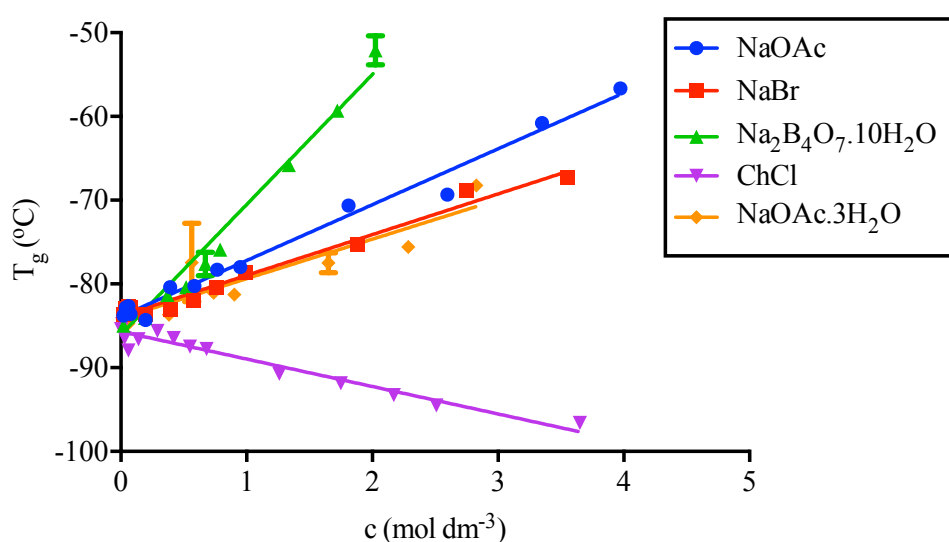

Figure 2. Glass transition onset temperature for a series of salt: glycerol mixture as a function of salt concentration with linear trend lines.

The positive trends in T_g in **Figure 2** suggest the inorganic salts tested have a reinforcing effect (kosmotropic) on the structure of glycerol as the heat energy required to transfer into the molten state increases with salt concentration. In contrast, the quaternary ammonium salt, QASs used in DESs appear to have a structure disrupting (chaotropic) effect on glycerol as the heat energy required to transfer into the molten state decreases with salt concentration until the eutectic point. At low QAS concentrations, the T_g of glycerol appears to initially increase, which is surprising as a linear response is observed for the inorganic salts studied. The [EMIM]Cl/AlCl$_3$ system shows a eutectic maximum at an approximate AlCl$_3$ mole fraction of 0.5, due to the presence of different anionic species at different molar ratios of [EMIM]Cl to AlCl$_3$.[18,19]

Viscosity

Figure 3 shows the viscosity of the salt: glycerol mixture as a function of salt concentration. At the highest concentrations measured for each sodium salt: glycerol system, viscosity varied from 487 ± 3 cP for a 2.83 M NaOAc·3H$_2$O mixture to 16300 ± 100 cP for a 3.98 M NaOAc mixture at 298 K. The range of viscosities measured is comparable with what is typically seen with DESs but are considerably more viscous that most commonly used ILs and molecular solvents.[15]
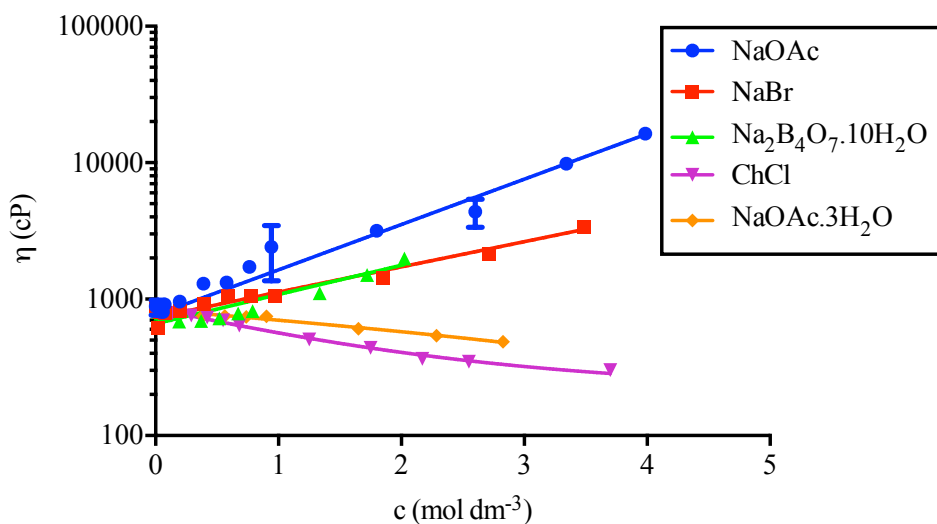

***Figure 3**. Viscosity measurements for a series of salt: glycerol mixture as a function of salt concentration at 298 K with linear trend lines.*

