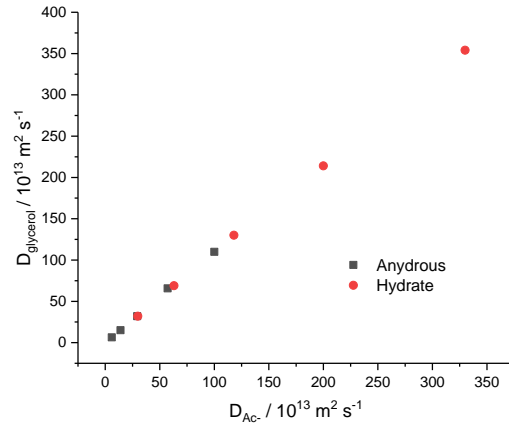


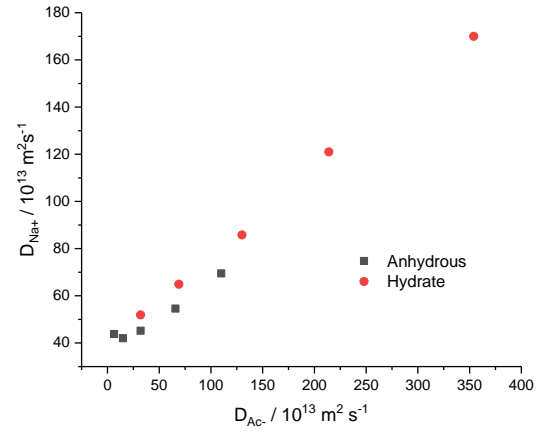
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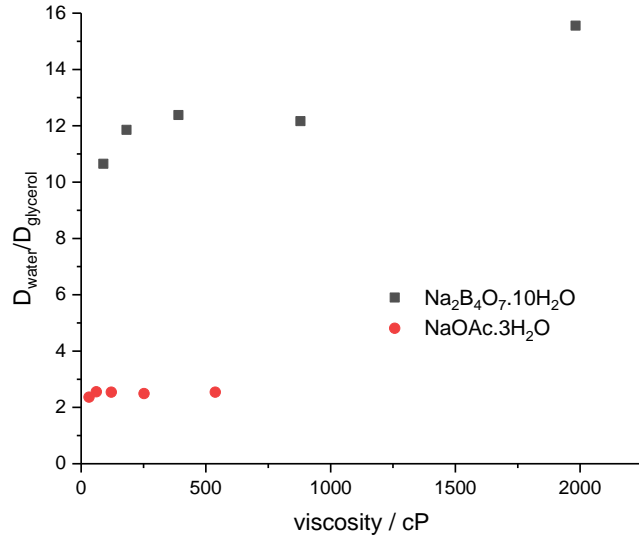


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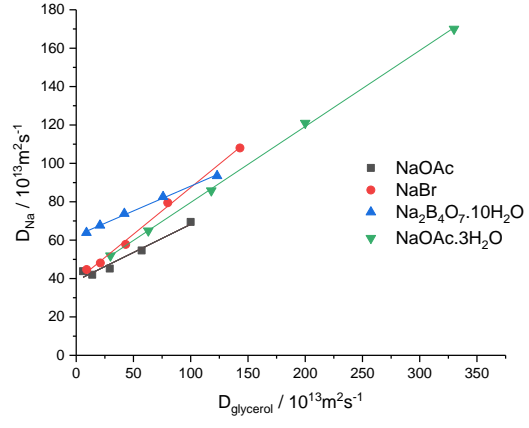
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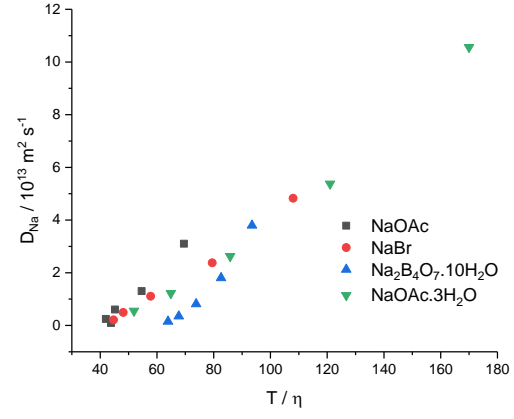


