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Diffusion Measurements To Understand Dynamics and Structuring in Solutions Involving a Homologous Series of Ionic Liquids

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The self-diffusion coefficients of each of the components in mixtures containing pyridine and each of the homologous series 1-alkyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imides in acetonitrile were determined using NMR diffusometry (*i.e.*, Pulsed Gradient Spin Echo). The nature of solvation was found to change significantly with the proportion of salt in the mixtures. Increased diffusion coefficients (when corrected for viscosity) for the molecular components were observed with increasing proportion of ionic liquid and with increasing alkyl chain length on the cation. Comparison of the molecular solvents suggests increased interactions in solution of the pyridine with other components of the mixture, consistent with the proposed interactions shown previously to drive changes in reaction kinetics. Discontinuities were seen in the diffusion data for each species in solution across different ionic liquids between the hexyl and octyl derivatives, suggesting a change in the structuring in solution as the alkyl chain on the cation changes and demonstrating the importance of such when considering homologous series.

Introduction

Ionic liquids were initially somewhat arbitarily defined as salts with a melting point below that of water,[1] though this definition has been expanded to take into account mixtures of salts and molecular solvents.[2] They are typically composed of charge diffuse, bulky cations ions[3] which frustrate crystallisation, leading to their characteristic lower melting points compared to typical salts. The charge is balanced by anions ranging from small halides to large, charge diffuse sulfonylimides.[4] However, being composed of ions mean that the forces between the components are strong (electrostatic) limiting their vapour pressure;[5] ionic liquids only evaporate under extreme conditions.[6] This feature, along with the fact that ionic liquids are non-flammable[7] and that their physical properties (such as miscibility with other solvents) can be altered by changing the constituent ions,[8] has seen ionic liquids being considered widely as alternatives to traditional molecular solvents in areas including catalysis,[9] solvent extraction[10] and electrochemistry.[11]

One area that has seen significant application of ionic liquids is in preparative chemistry.[12–17] However, immediately apparent from early studies (for a key early example, see Earle *et al.*[18]) was that the outcomes of chemical processes, such as the reaction rate and product selectivity, were different in ionic liquids compared to traditional molecular solvents. Subsequently, a significant amount of work has been carried out in order to understand these ionic liquid solvent effects, with the aim of being able to predict reaction outcomes (for a review, see Hawker *et al.*[19]).

Several aspects of reaction outcomes in ionic liquid mixtures are now well understood, notably that the solvent effects vary with the both the amount of ionic liquid in the reaction mixture[19–22] and the nature of the ionic liquid (that is, the constituent ions)[19,23–25] being critical. Such understanding has extended to the solute-solvent interactions responsible for solvent effects on fundamental processes and hence solvent design,[26] machine learning approaches to solvent choice[27] and quantification of key reactivity parameters.[28]

A key aspect of the above argument is that the prediction of ionic liquid solvent effects relies on understanding solute-solvent interactions. One point that is frequently overlooked in such situations is the organisation of the components of ionic liquids in solution; such organisation has been observed using, for example, X-ray scattering techniques[29] along with a variety of NMR methods.[30,31] Whilst the change in the nature of the solvent and organisation is sometimes invoked to explain changes in the outcomes with different proportion of ionic

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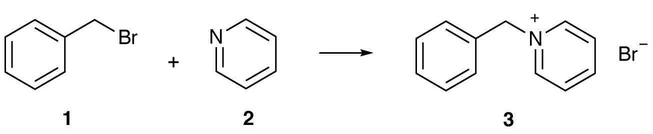
liquid (*i.e.* changing from ionic liquid dissolved in a molecular solvent to a molecular solvent dissolved in an ionic liquid), the effect of changing the nature of the ionic liquid and effects on solvent organisation are generally not considered.[32]

Importantly, in recent work considering the relationship between the rate coefficient for a well-studied reaction that proceeds through a bimolecular substitution process (that between pyridine **1** and benzyl bromide **2**, Scheme 1) and transverse NMR relaxation time (T_2),[33] a dependence on the origin of solvent effects was noted with the nature of the ionic liquid mixture.[34] In all cases in which the reaction was carried out in mixtures containing a high proportion of one of the homologous series **4** (Figure 1), the energetic origins of the changes in rate coefficient were the same and consistent with reported observations[26,35–38] – an increase in enthalpy of activation was outweighed by an increase in the entropy of activation. However, within these results there was a step-change in the values of the entropy and enthalpy data between the cases involving the hexylimidazolium-based ionic liquid **4c** and the octyl derivative **4d**. This change was argued to be as a result of increased ordering in solution with alkyl chain length and the resulting structuring in solution.