Except for NaOAc·3H$_2$O, the other sodium salts studied, at all concentrations, increased the viscosity of glycerol. Ionic species that have high charge densities are known to have a kosmotropic effect on polar solvents resulting in stronger solvent-solvent interactions.[20,21] In the context of viscosity, stronger solvent-solvent interactions implies greater resistive forces between shear planes, which results in a greater E_η that leads to a greater dynamic viscosity. Not all inorganic salts have a structure forming effect on the viscosity of water, and the observed effect is dependent on the components of the salt.[22] (See supplementary data file for a full Dole-Jones analysis of the data)

It has previously been shown that QASs decrease the viscosity of glycerol, oxalic acid, urea and other HBD as a function of QAS concentration.[2,23,24] This was rationalised as the QAS disrupts the hydrogen bonding network and decreases the viscosity due to weaker resistive forces between fluid shear planes, which lower E_η.[23] Chaotropic salts are known to show structure breaking effects via disruption of non-covalent intermolecular forces. This can

result in the formation of ion-dipole interactions between ions and the hydrogen-bonding species, which is thermodynamically favourable compared to the solvent intermolecular interactions.[25]

The role of water is not clear from the trends shown in **Figure 3** as NaOAc·3H$_2$O shows a decrease in viscosity as a function of salt concentration, whereas Na$_2$B$_4$O$_7$·10H$_2$O indicates in increase in viscosity. A comparison between NaOAc·3H$_2$O and NaOAc suggests the waters of hydration may be relatively free, implying the free water could act as a diluent. Unfortunately, a comparison between Na$_2$B$_4$O$_7$·10H$_2$O and Na$_2$B$_4$O$_7$ could not be achieved, as Na$_2$B$_4$O$_7$ is insoluble in glycerol.

There are conflicting arguments in the literature regarding the fluid behaviour of ILs and DESs, but component choice has been repeatedly regarded as the deciding factor.[26,27] The viscosity of approximately 2 M salt: glycerol mixtures were studied as a function of viscometer rotation speed. The NaBr, Na$_2$B$_4$O$_7$·10H$_2$O, ChCl, NaOAc·3H$_2$O systems and pure glycerol showed a Newtonian fluid response. The NaOAc system showed a positive gradient, which suggests the NaOAc: glycerol system is behaving as a *shear-thickening* fluid. (See supplementary data file) 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.[28] 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.[29] Jacquemin *et al.* found diisopropyl-ethylammonium based protic ionic liquids showed shear-thickening behaviour at shear rates greater than 4000 s^{-1}; however, they gave no indication as to why the phenomenon occurred.[30] Abbott *et al.* found that the eutectic mixture of ChCl and urea showed non-Newtonian fluid properties in the pure state. Upon the addition of 2.5 % water, the mixture was found to behave as a Newtonian fluid.[13] 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. 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.

Ionic Conductivity

Figure 4 shows the change in molar conductivity (Λ) as a function of the square root of salt concentration for a series of salt: glycerol systems. ChCl: glycerol mixtures show a decrease in molar conductivity up to 0.25 M suggesting the formation of ion pairs, followed by an increase to approximately 4 M, which is indicative of triple ion formation. Concentrations larger than 4 M cause a decrease in molar conductivity due to decreased ionic mobility.[31] NaOAc and NaBr mixtures with glycerol show a consistent decrease in molar conductivity across the measured concentration range, which appears to be due to the high viscosity of the liquids.[32].
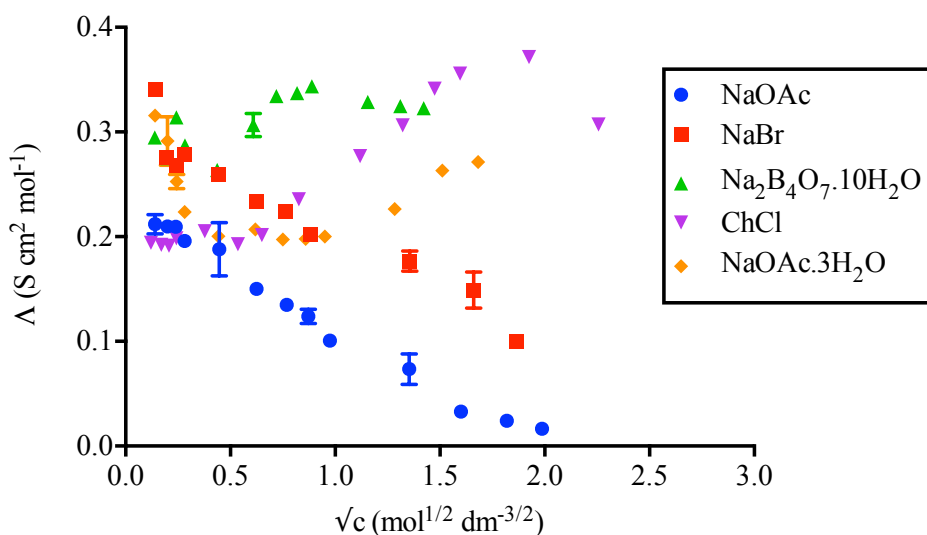

Figure 4. Molar conductivity measurements for a series of salt: glycerol mixtures as a function of the square root of salt concentration at 298 K.