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## $^{23}\text{Na}$ NMR $T_1$ relaxation measurements as a probe for diffusion and dynamics of sodium ions in salt-glycerol mixtures

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### Abstract

Mixtures of sodium salts with oxygen-containing molecules are useful from the perspective of applications such as sodium ion batteries but also because they fill the gap between deep eutectic solvents and molten salt hydrates. In a previous work, the physical properties (such as diffusion coefficients, conductivity, viscosity and glass transition temperature) of four salts, namely  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ,  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ ,  $\text{NaBr}$ , and  $\text{NaOAc}$ , were measured with glycerol. Pulsed-field gradient (PFG) NMR was also used to measure self-diffusion coefficients of  $^1\text{H}$ -bearing species. However, the technique was not able to measure diffusion of sodium ions due to the very fast NMR relaxation rate of such species, resulting in loss of PFG NMR signal. In the current work, this study is expanded to using  $^{23}\text{Na}$   $T_1$  relaxation measurements, which under certain assumptions, can be translated into diffusion coefficients. Analysis of the physical properties is then correlated with self-diffusion coefficient measurements to elucidate information about structure and ionic mobility. It is shown that  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ ,  $\text{NaBr}$  and  $\text{NaOAc}$  fit models for ionic conductivity and diffusion, which are consistent with ionic liquids where charge transport is limited by ionic mobility rather than the number of charge carriers. The waters of hydration of  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  do not appear to form a separate phase but instead are strongly coordinated to the cation. In contrast,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  appears to form a water-rich phase with enhanced sodium mobility.

*Keywords:* Deep Eutectic Solvents, Ionic Liquids, NMR relaxation, diffusion

## Introduction

Deep eutectic solvents (DESs) are a class of ionic liquids, which in the last two decades have been used in areas such as materials preparation,<sup>1</sup> gas-separation,<sup>2</sup> electrochemistry,<sup>3</sup> biomass valorization<sup>4</sup> and catalysis.<sup>5</sup> DES properties have been extensively studied focusing on the freezing point,<sup>6</sup> vapour pressure,<sup>7</sup> conductivity,<sup>8</sup> viscosity<sup>9</sup> and more recently diffusion.<sup>10, 11</sup> The knowledge of such properties plays a crucial role in applications and determines the suitability of a particular DES for a specific application. For example, the knowledge of viscosity is useful when using DESs in flow applications,<sup>12</sup> whereas ionic mobility and conductivity are essential knowledge for the design of electrochemical applications. It has previously been suggested that conductivity in ionic liquids is limited not by the number of charge carriers but by the availability of holes which are sufficiently large to enable ions to move in to them.<sup>13, 14</sup> This is a concept first developed for high temperature molten salts but found to be more applicable to ionic liquids due to their much larger ionic radii.<sup>15, 16</sup> It was shown that both conductivity and viscosity could be modelled using this approach. It was also shown that bulk diffusion, measured electrochemically, fitted the Stokes-Einstein equation but the radius of the mobile species corresponded to that of the hole rather than the electroactive species. This is because in bulk diffusion measurements there is a net transport of mass.

Studies of diffusion in DESs emerged relatively recently. In particular, the pulsed-field gradient (PFG) NMR technique, also known as NMR diffusometry, or sometimes referred to as pulsed gradient stimulated echo (PGSE) NMR, is a powerful, non-invasive tool to selectively probe diffusion in molecular<sup>17-21</sup> and ionic liquid<sup>22, 23</sup> mixtures, including diffusion of the different components within DESs, for example that of the ionic salt and of the hydrogen bond donor (HBD). A first study reported by D'Agostino et al.<sup>11</sup> on choline chloride-based DESs revealed that the molecular structure of the hydrogen bond donor can greatly affect the mobility of the whole system and that structuring phenomena within the HBD can lead to low diffusion coefficients, which in turn affects the viscosity of the DES. The Stokes-Einstein equation could be used for self-diffusion measurements as there is no net transfer of mass. A subsequent study on aqueous mixtures with DESs<sup>10</sup> revealed hydroxyl protons in the HBD can have a diffusion coefficient that is significantly different from that of the parent molecules, possibly due to exchange processes with water. Other methods, such as electrochemical measurements, have also been used to measure diffusion in DESs, showing values of diffusion coefficients similar to those reported for some ionic liquids.<sup>24</sup>