With the above argument in mind, it would clearly be of interest to evaluate the nature of organisation and dynamics in solution, particularly as to how this changes both with the proportion of ionic liquid in the reaction mixture but particularly with the nature of the ionic liquid, in this case the increased alkyl chain length on the cation. We have previously used self-diffusion to evaluate ionic liquids[39–41] and their mixtures[42] as these data provide molecular level insight into the dynamics and interactions in solution. The self-diffusion coefficient (D) can be related to the local environment through the Stokes–Einstein–Sutherland equation (1):[43–45]



Scheme 1. The reaction between pyridine **1** and benzyl bromide **2** to give the corresponding salt **3**, which has been widely evaluated in ionic liquids.[26,35–38]

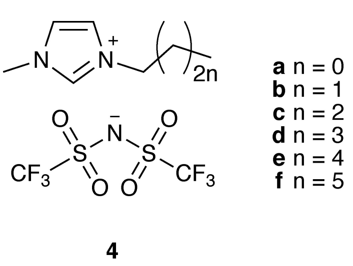


Figure 1. The homologous series of ionic liquids **4** used in this work; these salts are abbreviated as $[C_{2n+2}C_1im][N(SO_2CF_3)_2]$.

$$D = \frac{k_B T}{c \pi r \eta} \tag{1}$$

where k_B is the Boltzmann constant, T is the temperature, r is the effective hydrodynamic radius, η is the solvent viscosity, and the constant c is a measure of the boundary conditions for solvent particles at the surface of the solute. This constant nominally has two limits: where there are no interactions between the solvent and the particle ($c=4$, so called "slip" conditions), and where the particle interactions strongly with the solvent such that the solvent layer closest to the particle moves at the same velocity as the particle ($c=6$, "stick" conditions).

In the case of mixtures containing the ionic liquid **4b** and acetonitrile,[42] we showed that the boundary conditions vary from "sticky" at low proportions of salt **4b** in the solution ("ionic liquid dissolved in acetonitrile") to "slippery" at high proportions of salt **4b** in acetonitrile ("acetonitrile dissolved in ionic liquid"). Further, at higher proportions of ionic liquid **4b**, the preference for acetonitrile to be near the charged centre on the ions resulted in marked "cage" and "jump" effects, whilst self-diffusion of a series of solutes was found to vary with the nature of the heteroatom.

In this work, we extend what was considered previously to a much larger range of ionic liquids and include a constant concentration of the reagent pyridine **1**. Along with providing information as to how the solution structuring and dynamics changes with the length of the alkyl chain in the homologous series, an understanding of pyridine **1** dynamics and how it changes with the nature and proportion of the ionic liquid **4** present is anticipated to be particularly useful in understanding ionic liquid solvent effects on reaction outcomes.

Results and Discussion

Data Acquisition and Choice of Solvent Compositions

As introduced above, mixtures containing different proportions of one of the ionic liquids **4** in acetonitrile, with a constant concentration of pyridine **1** (approx. 0.5 M), were examined; the pyridine **1** concentration used matches that used in kinetics experiments.[34] The values of the χ_{IL} were increased in increments of approx. 0.1. At high proportions of the ionic liquid ($\chi_{IL} > 0.8$), either no molecular solvent was present ($\chi_{IL} = 1$) or it was not possible to have both molecular solvents present ($\chi_{IL} = 0.9$). In the latter cases, any differences as a result of different molecular solvents present will be commented upon but are found to be generally trivial.

Density and Viscosity Data

In order to analyse the diffusion data of these ionic liquid mixtures, complete density and viscosity data were determined. Along with the dependence of each of these properties on the proportion of each of the ionic liquids **4**, their temperature dependence over the range 293.15–333.15 K was evaluated. While the complete set of data is provided in the Supporting Information, several key points were clear.

For the density measurements, an increase in the amount of ionic liquid **4** in the reaction mixture resulted in increase in density of the solution; a representative plot for the data associated with ionic liquid **4c** is shown as Figure 2. This outcome is reasonable given that each of the ionic liquids **4** is more dense than acetonitrile. Further, these plots were non-linear and all of the mixtures were more dense than would be expected for an ideal solution, corresponding to negative volumes of mixing. This latter point suggests greater interactions between components of the mixture than within each component and has been seen previously in ionic liquid mixtures with molecular solvents (for a recent example, see Aparicio *et al.*[46]). Increases in the temperature of the mixtures resulted in the expected decrease in the density of the solution. Changing the length of the alkyl chain on the cation of the ionic liquid **4** resulted in a decrease in the density of the mixture and this change was more marked at the smaller carbon chain lengths. Once again, this observation is not unreasonable and is consistent with decreased interactions between components of solution as the size of the non-polar alkyl chain on the charged head group increased though there is the possibility that decreased packing efficiency may also contribute; it should be noted that on moving through the homologous series there is a distinct change in the volume of the cation. All of these data sets showed trends with no obvious discontinuities. The absolute values for the data for the butyl derivative **4b** were the same as those previously reported[42] for the equivalent mixtures not containing pyridine **1**. Likewise, in systems examined here at $\chi_{IL}=0.9$ with different molecular solvents (either acetonitrile or pyridine **1**) present, there was no measurable difference in the density values. All of these data indicate that for this physical property, the presence of pyridine **1** did not make an observable difference.