The NaOAc·3H$_2$O: glycerol system shows an initial decrease in molar conductivity followed by an increase above 0.25 M. This behaviour is usually characteristic of ion pair formation at lower concentrations followed by triple ion formation beyond the minimum. The trend displayed by the NaOAc·3H$_2$O: glycerol system is very different to that of the anhydrous system and suggests water is contributing to the charge transport mechanisms in this system. Water may help to solvate the sodium ions enabling more charge separation and showing a contribution from ion aggregates (e.g. triple ions) rather than molar conductivity being controlled just by ion transport. The Na$_2$B$_4$O$_7$·10H$_2$O:glycerol system does not show a clear trend in **Figure 4**, but molar conductivity is in the range 0.27 to 0.34 S cm^2 mol^{-1} implying little variance occurs. It suggests that water may be behaving differently than in Na$_2$B$_4$O$_7$·10H$_2$O: glycerol compared to the NaOAc·3H$_2$O: glycerol system. It has previously

been shown that addition of 5 wt% water to a range of ChCl: HBD systems significantly decreased viscosity and in turn increased molar conductivity.[13] At 0.08 M, $Na_2B_4O_7 \cdot 10H_2O$ in glycerol the water content of the system is 5.5 wt%, and at 2.02 M, the water content is 69.2 %. Despite the significant water contents, little variance in molar conductivity occurs, which suggests some of the waters of hydration are bound sto the sodium cation and the tetraborate anion. The anion can be more precisely written as $[B_4O_5(OH)_4]^{2-}$ showing that two of the water molecules are covalently bound to the anion.

At their maximum concentrations, the sodium salt: glycerol systems showed molar conductivities in the range 0.02 to 0.32 S cm^2 mol^{-1}, whereas ILs are typically in the 0.35 to 10 S cm^2 mol^{-1} range, and DESs are 0.05 to 3 S cm^2 mol^{-1}.[1,15] The sodium salt: glycerol systems measured are significantly lower than those generally experienced for ILs however, ILs are normally less viscous than the sodium salt: glycerol mixtures and DESs allow for a much greater ion mobility.[15]

Figure 5 shows the logarithmic plots of molar conductivity *vs*. fluidity for a series of approximately 2 M sodium salt: glycerol systems as a function of temperature. Molar conductivity has been substituted for molal conductivity to provide an absolute concentration factor that did not vary with temperature. In all instances, there is a clear linear trend between molal conductivity and fluidity. The slopes of these lines, known in the literature as Walden products (molar conductivity × viscosity) are summarised in **Table 1**.
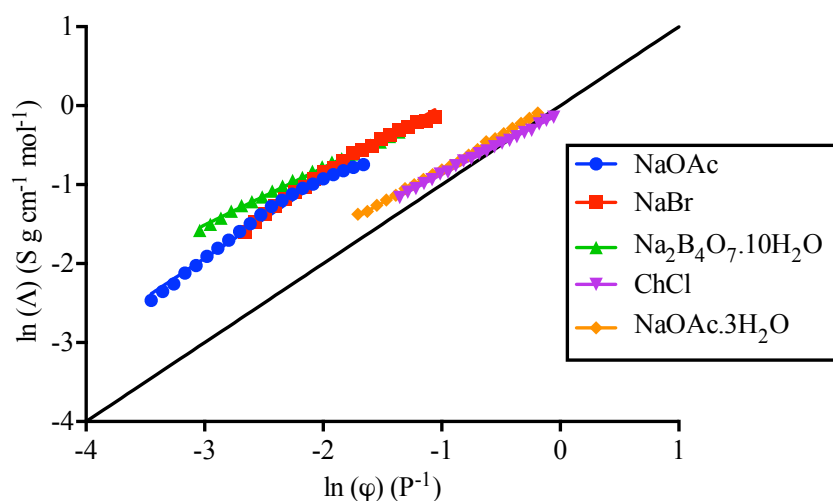

Figure 5. *Walden plots for a series of approximately 2M salt: glycerol mixtures as a function of temperature.*

The Walden product describes the effect of fluidity on molar conductivity. The NaOAc, NaBr and $Na_2B_4O_7 \cdot 10H_2O$ systems all show very similar, comparatively high, Walden products showing that fluidity has a significant effect on conductivity. Systems where the molar conductivity lies above the black equivalence line (NaOAc, NaBr and $Na_2B_4O_7 \cdot 10H_2O$ in Figure 5) are generally described as superionic glasses.

Table 1. Walden products of salts in glycerol.

Salt: glycerol system	Walden product (S g cm^{-1} mol^{-1} P)
NaOAc	2.63 ± 0.10
NaBr	2.45 ± 0.08
$Na_2B_4O_7 \cdot 10H_2O$	2.42 ± 0.05
ChCl	0.79 ± 0.01
$NaOAc \cdot 3H_2O$	1.02 ± 0.01

ILs typically have Walden products in the range $0.30 - 1.00$ S cm^2 mol^{-1} P.[15] The $NaOAc \cdot 3H_2O$ and the ChCl systems both show lower Walden constants. This could be because the first three liquids exhibit greater structure compared to the other two. This certainly fits with the data in Figure 3 and confirms that the latter two are structure breaking. For both NaBr and NaOAc the salt decreases the free volume of the liquid which in turn increases the viscosity and Tg and results in low molar conductivities which would be expected for structure making salts (see supplementary data file). The hydrate salts, however behave differently. $NaOAc.3H_2O$ shows a decrease in free volume accompanied by a decrease in viscosity whereas $Na_2B_4O_7 \cdot 10H_2O$ shows an increase in free volume but an increase in viscosity. This must be due to the behaviour of the hydrate water molecules. To probe this further diffusional measurements were carried out to understand the mobilities of the individual species.