Subsequent studies have revealed that inorganic salts can form eutectic mixtures with a variety of amides, polyols and carboxylic acids. These include aluminium chloride,<sup>25</sup> ferric chloride<sup>26</sup>

and zinc chloride.<sup>27</sup> These are liquid through the disproportionation of the metal salt to form both anionic and cation species. It was found that transition metal hydrate salts could also be used and in this case disproportionation does not occur.<sup>28</sup> This idea was extended to a range of sodium salts such as borax, sodium acetate and sodium bromide which formed liquids when mixed with glycerol. Choline chloride mixed with glycerol resulted in a decrease in the liquid viscosity whereas the sodium salts increased the liquid viscosity.<sup>29</sup> This study is fundamental as it spans the compositional space between ionic liquids, DESs, molten salt hydrates<sup>30</sup> and concentrated brines.

In this work, the conductivity and viscosity of these liquids are analysed in more detail and compared with a model derived from hole theory.<sup>13</sup> Deviations between this models and experimentally determined values are explained in terms of inhomogeneity of the liquids and we use <sup>23</sup>Na *T*<sub>1</sub> relaxation measurements, under certain assumptions, to derive diffusion coefficient data. In particular, using the theoretical approach developed by Mitchell et al.<sup>31</sup>, which relates *T*<sub>1</sub> relaxation of quadrupolar nuclei with diffusion coefficients. We calculate diffusion coefficients of sodium ions and compare those with the other species diffusing in the liquid to gain information about homogeneity and phase behaviour.

### Experimental

Glycerol (Fisher Scientific) was heated to 50 °C and mixed with one of the four salts NaOAc (Fisher Scientific), NaBr (Sigma-Aldrich), Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (Sigma-Aldrich) or NaOAc·3H<sub>2</sub>O (Fisher Scientific) using an overhead stirrer (Stuart Scientific, 500 rpm) until all the components formed a homogeneous liquid phase. The molar concentration of salt in glycerol was 1.80 M for NaOAc, 1.85 M for NaBr, 2.02 M for Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O and 2.28 M for NaOAc·3H<sub>2</sub>O. All liquids were stored at 50 °C. 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 °C and viscosity measurements were taken down to 25 °C. The electrical conductivities of all the ionic solvents were measured using a conductivity probe (Jenway 4510, cell constant *K* = 0.96 cm<sup>-1</sup>), which was fitted with an integral temperature probe. Conductivity was measured over the temperature range 25 – 45 °C. All the <sup>1</sup>H and <sup>23</sup>Na NMR data (diffusion and relaxation) used for the subsequent analysis were taken from previously reported literature.<sup>29</sup>

## Methodology

The relaxation behaviour of quadrupolar  $^{23}\text{Na}$  nuclei, spin = 3/2, in electrolyte solutions, assuming the motional narrowing (i.e., fast tumbling) regime can be described with a single relaxation rate according to:<sup>31, 32</sup>

$$\frac{1}{T_1} = \frac{(e^2qQ)^2}{10} \left[ 1 + \frac{\theta^2}{3} \right] \tau_c \quad (1)$$

whereby  $eq$  refers to the electric field gradient at the Na nucleus,  $eQ$  is the nuclear quadrupole moment,  $\theta$  describes the asymmetry of the electric field gradient and  $\tau_c$  is the rotational correlation time for  $\text{Na}^+$  ions. Writing  $\tau_c$  according to the Debye relationship and assuming the  $\text{Na}^+$  ions diffuse as solid spheres in a Stokes-Einstein manner, the following expression relating  $T_1$  with the diffusion coefficient,  $D$  can be derived:<sup>31, 32</sup>

$$\frac{1}{T_1} = \frac{1}{45} \frac{r_0^2}{D} (e^2qQ)^2 \left[ 1 + \frac{\theta^2}{3} \right] \quad (2)$$