For the viscosity data, an increase in the amount of ionic liquid **4** in the reaction mixture led to a notable increase in the viscosity of the solution for all ionic liquids; a representative plot for the data associated with ionic liquid **4c** is shown as Figure 3. This observation is reasonable given that increasing the proportion of ionic liquid **4** in the mixture increases the extent of interaction between components in solution. Increases in temperature of the mixture gave the anticipated decrease in viscosity for all of the systems considered. Changing the nature of the cation of the ionic liquid **4** by varying the length of the alkyl chain resulted in increases in the viscosity with increasing alkyl chain length; such an outcome can be argued in terms of it being more dif- ficult for fluids containing ionic liquids with long alkyl chains to flow. This phenomenon has been seen previously and has been argued to be due to some combination of an increase in the van der Waals interactions between the side chains and the formation of nanodomains of the imidazolium cations with hexyl and longer substitutents.[47] All of these data sets showed trends with no discontinuities. The data for the butyl derivative **4b** were slightly different (even given the uncertainties in the data) from those previously reported for the mixtures in the absence of pyridine **1**; they were greater in the presence of pyridine **1**. Similarly, in our systems **4b-f** at χIL$=0.9$ with different molecular solvents, the viscosity was greater in mixtures containing pyridine **1** than those with acetonitrile; the slight increase indicates that the presence of pyridine **1** sufficiently changes interactions in solution to decrease the fluidity of the mixture.

Co-solvent Influences on Diffusivity in Mixtures Containing the Ionic Liquid 4b

Initially, let us consider the data for the ionic liquid **4b**, which contains a cation with a butyl side chain ($[C_4C_1im]^+$, see Supporting Information for full details). The ionic liquid **4b** is picked as the archaetypal ionic liquid, allowing both comparison with literature and a reference for the rest of the homologous series.[34] Immediately apparent is that the self-

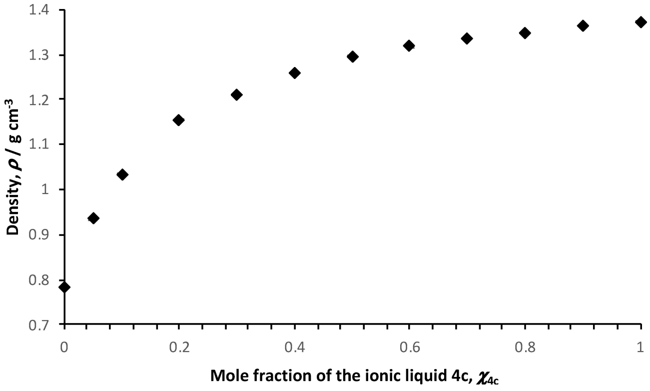


Figure 2. A plot of the density (ρ) *versus* solvent composition for mixtures containing different proportions of the ionic liquid $[C_6C_1im][N(SO_2CF_3)_2]$ **4c** and acetonitrile at 25.0 °C. Uncertainties fall within the size of the markers used.

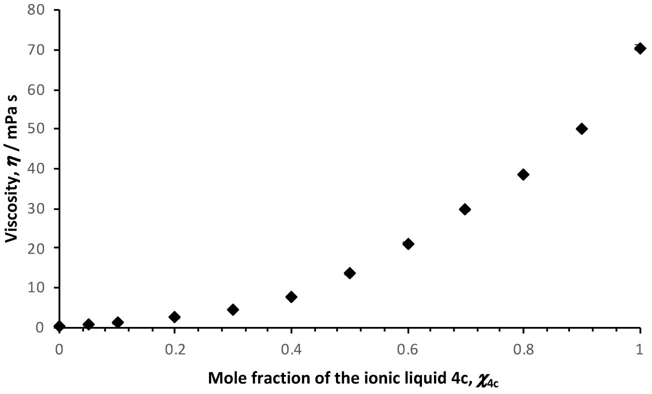


Figure 3. A plot of the density (η) *versus* solvent composition for mixtures containing different proportions of the ionic liquid $[C_6C_1im][N(SO_2CF_3)_2]$ **4c** and acetonitrile at 25.0 °C. Uncertainties fall within the size of the markers used.