^{1}H PFG NMR measurements

A typical PFG NMR signal decay measured for the samples studied in this work is shown in **Figure 6A**, which shows the diffusion attenuation of NaOAc sample at 298.15 K. It is possible to observe the signal attenuation of the NMR resonances of the different species, in particular the hydroxyl and aliphatic resonance of glycerol at 4.54 ppm and 2.68 ppm, respectively, and the resonance of the OAc$^-$ anion at 1.03 ppm. The figure also shows the usefulness and potential of this technique, which is able probe multi-component diffusion

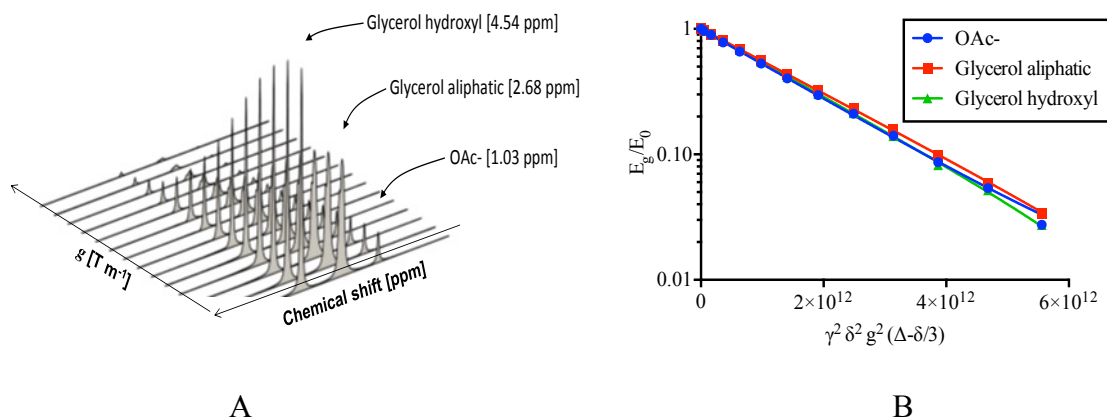even in cases of such samples, whereby the NMR resonances are broadened due to the significant high values of viscosity.[13]

Glycerol hydroxyl [4.54 ppm]
Glycerol aliphatic [2.68 ppm]
OAc- [1.03 ppm]

g [T m^{-1}]
Chemical shift [ppm]

E_g/E_0

OAc-
Glycerol aliphatic
Glycerol hydroxyl

$\gamma^2 \delta^2 g^2 (\Delta - \delta/3)$

| A | B |

***Figure 6**. Typical NMR spectrum of the NaOAc: glycerol system (A) and associated characteristic signal decay profile (B).*

From the plot in **Figure 6B** it is possible to obtain the Stejkal-Tanner plot,[33] i.e., $E(g)/E_0$ vs. $\gamma_H^2 g^2 \delta^2 (\Delta - \delta/3)$, which is then used to extrapolate the value of self-diffusion coefficient by taking the negative of the slope of this plot. As an example of such plots, **Figure 6B** shows the log attenuation plots the glycerol and acetate resonances of the NaOAc. The reproducibility of the measurements had a relative error of approximately 3%.

A summary of the diffusion measurements at variable temperature is shown in **Figure 7** in terms of self-diffusion coefficients plotted against $1000/T$. **Figures 7A** and **B** show the self-diffusion coefficient for the NaOAc: glycerol and NaBr: glycerol systems. In both cases there is relatively good agreement between the measured self-diffusion coefficients and that calculated by the Stokes Einstein equation. The $Na_2B_4O_7 \cdot 10H_2O$: glycerol and $NaOAc \cdot 3H_2O$: systems in **Figures 7C** and **7D**, shows poor agreement for both the glycerol hydroxyl protons which are in some cases underestimated by an order of magnitude. This suggest water plays a significant role in delocalising the hydroxyl protons whilst having only a nominal effect on the aliphatic parent molecule, which agrees with the uncharacteristically high diffusivity of the hydroxyl protons in such a viscous medium. This suggests the aliphatic glycerol parent species and the acetate anion are more mobile in the $NaOAc \cdot 3H_2O$ system, compared to the aliphatic glycerol parent species and the tetraborate anion in the $Na_2B_4O_7 \cdot 10H_2O$ system, hence the lower observed macroscopic viscosity. The diffusivity of the hydrate waters is more restricted than would be expected from a pure water phase, showing that the system is quite complex and not just two separate phases.