This expression allows calculations of the diffusion coefficient,  $D$ , of a certain species in solution once its  $T_1$  values are known. Hence, Equation (2) represents a very useful tool for estimating diffusion coefficients of  $\text{Na}^+$  in solutions when direct measurements are not possible. Equation (2) has been shown to predict well diffusion of  $\text{Na}^+$  in NaCl aqueous solutions.<sup>33</sup> In using Equation (2) we assume the quadrupole coupling coefficient,  $e^2qQ$ , of  $\text{Na}^+$  to be  $4.8 \times 10^6 \text{ rad s}^{-1}$ , the asymmetry parameter to be  $\theta = 0$  and the radius of the  $\text{Na}^+$  ions to be  $r_0 = 0.210 \text{ nm}$ .<sup>31</sup> It is noted that the quadrupole coupling coefficient of  $\text{Na}^+$  will depend on the coordination environment and hydration state and that the value chosen assumes hydrated ions; such value is however similar to that of  $\text{Na}^+$  in different coordination environments.<sup>34</sup>

The calculated  $\text{Na}^+$  diffusion coefficients were benchmarked with the Stokes-Einstein model:<sup>35</sup>

$$D = \frac{k_B T}{6\pi\eta r_0} \quad (3)$$

where  $k_B$  is the Boltzmann constant,  $T$  the temperature,  $r_0$  the radius of the diffusing species, and  $\eta$  the viscosity of the mixture.

## Results and discussion

Table 1 shows the physical properties of glycerol with mixtures of four sodium salts, namely  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ,  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ ,  $\text{NaBr}$ , and  $\text{NaOAc}$ . While some of these data have been previously presented, they have not been analysed in depth. Despite having similar concentrations, there is a significant difference in the conductivity and molar conductivity. Clearly, each salt has a different structuring role on glycerol. Pure glycerol is viscous due to the extensive network of intermolecular hydrogen bonds. The addition of salts such as choline chloride to glycerol has been found to decrease the viscosity of the resulting DESs.<sup>36</sup> The data in Table 1 show that  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ,  $\text{NaBr}$ , and  $\text{NaOAc}$  increase the viscosity of the mixture compared to pure glycerol whereas  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  causes the viscosity to decrease by a similar amount as choline chloride. It would be expected that ions with a high charge density will increase the interaction between species and decrease mobility. If the ion-ion or ion-dipole interactions increase, the components will be constricted decreasing the free volume of the liquid (i.e., molar volume – volume per mole of the constituent components) and decreasing ionic mobility, since ionic mobility is related to free volume. Interestingly Table 1 shows that the free volume of  $\text{NaBr}$ ,  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  and  $\text{NaOAc}$  decrease compared to pure glycerol ( $V_{\text{free}} = 17.9 \text{ cm}^3 \text{ mol}^{-1}$ ) whereas that of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  increases significantly despite an increase in viscosity. For most ionic liquids this would simply be explained by the viscosity of the liquids but the data in Table 1 show that there is not the expected correlation between molar conductivity and fluidity. For example,  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  has a lower conductivity than  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  despite having a much lower viscosity.

**Table 1.** Physical properties of mixtures of glycerol with four sodium salts at 298 K.

Property	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	$\text{NaOAc} \cdot 3\text{H}_2\text{O}$	$\text{NaBr}$	$\text{NaOAc}$
Concentration / $\text{mol dm}^{-3}$	2.02	2.28	1.88	1.80
Density / $\text{g cm}^{-3}$	1.412	1.207	1.374	1.290
Free volume / $\text{cm}^3 \text{ mol}^{-1}$	27.29	12.18	16.25	16.91
Conductivity / $\text{S cm}^{-1}$	$6.53 \times 10^{-4}$	$6.02 \times 10^{-4}$	$3.25 \times 10^{-4}$	$1.35 \times 10^{-4}$
Viscosity / cP	1982	538	1420	3169
Molar conductivity / $\text{S cm}^2 \text{ mol}^{-1}$	0.323	0.264	0.173	0.075
Calculated conductivity / $\text{Scm}^{-1}$	$0.82 \times 10^{-4}$	$7.64 \times 10^{-4}$	$4.54 \times 10^{-4}$	$2.30 \times 10^{-4}$
$E_a$ (conductivity) / $\text{kJ mol}^{-1}$	48.09	51.01	56.98	70.24
$E_a$ (viscosity) / $\text{kJ mol}^{-1}$	-66.18	-59.85	-63.28	-70.52

Error analysis and more physical data for these systems are published elsewhere.<sup>37</sup>