diffusion coefficients for the species concerned vary over several orders of magnitudes depending on the solvent composition examined. This outcome is not surprising given that the viscosity of the systems dramatically change with proportion of ionic liquid (*vide supra*) and the self-diffusion coefficients are dependent on the viscosity of the mixture. As such, the observed trends of a continuous decrease in self-diffusion coefficient data for all four species (the cation and the anion of the ionic liquid **4b**, acetonitrile and pyridine **1**) is reasonable. The data for the diffusion coefficients for the anion, the cation and acetonitrile were generally the same as previously reported[42] for the equivalent mixtures not containing pyridine **1**, noting two points. The values of the self-diffusion data for the ionic components were, if anything slightly smaller in the case reported here, suggesting that there may be a decrease in the ability of molecules to move on addition of pyridine **1** to the reaction mixture though it is noted the effects on the diffusion coefficients here are small. It is also of interest that the uncertainties of the data are lower in this case, for all of the systems considered. Whilst this effect is due to using uncertainties from data fitting for the anion and acetonitrile data (rather than an estimate based on cation uncertainties), it is interesting that the uncertainty in the cation data (which is based on the same range of diffusion coefficients for the different signals, as previously[42]) is much smaller. Whilst particular care has been taken in ensuring appropriate variables are used in the attenuation curve and biexponential fits have been checked in all case to ensure only one environment in one species is being observed, one potential experimental source of this (real) improvement is the use of capillary tubes in the NMR analyses, minimising any issues associated with convection.[1][45,48]

To gain a better understanding of the effects of changing the solvent composition on the diffusion of the species in mixtures containing ionic liquid **4b**, we will use a methodology introduced previously, where rather than considering simply the variation in the diffusion coefficient with the mole fraction of ionic liquid in the mixture, the product of the diffusion coefficient with the viscosity of that mixture ($D\eta$) and its variation with solution composition is evaluated. Considering the Stokes–Einstein–Sutherland equation (Eq. 1), such a plot would expected to be a constant value unless the either the hydrodynamic radius of the species being considered, the boundary conditions, or both, changed with solvent composition.[2]

The normalised diffusion data (as introduced above), for each of the components in the solution are presented in Figure 4, which shows the product of $D\eta$ and how it changes with solvent composition. Immediately apparent is that the plots are not simply horizontal lines; there is an upward trend in the data for each of the components of the solution that indicates a change in solvent structure with composition. This outcome is consistent with results for the equivalent mixtures in the absence of pyridine **1**,[42] as are the absolute values presented (with minor deviations based on the differences in the self-diffusion coefficients discussed above). These data indicate that interactions in these mixtures are generally the same, with little change in substituting pyridine **1** for acetonitrile.

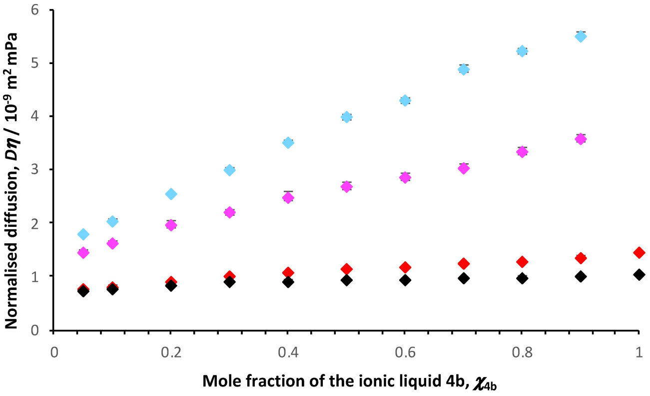


Figure 4. A plot of the normalised diffusion ($D\eta$) for acetonitrile (cyan), pyridine **1** (pink), the $[C_4C_1im]^+$ cation (red) and the $[N(SO_2CF_3)_2]^-$ anion (black) *versus* χ_{IL} of the ionic liquid **4b** in the mixture at 25.0 °C. Error bars represent the compounded uncertainty of the error associated with the NMR diffusion experiments (for D) and the deviation coefficient of the viscometer for the viscosity data; most of these fall within the size of the markers used.

Importantly, several key points can, and should, be reiterated from previous work.[42] The increase in the value of $D\eta$ with the proportion of ionic liquid in the reaction mixture is consistent with a change in the boundary con ditions (as measured by the constant c); as previously, this increase is considered more probable than a change in the hydrodynamic radius and likely arises from a decrease in the frictional forces between the ions. The trend in the acetonitrile data is similar, but the proportional change in $D\eta$ is greater than for the ions, consistent with these molecules experiencing greater lubrication than the ions. Of interest, at high proportions of ionic liquid, $\chi_{IL} = 0.9$, previously observed decreases in the $D\eta$ data for acetonitrile at $\chi_{IL} > 0.8$ were not seen. Those decreases were attributed to the formation of a a strong solvation shell of ions about acetonitrile molecules, which may be disrupted in these cases due to the presence of pyridine **1**.