NMR diffusion measurements show a single average diffusion coefficient that describes the hydroxyl proton of glycerol and water protons, suggesting an exchange of protons between the two species diffusing at that average rate. Such phenomena have previously been observed when studying diffusion in alcohol/water solutions.[34] This also implies that glycerol hydroxyls are diffusing in a rather "independent" fashion relative to their aliphatic parent molecules, which agrees with previous observation on aqueous DES samples.[13] Otherwise, the NMR signal decay for the glycerol OH/water peak would clearly show a much slower second component with values of close to the self-diffusivity of the glycerol aliphatic chain, which is not the case.
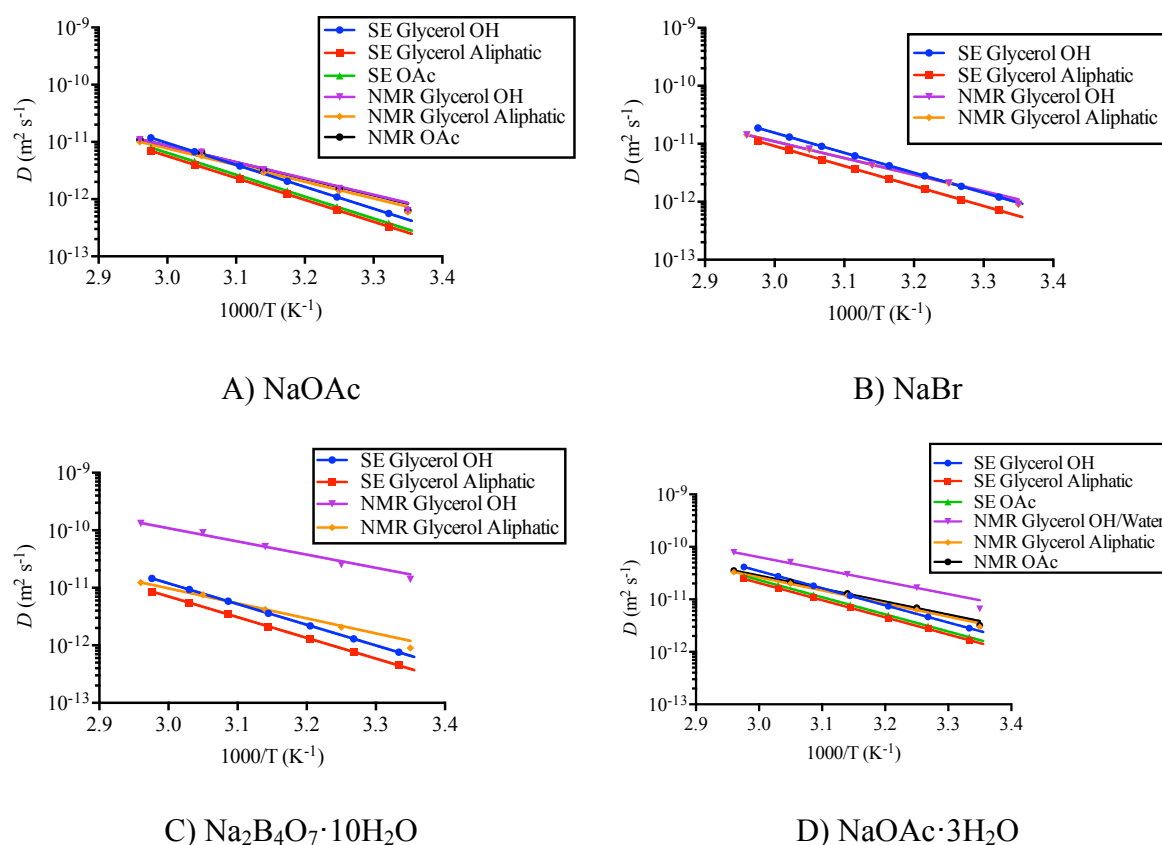

A) NaOAc

B) NaBr

C) $Na_2B_4O_7 \cdot 10H_2O$

D) $NaOAc \cdot 3H_2O$

Figure 7. *Self-diffusion coefficients measured by NMR and calculated using Stokes-Einstein (SE) versus inverse temperature for a range of salt: glycerol mixtures. Within each plot there are trends from PFG NMR and trends from the Stokes-Einstein equation.*

The above observations agree with the molar ionic conductivity behaviour reported in **Figure 4**, as the NaOAc: glycerol has the lowest molar ionic conductivity and $Na_2B_4O_7 \cdot 10H_2O$: the

highest. This suggests that free hydroxyl protons may be involved in the charge transport mechanism as the molar ionic conductivities of the sodium salt: glycerol systems appear to be dependent on the mobility of the glycerol hydroxyl protons. The relatively free nature of the hydrate waters in the $Na_2B_4O_7 \cdot 10H_2O$: glycerol system may explain why the free volume of this system increases with salt concentration, whereas the free volume of the $NaOAc \cdot 3H_2O$ glycerol system decreases with salt concentration. (See supplementary data file)

The diffusion data as a function of temperature were fitted with an Arrhenius expression $D(T) = D_0 \exp(-E_a/RT)$ and plotted on a vertical log scale, from which it is possible to calculate the activation energy barrier for diffusion, E_a. The values of activation energy for diffusion are reported in **Table 2**:

Table 2. *Activation energies of NMR self-diffusivity.*

Sample	Activation energy of diffusivity (kJ mol^{-1})			
	Glycerol OH	Glycerol OH/ Water	Glycerol aliphatic H	Acetate aliphatic H
NaOAc	53.4 ± 2.9	-	54.5 ± 1.7	53.9 ± 2.9
NaBr	53.4 ± 1.2	-	54.0 ± 0.9	-
$Na_2B_4O_7 \cdot 10H_2O$	-	42.9 ± 3.0	48.8 ± 2.1	-
$NaOAc \cdot 3H_2O$	-	44.9 ± 2.5	47.9 ± 0.9	47.3 ± 1.1

The E_a values are similar to those for other ionic liquids[23] but **Table 2** shows that the presence of water decreases E_a for diffusion which can be seen by comparing the dry and hydrate NaOAc samples. E_a for the glycerol hydroxyl/water protons in exchange are significantly lower than those measured for the glycerol hydroxyl diffusion only.

In terms of relating the viscosity of the sample with the experimental NMR diffusion coefficients, it is clear that in general the samples with lower self-diffusion coefficient of the various ^1H different species are those with the highest viscosity. However, the mobility of the ^1H species is not sufficient to fully explain the viscosity data. Indeed, comparison of the NaBr data in Figure 7B with sample $Na_2B_4O_7 \cdot 10H_2O$, might lead to the conclusion that the latter should be less viscous. Both samples have similar diffusivity values for the glycerol aliphatic chain; the latter, however, shows an increased mobility of the glycerol hydroxyl protons in

exchange with water despite $Na_2B_4O_7 \cdot H_2O$ having a higher viscosity. This suggests that the $Na_2B_4O_7$ plays a crucial role in increasing the viscosity of this sample due to solution ordering.

Measurements of diffusion coefficients for Na^+ ions in these samples were not possible due to the very high solution viscosity; this, together with the quadrupolar interaction involved in ^{23}Na NMR makes the relaxation times of these species extremely short precluding PFG NMR measurements even by minimising the echo time in the pulse sequence. Indeed, we measured T_1 values for these samples of the order of μs, which are extremely small. Given that the T_2 transverse relaxation is equal or less then T_1,[35] no ^{23}Na NMR signal could be detected.

To circumvent this problem, T_1 relaxation measurements were carried out on both ^1H and ^{23}Na to give useful information on rotational dynamics[36] and gain further information on the microscopic behaviour.

^1H and ^{23}Na NMR T_1 relaxation measurements

The ^1H T_1 relaxation times for the proton species in the different samples as a function of temperature are reported in **Figure 8**. Minima in the T_1 relaxation times can be observed in many cases, which has been previously observed by Remsing *et al.*[37] and Hayamizu *et al.*[36] when studying ionic liquids with similar viscosities and diffusivities to those reported in this work.