It has previously been suggested that the conductivity of ionic liquids is limited by the mobility of charge carriers and not by their number. The high viscosity is limited by the free void volume of the liquid where the fraction of ions that can move into a suitably sized hole is effectively at infinite dilution ( $\sim 10^{-6}$ ). Accordingly, the Nernst-Einstein equation can be applied to a given ion to determine the molar conductivity of a given ion,  $\lambda_+$ , according to:

$$\lambda_+ = z^2 F e / 6 \pi \eta R_+ \quad (4)$$

where  $z$  is the charge on the ion,  $F$  is the Faraday constant,  $R_+$  is the radius of the ion and  $e$  is the electronic charge. This explains why the molar conductivity of an ionic liquid often varies linearly with fluidity,  $\eta^{-1}$ . Equation (4) can be expressed in terms of the solution conductivity,  $\kappa$ , using Equation (5):

$$\kappa = \frac{z^2 F e}{6 \pi \eta} \left( \frac{1}{R_+} + \frac{1}{R_-} \right) \frac{\rho}{M_w} \quad (5)$$

where  $\rho$  is the density,  $R$  is the size of the cation (+) and anion (-) and  $M_w$  is the molar mass of the ionic fluid. Equation (5) was used to calculate a conductivity case on a hole theory<sup>14</sup> and the data are shown in Table 1. It can be seen that the calculated conductivity values for NaOAc·3H<sub>2</sub>O, NaBr, and NaOAc mixed with glycerol are of a similar magnitude to the measured values. The value calculated for Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O is a factor of 8 smaller than the measured value, which suggests that the ionic mobility is different from that expected for a homogeneous fluid where free volume limits the movement of ions. The one obvious difference for Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O is the large number of waters of hydration. This has the potential to form a non-homogeneous phase as was found for water mixtures with choline-chloride based DESs.<sup>38-40</sup> Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O is the only mixture with glycerol that results in a significant increase in free volume compared to pure glycerol. An additional method to determine the ability of species to move is by measuring the surface tension,  $\gamma$ , of the liquid as this can be related to the average void radius,  $r$ :

$$4\pi r^2 = 3.5 kT / \gamma \quad (6)$$

where  $k$  is the Boltzmann constant. Interestingly these liquids all have high surface tensions meaning that the hole radius is relatively small but the surface tensions are relatively similar ( $\gamma$

(borax) = 77.73 mNm<sup>-1</sup>  $\gamma$  (NaOAc) = 63.45 mNm<sup>-1</sup>). Accordingly, the average void radii are also similar, ( $r$  (borax) = 0.121 nm and  $r$  (NaOAc) = 0.134 nm).

The change in viscosity and conductivity with temperature can be modelled using an Arrhenius-like equation to obtain values of activation energies. This is a common approach used for ionic liquids and DESs. This has been done for the four systems discussed here and the data are presented in Table 1. It can be seen that the data for all the systems except borax are similar to each other (note the sign convention is that viscosity is negative whereas conductivity is positive as the former decreases whereas the latter increases with increasing temperature).

The structure of the liquid and the mobility of the charge carrier can be further investigated using the PFG NMR and NMR relaxation data. Table 2 reports the values of <sup>23</sup>Na self-diffusion coefficients, calculated using Equation (2), together with those for other <sup>1</sup>H-containing species and bulk viscosity values of the liquids. As expected, an increase in temperature leads to a decrease of viscosity and an increase in self-diffusion coefficients, the latter consistent with the Bloembergen, Purcell and Pound (BPP) theory of relaxation of liquids.<sup>41</sup>