While there are a number of similarities with reported data, it should be noted that the trends with changing solvent composition in the cases shown are notably smoother than previously.[42] The origin of the smoothness is not immediately clear, though the reduction in the uncertainties relatively to previously should again be noted. As such, numerous slight changes in solvent environment implied previously are not seen here. This difference may be a function of the multi-component mixture present here, with the presence of pyridine **1** meaning that the quite abrupt changes in solvent composi-

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[1] The data for the components of ionic liquid **4b** in the absence of pyridine **1** and acetonitrile (*i.e.* $\chi_{IL} = 1$) is slightly different from that reported previously by us,[42] supporting this argument. Note that the value lies within the range calculated previously in literature[49–51]

[2] An alternative analysis, involving a plot of D *vs* $1/\eta$, in principle can be used to for similar purposes, with deviation from linearity indicating changes to indicated parameters. However, quantifying the changes with solvent composition is more straightforward on the plots used here.

tion (for example, from acetonitrile dissolved in ionic liquid to ionic liquid dissolved in acetonitrile) are smoothed by the presence of a fixed amount of pyridine **1**.

With the above in mind, it worth now considering the component that is 'novel' in these mixtures, pyridine **1**. Whilst the general trend in $D\eta$ is the same as for the other components, increasing with proportion of the salt **4b** in the reaction mixture, the extent of that increase is intermediate between that observed for the acetonitrile (approx. 2.5 times). Further, the intermediate value of the normalised diffusion data is consistent with the molecular size of pyridine **1** and the resulting hydrodynamic radius.

Of interest, however, is the relative diffusion data for the two uncharged components of the mixtures as the proportion of the salt **4b** present changes (Figure 5), which decreases with increasing amount of ionic liquid **4b**, noting that the larger uncertainties as a result of compounding means that many adjacent measurements (such as the last two) have the same value. This change suggests that interactions of each of the molecular species with the components of solution change with increasing proportion of the salt **4b**. This outcome is consistent with what has been seen previously with different solutes in the butylimidazolium salt **4b**, where it was found that nitrogen containing substrates diffused at a relatively slower rate compared to equivalent oxygen containing substrates.[42] Importantly, this decreased diffusion suggests increased interactions between pyridine **1** and the other components of the mixture as the amount of ionic liquid present increases. Such increased interactions have been invoked previously to explain rate coefficient enhancement for the reaction of species **1** and **2**,[26,35–38] and so this observation introduces the potential to use these data to predict reaction outcome.

Trends in Diffusivity Across Mixtures Containing the Homologous Series of Ionic Liquids 4a,4c–f

The equivalent self-diffusion coefficients were obtained for mixtures containing each of the other alkylimidazolium salts **4a,4c–f** in order to examine the effect of changing the alkyl chain length (for full data, see Supporting Information). Immediately, the trends in diffusion coefficients for each species with the proportion of salt in the reaction mixture are the same, with a significant decrease with increasing amount of salt. Once again, this matches the observed increase in viscosity with proportion of ionic liquid in the reaction mixture.

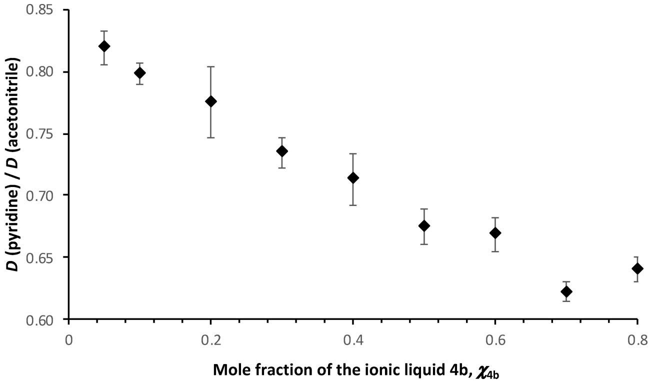

Figure 5. A plot of the ratio of *D* for pyridine **1** and acetonitrile *versus* χ_{IL} of the ionic liquid **4b** in the mixture at 25.0 °C. Uncertainties reported are compounded from the uncertainties in individual diffusion measurements.

Approaching the analysis as above, normalising the diffusion using the observed viscosity, allows comparison between systems. In the case of the ethyl derivative **4a**, the data were similar to that for the butyl derivative **4b**; particularly the normalised diffusion data for the anion of the ionic liquid were effectively the same for each mole fraction of salt, irrespective of which cation was present. The only significant change was the higher values for the cation of the salt **4a** rather than that of salt **4b**, which is entirely consistent with the size of the cation being smaller (*vide supra*). The ratio of the diffusion coefficients for the molecular solvents identified as changing in the butyl case **4b** follows the same trend for the ethyl case **4a**, noting that this ratio does not explain the rate coefficient difference seen between those two solvents for the reaction shown in Scheme 1.

The results in the hexyl derived system **4c** are consistent with the other systems. Of interest, however, is that the normalised data for both acetonitrile and pyridine **1** increased with increasing length of the alkyl chain on the salt. (The ratio of the two diffusion coefficients changed in a similar fashion to described previously, Figure 5.) This change in behaviour may be a function of the increase lubricity of the longer chain cation, effectively reducing the friction between the components of solution. Alternatively, this could be result of some degree of organisation and a greater degree of "cage"/"jump" effects.[52,53] It should be noted that this argument only applies to the molecular solvents in the mixture; the normalised anion data remains effectively unchanged (again) suggesting no change to the nature of solvation of the anion as a function of the ionic liquid cation. The cation diffusion data is notably different to previously, consistent with an increase in the size of the cation, a larger hydrodynamic radius and a decreased diffusion coefficient. Otherwise, the trend with mole fraction of ionic liquid, of increasing normalise diffusion with proportion of salt, remains the same irrespective of the nature of the salt.