For non-viscous liquids, T_1 usually increases with temperature, i.e., T_1 increases with temperature as the rotational correlation time decreases due to a faster molecular tumbling rate.[35] However, for very viscous samples, minima in T_1 can be observed, as a result of the Bloembergen-Purcell-Pound (BPP) theory of liquid relaxation.[38] The presence of minima indicates a transition from the slow tumbling (or diffusion limit) relaxation regime, where $\omega_0\tau > 1$ to the fast tumbling (or extreme narrowing) relaxation regime, where $\omega_0\tau < 1$. Here ω_0 is the frequency and τ is the correlation time for molecular tumbling.[35] As the temperature increases a transition from diffusion limit regime (low mobility, higher correlation times) to extreme narrowing (fast mobility, lower correlation times) occurs.
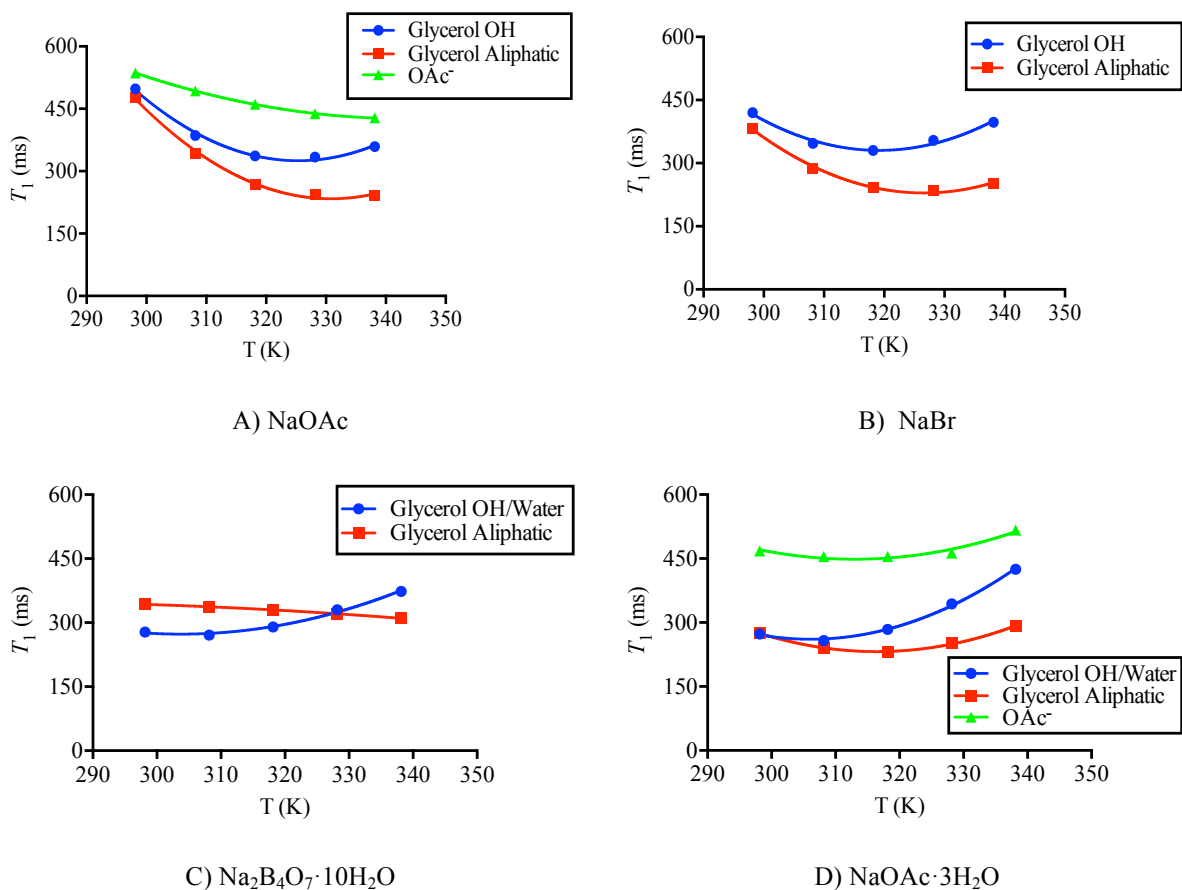
Figure 8. ^1H T_1 *relaxation times versus temperature for a range of salt: glycerol mixtures. Changes in T_1 relaxation times as a function of temperature are linked to changes in molecular dynamics.*

Analysis of the T_1 trends using the BPP theory shows that the faster the mobility of the species under investigation, the lower the temperature at which this transition from slow to fast regime occurs, in other words, more mobile species will be in the fast regime at lower temperatures.[35]

In NaOAc, **Figure 8A**, this transition occurs above 328 K for the glycerol OH, whereas it is not observed at all for the glycerol aliphatic and the acetate anion, which both remain in the slow tumbling regime. This is consistent with the much higher viscosity and lower mobility of these species compared to the mobility in NaBr, **Figure 8B**. It is noted that NaOAc is the sample with the highest viscosity among the sample studied here. For NaBr this transition occurs at about 318 K for the glycerol OH and at 325 K for the glycerol aliphatic, which is reasonable as in general we expect the hydroxyls to be more mobile than the aliphatic chains.

In **Figure 8D** the NaOAc·3H$_2$O, has the highest mobility (lowest viscosity) and highest diffusivity values of all species with the transition for the glycerol OH/water occurring at 308 K and that for the glycerol aliphatic, at about 315 K which is consistent with the other results.

In Na$_2$B$_4$O$_7$·H$_2$O, **Figure 8C**, the transition for the glycerol OH/water peak is observed at about 308 K, a value lower than the minimum for the glycerol OH observed in NaBr, which is consistent with the higher mobility of these protons in exchange with water as measured by PFG NMR. However, the glycerol aliphatic fails to undergo this transition and remains in the slow tumbling regime. This may therefore explain the observation that, despite the presence of mobile water, overall, this sample has a viscosity significantly higher than that of NaBr. In addition, it is noted that the diffusivity values of the glycerol aliphatic in Na$_2$B$_4$O$_7$·H$_2$O + glycerol are lower than those observed in NaBr, which is consistent with the restricted mobility.