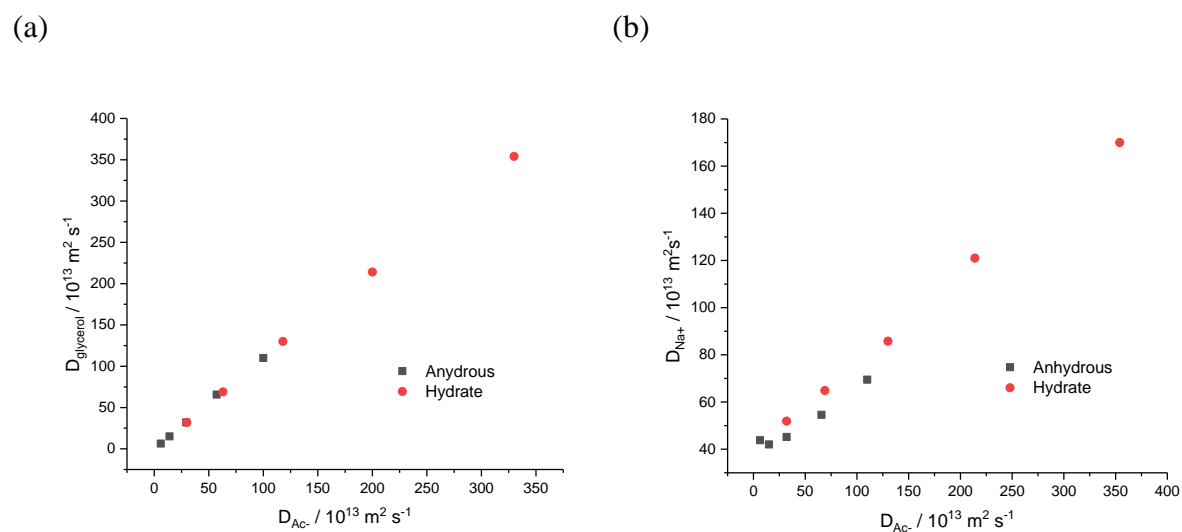
**Table 2.** Self-diffusion coefficients derived from <sup>1</sup>H PFG (for proton bearing species) and <sup>23</sup>Na  $T_1$  NMR relaxation data (for sodium ions).

Salt:glycerol system	Viscosity (cP)	T (K)	Self-diffusion coefficient (10 <sup>-13</sup> m <sup>2</sup> s <sup>-1</sup> )				Na <sup>+</sup>
			Glycerol OH	Glycerol OH/ Water	Glycerol aliphatic H	Acetate aliphatic H	
NaOAc	3169	298	6.30	-	5.95	6.34	43.8
	1250	308	15.4	-	14.0	15.0	42.0
	526	318	32.6	-	29.3	32.0	45.2
	252	328	66.0	-	57.2	65.7	54.6
	109	338	110	-	100	110	69.5
NaBr	1420	298	9.10	-	9.10	-	44.7
	624	308	21.1	-	21.1	-	48.1
	287	318	43.1	-	43.2	-	57.8
	138	328	81.0	-	80.0	-	79.5
	70	338	142	-	143	-	108
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	1982	298	-	140	9.00	-	63.9
	879	308	-	253	20.8	-	67.7
	390	318	-	520	42.0	-	73.8
	182	328	-	900	75.9	-	82.6
	89	338	-	1310	123	-	93.5
NaOAc·3H <sub>2</sub> O	538	298	-	75.9	29.9	32.0	51.9
	252	308	-	157	63.0	69.0	64.9
	121	318	-	300	118	130	85.8
	61	328	-	511	200	214	121
	32	338	-	780	330	354	170

Error analysis for these systems are published elsewhere.<sup>37</sup>

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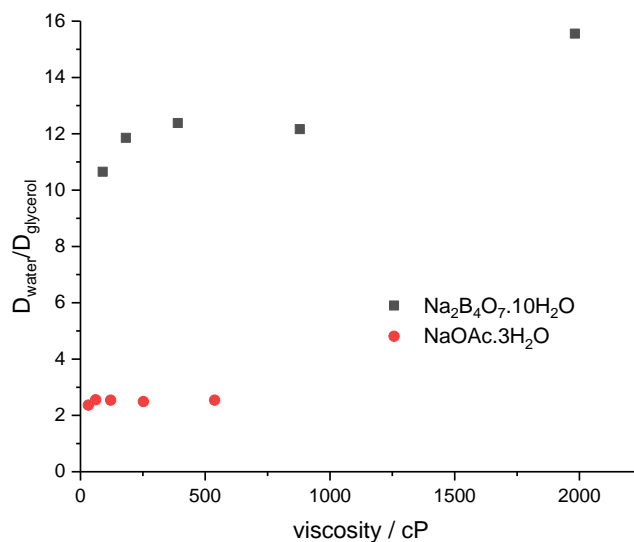
**Figure 1.** Self-diffusion coefficients calculated using NMR data for (a) glycerol and (b) sodium, using Equation (2), as a function of self-diffusion coefficient for acetate for the hydrated ( $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ ) and anhydrous ( $\text{NaOAc}$ ) form of sodium acetate.