It is with the octyl system **4d** that the first significant changes in the solvent behaviour can be seen, demonstrating the importance of considering the entire homologous series. Whilst certain features of the diffusion data addressed above are also relevant in this case (such as the fact that the normalised diffusion data for the anion appear independent of the cation, and there appears to be even further increased lubricity of the molecular solvents as the cation chain length increases), the biggest difference can be seen in the diffusion of the cation. Whilst in previous cases, the change in the normalised diffusion with proportion of salt was approximately linear, the distinct change in the octyl case **4d** is that there is an approximately linear change to $\chi_{IL} = 0.5$, followed by little change after that. Immediately, this suggests a degree of organisation in the system as the alkyl chain on the imidazolium cation becomes longer.

This effect becomes even more marked as the alkyl chain on the imidazolium salt is increased further in length to the decyl **4e** and dodecyl **4f** systems, with the sharpest change in diffusion of the cation in the mixture happening at low proportions of the salt. These effects suggest that there is a change in the nature of the interactions in solution as the alkyl chain length increases, with more organisation at longer chain length. Other changes that have been noted previously, including decreased normalised diffusion data for the larger cation, similar diffusion data for the anion and increased lubricity resulting in faster diffusion of the molecular solvents at higher mole fractions of salt, are consistent with before (though the large increases in normalised diffusion coefficients suggest a significant amount of "cage"/"jump" events). Likewise, the ratio the two diffusion coefficients changed in a similar fashion to as was described previously (Figure 5).

Further insights into the changes that have occurred in the ionic liquid systems investigated can be derived by comparing data at the extreme ends of the homologous series. As such, consider Figure 6, which includes the normalised diffusion data for two the components of mixtures containing ionic liquids **4a** and **4f**. Considering first the diffusion of the cation of the ionic liquids (Figure 6, top), the continual increase in the case of the ethyl derivative **4a** compared to the effective plateau after $\chi_{IL} = 0.4$ is consistent with significant structuring in the solution in the case of the longer chain $[C_{12}C_1im][N(SO_2CF_3)_2]$ **4f**. However, the anion data do not vary significantly between the two cases, showing that the interactions involving the anion are, relatively, independent of this structuring. The significant changes in the diffusion coefficients for the molecular solvents acetonitrile and pyridine **1** on changing the ionic liquid component of the mixture (Figure 6, bottom) shows that both ionic liquids effectively lubricate their motion through solution.

However, the ratio of the diffusion coefficients of the molecular species varies with the ionic liquid component of the mixture (Figure 7). Importantly, it can be seen that there are changes in the ratio of these diffusion data, particularly at low proportions of the ionic liquids. These changes suggest that the structuring in solution does affect inter- actions involving the molecular solvents (and affects them differently from one another), particularly when comparing two ionic liquids, one that would be expected to not selfassemble at low proportions in a mixture (**4a**) and one that would be expected to self-assemble at low proportions in a mixture (**4f**).