In order to have further insight into the molecular dynamics in these samples, ^{23}Na NMR T_1 relaxation time measurements have also been carried out to probe the behaviour of the Na$^+$ ions and see how this correlates with the viscous properties of these liquids. Compared to ^{1}H NMR, ^{23}Na NMR spectra are very broad due to the very high viscosity and quadrupolar interactions in the liquids.[39] The results are shown in **Figure 9**. The ^{23}Na T_1 relaxation times are much shorter than the ^{1}H T_1 values of the other species due to ^{23}Na being quadrupolar with enhanced relaxation.[39] The analysis of these relaxation times can also be carried out using the BPP theory approach for liquids as it has previously been done for other quadrupolar species.[37]
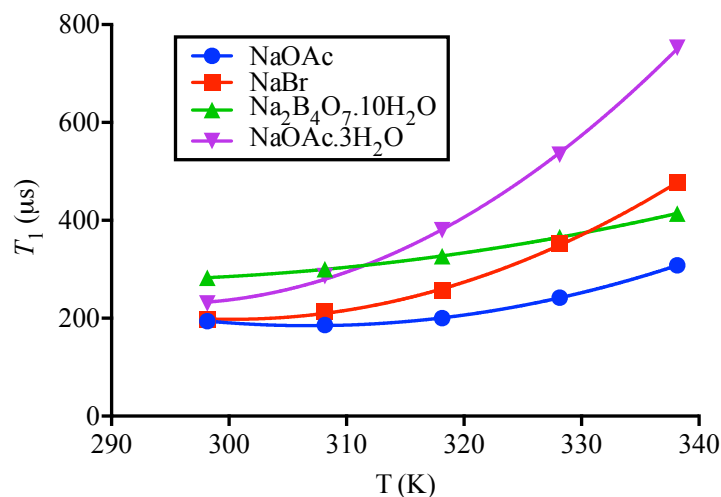
Figure 9. *T_1 relaxation times ^{23}Na versus temperature for a range of salt: glycerol mixtures with non-linear trend lines. The results show that Na ions have a significantly different molecular dynamics in the different salts.*

The NaOAc sample, **Figure 9**, is the only one showing a minimum for the ^{23}Na T_1 in the range of temperature studied, which implies a transition from the slow to fast regime. In all the other samples, the value of T_1 increases with temperature in all cases. This implies that at those temperatures we are already in the fast regime for these samples as opposed to the case of NaOAc, which ties in with the much higher viscosity of this sample compared with the other ionic liquids.

Compared to the trend observed for ^{1}H T_1 relaxation times, we can see a much steeper rise of the ^{23}Na T_1 values with temperature. This pronounced increase correlates well with the changes in viscosity observed and indicates a weakening of inter-ionic interactions.[37] The rather different trend of ^{23}Na T_1 as a function of temperature compared to the other ^{1}H species also suggests that the dynamic of these ions is independent to a large extent from that of the other species. Indeed, unlike the ^{1}H species, for all the samples we can see a fully developed trend in the fast tumbling regime for ^{23}Na T_1 times and we note that the trend for the absolute values of ^{23}Na T_1 in the high temperature range, i.e., fast narrowing, reflects well that of viscosity: the less viscous the sample, the higher the T_1 relaxation time values (i.e., slower $1/T_1$ relaxation rate), which is in agreement with the BPP theory. We can also see that the addition of water to NaOAc has a significant impact on the T_1 behaviour. When water is added the increase in ^{23}Na T_1 become much faster and reaches much higher values, which implies an enhanced molecular dynamics in agreement with the dramatic decrease of viscosity observed.

In summary, the macroscopic viscous properties of these liquids are determined by a series of dynamic phenomena at molecular level and the ^{1}H and ^{23}Na NMR measurements carried out in these work are able to elucidate such phenomena, which are responsible for the macroscopic behaviour of these liquids. Translational and rotational motion at microscopic level was studied using diffusion and T_1 relaxation measurements and the results correlate well with the macroscopic behaviour of these liquids. The presence of water enhances significant the molecular dynamics of the species in NaOAc. However, an unusually low viscosity for the $Na_2B_4O_7 \cdot 10H_2O$ sample is observed despite the presence of water and relatively fast translation motion of this water in fast exchange with the glycerol hydroxyl. The ^{23}Na NMR T_1 relaxation measurements suggest that the mobility of $Na_2B_4O_7$ species play an important role in determining the macroscopic behaviour of these liquid.

Conclusions

It has been shown that concentrated mixtures can be prepared using alkali metal salts and glycerol. The mixtures are not true eutectics (the melting point does not have a minimum as a function of concentration) but they have densities, viscosities and ionic conductivities comparable to DESs and ILs. All of the systems investigated showed Newtonian fluid behaviour over the rotation rate range of the rotational viscometer used, except for the NaOAc: glycerol system where a shear thickening response was observed.

PFG NMR showed that the self-diffusion coefficients of the ions and molecules are in the range 10^{-11} - 10^{-13} m^{2}s^{-1} which is similar to many DES and IL systems. For NaBr, the glycerol aliphatic and hydroxyl protons appear to be diffusing together, whereas in the NaOAc: glycerol system the glycerol hydroxyl protons appear to be diffusing with the acetate anion.

There appears to be a clear link between dynamic viscosity and the self-diffusivity of a species as well as between ionic conductivity and diffusion of free hydroxyl protons; however the role of water complicates the diffusion mechanism. Hydrate waters increase species self-diffusivity, and reduce the viscosity of the $NaOAc \cdot 3H_2O$: glycerol system however, water in this system appears to be more restricted compared to the $Na_2B_4O_7 \cdot 10H_2O$ system. In all of the systems investigated, the Stokes-Einstein relationship underestimated the self-diffusion coefficients of all of the ^{1}H species probed.

The use of ^{1}H PFG NMR diffusion measurements together with ^{1}H and ^{23}Na T_1 relaxation measurements show that translation and rotational dynamics of ^{1}H and ^{23}Na species are intimately connected to the macroscopic behaviour of these systems in terms of ionic conductivity and viscosity.

Acknowledgements

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