Figure 1a shows the diffusion coefficient of the acetate anion correlated with the diffusion coefficient for glycerol both in the anhydrous and hydrate salt mixtures. Both show a linear trend and both overlap as would be expected. This shows that both species are diffusing in a medium with a composition which changes fluidity the same with temperature, i.e., if there is heterogeneity in the liquid composition both glycerol and the anion are in regions of the same composition. It was recently shown that the addition of water to a choline chloride- glycerol DES resulted in significantly increase diffusion of water molecules than would be expected from the bulk viscosity.<sup>10</sup> From this it was concluded that the mixture was heterogeneous and this was later confirmed using X-ray diffraction studies.<sup>42</sup> Adding two mole equivalents of water to the choline chloride-glycerol DES resulted in significant changes in physical properties such as viscosity and conductivity and dynamic light scattering and NMR diffusion measurements showed inhomogeneity in the water distribution.<sup>10, 40</sup> In the case of the sodium acetate-glycerol the hydrate salt has 3 mole equivalents of water and so heterogeneity may be expected. The anhydrous mixture is 5.9 times more viscous than the mixture with the hydrated salt but the conductivity of the latter is only 4.5 times that of the former. Interestingly the molar free volume of the hydrate salt mixture is considerably less than the anhydrous mixture suggesting that the waters of hydration are tightly bound to the sodium cations.

Figure 1b correlates the diffusion coefficient of the acetate containing species with the diffusion coefficient for sodium ion both in the anhydrous and hydrate salt mixtures. The ratio of diffusion coefficients of sodium: acetate ions are slightly larger in the hydrated mixture than the anhydrous liquids. This suggests that the sodium ions are proportionately slightly more mobile in the hydrated liquid than the anhydrous liquid. This could be because the sodium ions are differently hydrated or because they are present in the water rich phase as was the case in DESs where water was deliberately added. However, the fact that the conductivity predicted is relatively similar to that calculated from a continuum model suggests that while water may affect the relative interactions between all the components it is likely to be strongly associated with the sodium cation so there may be a trade-off between an effective viscosity decrease and a hydrodynamic radius increase.

In Table 1 the major discrepancy was between the measured and calculated conductivities of the glycerol- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  mixture. Clearly, the large number of waters of hydration would enable a heterogeneous phase to form. To put this into perspective the molar ratio of glycerol: water is 0.68 and the molecular volume ratio of glycerol: water is 3.3:1. This shows that glycerol is still the major phase by volume. For the glycerol- $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  mixtures the molar ratio of glycerol:water is 2 and the molecular volume ratio of glycerol:water is 9.7.

To demonstrate the difference in structure between these two mixtures the ratio of the self-diffusion coefficients for water and glycerol were determined for the  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  mixtures with glycerol as a function of viscosity and the results are shown in Figure 2. It can be seen that for the  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  mixture the ratio of diffusion coefficients remains constant at approximately 2.5. For the  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  mixture with glycerol the ratio is approximately 15 showing how proportionately more mobile the water is. This must result from the water being in a separate phase. As the temperature increases the viscosity decreases and the ratio of self-diffusion coefficients for water and glycerol decreases slightly to 10 showing that there is definitely a more mobile second phase but the liquid is probably slightly less heterogeneous.