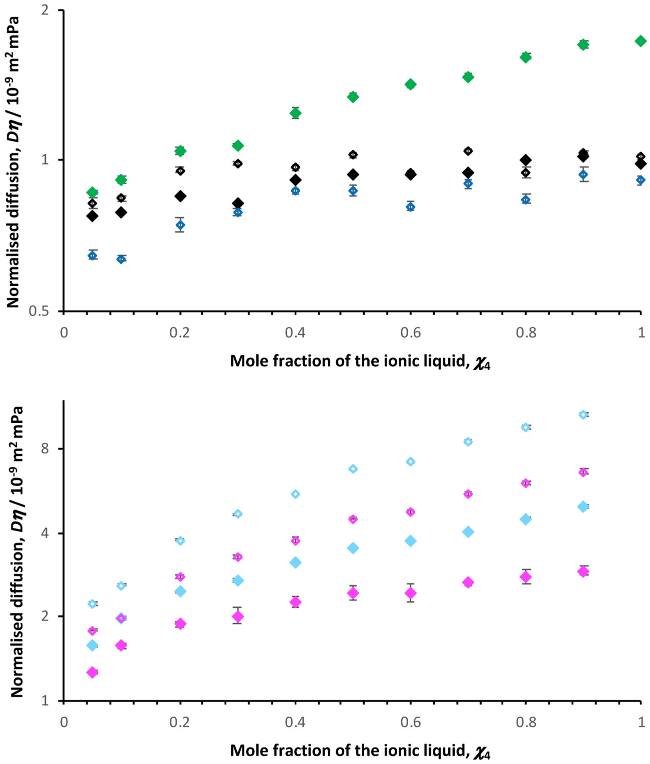

Figure 6. A plot of the normalised diffusion ($D\eta$) for the ionic liquid cation (green or blue) and the $[N(SO_2CF_3)_2]^-$ anion (black) **(top)**, and acetonitrile (cyan) and pyridine **1** (pink) **(bottom)** *versus* χ_{IL} of the ionic liquid in the mixture for mixtures containing either $[C_2C_1im][N(SO_2CF_3)_2]$ **4a** (solid diamonds) or $[C_{12}C_1im][N(SO_2CF_3)_2]$ **4f** (open diamonds) at 25.0 °C. Note the different scales on each plot. Error bars represent the compounded uncertainty of the error associated with the NMR diffusion experiments (for D) and the deviation coefficient of the viscometer for the viscosity data; most of these fall within the size of the markers used.

Discontinuities and Structuring in Solution

Having shown the extremes of the homologous series used, particularly the difference in diffusion coefficients and a rationale based on underlying organisation in solution, it of interest to consider the entire series **4a–f**. With the above changes in diffusion data with the nature of the imidazolium salt, it is useful to consider visualising how these data change and further correlate those changes to structure in solution. These are best represented using plots of the diffusion coefficient of each species in the reaction mixture and how that changes with the constituent ions of the ionic liquid. A representative example of such data is shown in Figure 8 for the homologous

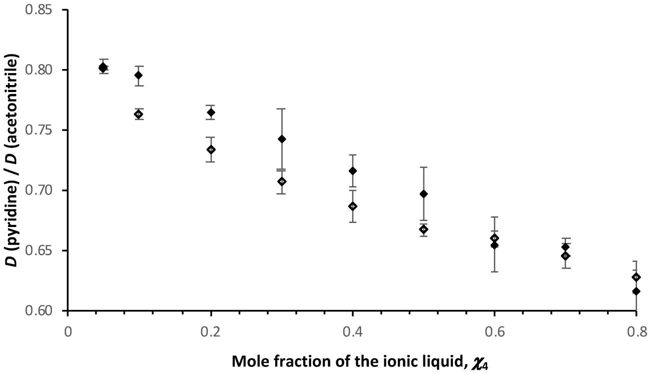

Figure 7. A plot of the ratio of D for pyridine **1** and acetonitrile *versus* χ_{IL} of the ionic liquid in the mixture for mixtures containing either $[C_2C_1im][N(SO_2CF_3)_2]$ **4a** (solid diamonds) or $[C_{12}C_1im][N(SO_2CF_3)_2]$ **4f** (open diamonds) at 25.0 °C. Uncertainties reported are compounded from the uncertainties in individual diffusion measurements.

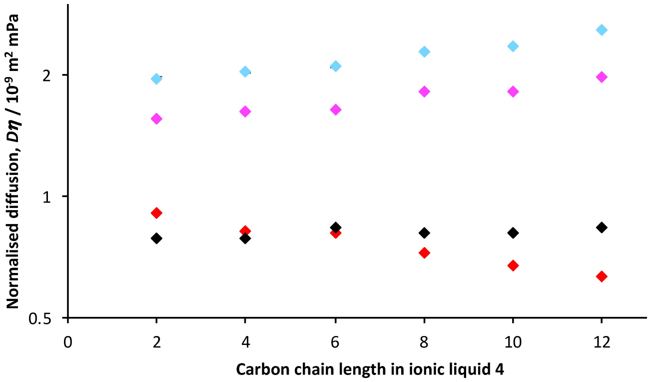

Figure 8. A plot of the normalised diffusion ($D\eta$) for acetonitrile (cyan), pyridine **1** (pink), the cation of the ionic liquid (red) and the anion of the ionic liquid (black) with changing size of the alkyl cation in the ionic liquid ($\chi_4 = 0.1$) at 25.0 °C.

series **4** at $\chi_{IL} = 0.1$. Of particular note is that there appears to be a discontinuity in the diffusion data between the hexyl **4c** and octyl **4d** ionic liquids. This change is consistent with what was seen in the kinetic data (where a step change in the activation parameters was observed between the data in salts **4c** and **4d**[34]) and what has been observed in surface structuring of related systems.[54] The data suggest that there is a change in organisation, likely as a result of structuring of the ionic liquid components. In the case of the molecular solvents, the discontinuity is seen as an increase in the normalised diffusion for the acetonitrile and the pyridine **1**, suggesting a jump in the lubricity of the mixture, consistent with these molecules being separated from (and lubricated by) the organised ionic liquid components. In contrast, this discontinuity appears as a decrease in the normalised diffusion for both ionic components of the mixture, again consistent with increased organisation of the ionic liquid components.