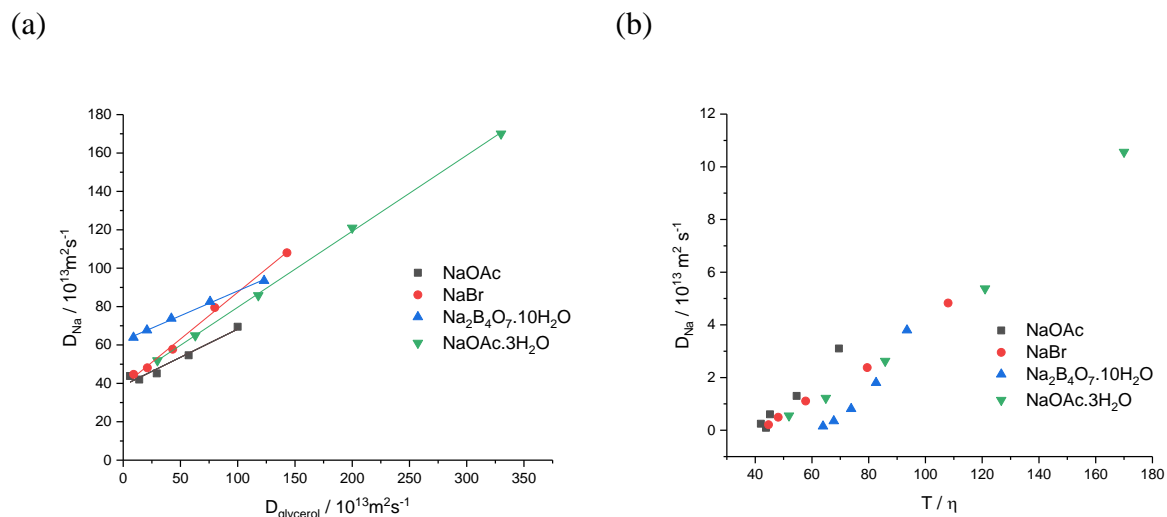
**Figure 2.** Ratio of self-diffusion coefficients for water and glycerol for the  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  mixtures with glycerol as a function of viscosity.

These data start to show some of the differences observed in physical properties in Table 1.  $\text{NaBr}$  and  $\text{NaOAc}$  are clearly homogeneous liquids and the conductivity fits with a model previously derived for ionic liquids.  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  decreases the viscosity of the mixture compared to  $\text{NaOAc}$  because the water molecules solvate the sodium cation. The observations that the ratio of diffusion coefficients of glycerol and water remains constant at different temperatures and the conductivity fits an ion mobility model suggests that the waters of hydration do not form a separate phase. For  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  the observation that the ratio of diffusion coefficients of glycerol and water changes significantly at different temperatures coupled with a significant discrepancy in the calculated conductivity suggests that the waters of hydration do form a separate phase.

These ideas can be confirmed by comparing the self-diffusion coefficients for sodium and glycerol, which are shown in Figure 3a. At lower temperatures, the self-diffusion coefficients for sodium correlate well with those for glycerol for the  $\text{NaBr}$ ,  $\text{NaOAc}$  and  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  systems confirming that they are homogeneous. Slight deviations at higher temperatures probably originate in differences in ionic atmosphere effects exhibited by the different anions. The higher mobility for sodium in the  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  liquid (approximately 50% higher at low temperature) must result from being in a water-rich phase. This decreases as the temperature increases presumably because the water becomes more evenly dispersed.

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**Figure 3.** Self-diffusion coefficients for sodium cations calculated using NMR data and Equation (2) (a) as a function of self-diffusion coefficient for glycerol and (b) as a function of temperature divided by viscosity.

Figure 3b shows a fit of the  $\text{Na}^+$  diffusion data in Table 2 to Equation (3). The data for NaBr, NaOAc and  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  fit roughly linearly with similar slopes whereas that for  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  is non-linear. It would be expected that the slopes would be the same as the size of the  $\text{Na}^+$  ion remains constant, however the dependency of the diffusion coefficient on the ion radius in Equation (2) ( $D$  is proportional to  $r^2$ ) will exaggerate errors in the assumed radius. Difference in the slope of the NaOAc and  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$  could also result from differences in the hydrodynamic radius of the sodium ion, i.e., the sodium is probably hydrated in the latter case. The non-linear behaviour of the  $\text{Na}^+$  ion in  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  probably originates from the non-uniform distribution of water molecules at lower temperature which becomes more uniform at the temperature increases and hence the local viscosity will change with temperature.

### Conclusions

This study has shown that waters of hydration can play an important role in determining the mobility of ions in eutectic mixtures. It is shown that for small ions such as  $\text{Na}^+$ , a small number of waters of hydration remain strongly bound to the cation and can significantly improve ionic mobility without behaving like free water molecules. This is different to the behaviour of water in DESs with non-coordinating quaternary ammonium cations. This may have some

implications for the use of group 1 metal salts as it implies that higher conductivities and lower viscosities could be obtained by addition of a small, highly coordinating molecule such as water to decrease the effect of ordering on the liquid. The addition of excess water results in separate phase formation, which while increasing conductivity, will have the effect of adding effectively bulk water to the liquid.

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### Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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