Conclusions

This extensive study of diffusion coefficients in mixtures containing one of a homologous series of ionic liquids has shown several key points on the dynamics and structuring in these systems. Firstly, across the entire series of ionic liquids **4a**–**4f** considered, the normalised diffusion data for each species in solution increased with proportion of salt in the reaction mixture. This change is consistent with a change in boundary conditions from a "stick" regime at low proportions of ionic liquid to a "slip" regime at high χ_{IL}. It might be said that the ionic liquid components lubricate the interactions of molecules and this lubrication is more effective for the long chain alkyl systems.

Secondly, across all of the systems **4a–f** considered, the ratio of the diffusion coefficients for the components of the molecular solvents changes with the proportion of ionic liquid present in the reaction mixture. Particularly, these changes showed that interactions in solution involving the pyridine **1** increased with the proportion of ionic liquid. Since this interaction has been identified as being responsible for the changes in rate coefficients for reactions involving pyridine **1** as a nucleophile in ionic liquids, this trend correlates with the mole fraction dependence of reaction outcome. Importantly, there is the potential to use these measurements to predict ionic liquid solvent effects.

Finally, whilst there are changes in the observed dynamics of the components of the solution with the length of the alkyl chain in ionic liquid **4** (and these are reasonable given the increased hydrophobicity of the cation), there are discontinuities on moving from the hexyl to the octyl systems. These changes are seen at all solvent compositions and indicate that there is different structuring in solution in each of the ionic liquid cases, with the critical point being that chain length drives the self-assembly. This outcome is consistent both with measures of organisation at a surface,[54] and kinetics and relaxation experiments[34] which show a step change in activation parameter data between these two alkyl chain lengths. Such a result is important as it reinforces the importance of organisation in solution and the impact that it can have on reaction outcome in these solvent mixtures.

Experimental

Materials

Pyridine **1** and acetonitrile are commercially available; the former was distilled and stored over 3 Å molecular sieves at −20 °C until use, while the latter was distilled from phosphorous pentoxide and stored over molecular sieves, under an inert nitrogen atmosphere until use.[55] Each of the ionic liquids **4** was prepared as described in the literature, through alkylation of *N*-methylimidazole with the appropriate bromoalkane followed by anion metathesis.[34] The ionic liquids were dried *in vacuo* and found to be <100 ppm water by Karl Fischer titrimetry.

Density and Viscosity Measurements

Samples containing different proportions of each of the ionic liquids **4** in mixtures with acetonitrile and pyridine **1** were prepared; details of the composition of these stock solutions can be found in the Supporting Information. Density measurements were carried out at over the range 20.0 °C to 60.0 °C using an Anton Paar DMA 4100 M density meter with an oscillating U tube. The viscosity measurements were carried out at over the range 20.0 °C to 60.0 °C using a Lovis 2000 ME microviscometer using the Rolling Ball Principle. All density and viscosity data is presented in the Supporting Information.

Self-diffusion Coefficient Measurements Using NMR Spectroscopy

NMR diffusion measurements were performed at 25.0 °C on a Bruker Avance 300 (300 MHz), a Bruker Avance 400 (400 MHz) or a Bruker Avance 600 (600 MHz) spectrometer, with a 5 mm BBFO probe and a z-axis gradient with a maximum gradient strength of $0.5\ \mathrm{T\,m^{-1}}$, calibrated *via* a D_2O standard. Sample geometry was kept constant for all diffusion measurements, using a 35 mm sample height inside a 1 mm inner-diameter capillary to mitigate any contributions from convective motions in the sample. For each nuclei examined, a recycle delay greater than five times the measured T_1 value of the slowest relaxing signal was used, with a Pulsed Gradient Stimulated Echo pulse sequence (PGSTE)[45,56,57] to determine the self-diffusion coefficient of each species. The magnetic field gradient amplitude (g) was varied from 0.5–90.5 % of the maximum gradient with a step size of 4.5 % between 0.5–45.5 %, followed by a step size of 9 % between 45.5–90.5 %. The diffusion time ($\triangle$) was varied between 0.155–0.8 s and the magnetic field gradient duration (δ) was varied between 1.0–5.0 ms, with the specific value of both $\triangle$ and δ chosen for each system to achieve a final signal attenuation exceeding 95 % of the initial signal amplitude. For the $[N(SO_2CF_3)_2]^-$ anion the self-diffusion coefficient was determined using ^{19}F NMR spectroscopy, and for all other species examined ^1H NMR spectroscopy was used. D was determined by fitting the attenuation of the stimulated echo signal to (2):[45,56,57]

$$E = \frac{S}{S_{g=0}} = \exp(-\gamma^2 g^2 \delta^2 D(\Delta - \delta/3)) \tag{2}$$

where S is the intensity of the stimulated echo signal and γ is the gyromagnetic ratio using a Levenberg-Marquardt nonlinear least squares regression with scipy.optimize.curve fit[58] (see Supporting Information). Complete tables of the diffusion data are provided in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: diffusion coefficients · ionic liquids · microscopic interactions · solution structure

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