Charge localization affects
the liquid phase structure
and transport properties

How Mixing Tetraglyme with the Ionic Liquid
1-n-hexyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide Changes Volumetric
and Transport Properties: An Experimental and
Computational Study

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Abstract

The viscosity and density of the ionic liquid (IL) 1-n-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_6mim][NTf_2]$), the molecular solvent tetraethylene glycol dimethyl ether (tetraglyme or G4) and their binary mixtures were measured experimentally as a function of temperature. The same systems were also studied using classical molecular dynamics (MD) simulations. The viscosities of the $[C_6mim][NTf_2]$ /G4 mixtures decrease with increasing G4 concentration, though not as much as an ideal mixing model would predict. Detailed analysis of the MD results reveals that G4 preferentially solvates cations, leading to a reduction in the interaction energy between cations and anions and a subsequent enhancement in anion mobility. A similar effect has been reported when glymes are mixed with salts containing alkali metal cations, with the resulting mixtures being called “solvate” ionic liquids. The simulations predict that the ionic conductivity will be maximized when the G4 mole fraction is around 10-20%. The ability of G4 to effectively solvate the cations stems from localized charges on the oxygens. The simulations predict that solvents having large localized positive charges would preferentially solvate anions, leading to enhanced cation mobility.

Keywords: ionic liquid, tetraglyme, viscosity, electrolytes, chelate effect

1 Introduction

Ionic liquids (ILs) are salts possessing many properties that make them attractive for use in a wide range of applications including chemical separation,¹⁻³ synthesis,^{4,5} solar cells,⁶ electrochemistry,^{7,8} and catalysis.⁹ These properties include a low melting point (often below room temperature), excellent thermal and electrochemical stability and negligible vapor pressure.

One of the biggest drawbacks of ILs is that they tend to be more viscous than conventional solvents, which poses problems in a number of application areas. A large amount of work has been carried out to discover combinations of cations and anions that reduce viscosity (or increase diffusivity). Some simple “design rules” have been used to search for ILs with low viscosity. It is generally thought that larger ions lead to higher viscosity, which is often the case.¹⁰ There are, however, exceptions.¹¹⁻¹³ For example, when the cation 1-n-butyl-3-methylimidazolium ($[C_4mim]$) is paired with the “planar” pyrrolide ($[Pyl]$) anion, the dynamics are significantly higher than when the $[C_4mim]$ cation is paired with the bis(trifluoromethylsulfonyl)imide ($[NTf_2]$) anion, despite the fact that $[Pyl]$ is “bigger” than $[NTf_2]$. This trend is thought to be the result of differences in the liquid phase packing structure of the two ILs.¹⁴ It has also been suggested that dynamics will increase (and viscosity decrease) if the interaction between the cation and anion is reduced. Under this “rule”, the dynamics of 1-n-butyl-2,3-dimethylimidazolium hexafluorophosphate ($[C_4mmim][PF_6]$) should be greater than that of 1-n-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$), since in the former IL a methyl group is blocking the favorable hydrogen bonding C2 ring position. The opposite trend is observed; $[C_4mmim][PF_6]$ has a higher viscosity than $[C_4mim][PF_6]$.^{15,16} This trend is thought to be related to the entropy of the liquid phase.^{17,18} When chemical reaction is involved, the transport properties of ILs become even more complicated.¹⁹

While the dynamics of ILs can be modulated by combining different cations and anions, or even by mixing different ILs,^{20,21} an easier way to obtain a lower viscosity is to simply mix ILs with low viscosity additives such as molecular solvents. It has been found that the

addition of a small amount of a low viscosity solvent can have a large effect on the mixture viscosity.^{22–28} The amount the viscosity decreases is unpredictable and depends on the nature of both the solvent and the ions composing the IL; a molecular solvent with a lower viscosity does not always decrease the viscosity more than a solvent with higher viscosity.²⁶ There is clearly a need for a better understanding of how and why molecular solvents change the dynamics of IL solutions.

An obvious disadvantage of mixing molecular solvents with ILs is that the extremely low volatility of the IL is compromised by the finite vapor pressure of the diluent. One strategy to overcome this is to mix ILs with molecular solvents that are themselves of very low volatility. One such class of compounds are the glymes, which are oligoethers having a $\text{CH}_3\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{CH}_3$ structure. In addition to having low volatility, glymes are effective at dissociating salts because of the electron donating nature of their ether oxygen groups. They also tend to have high thermal and electrochemical stability, which has led many groups to investigate mixing glymes with alkali metal salts (most commonly $\text{Li}^+ [\text{NTf}_2]$) for use as electrolytes in batteries.^{29–36} The alkali metal cation tends to coordinate with the oxygen atoms of the glyme, which can significantly lower the melting point of the salt. Such systems usually retain the attractive properties of pure ILs but the transport properties are improved. They are considered a new class of ILs and have been termed “solvate ILs”.³⁷ Tetraethylene glycol dimethyl ether (tetraglyme or G4) is a particularly promising glyme. It has a vapor pressure of only 0.132 kPa at 100° C³⁸ and readily dissolves many salts.

While there are many studies devoted to the properties of Li-based solvate ILs, much less work has been done investigating the properties of mixtures containing glymes and more conventional ionic liquids. Gurkan et al.³⁹ diluted three different phosphonium-based ILs with G4 in order to reduce the viscosity enough to measure CO_2 reaction rate constants for amine-functionalized ILs. They measured the mixture viscosities as a function of temperature and found that the addition of G4 significantly lowered the viscosity. We are unaware of any studies by other research groups that have investigated the properties of conventional imidazolium-based ILs mixed with glymes. In the current work, the density and viscosity

of the IL 1-n-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_6mim][NTf_2]$) and its mixtures with tetraglyme were measured at different temperatures and concentrations. Molecular dynamics (MD) simulations were also carried out on the mixtures in order to compute the density, self-diffusivity, viscosity, ideal ionic conductivity and liquid structure. The simulations provide molecular-level insight into the factors responsible for the trends observed in the transport properties as a function of G4 concentration.

2 Experimental Methods

The ionic liquid $[C_6mim][NTf_2]$ was synthesized in our lab from the starting material of methylimidazole. The methylimidazole (99% purity Sigma Aldrich) was further purified by distillation with KOH and boiling chips. After distillation, hexylbromide was added dropwise to the methylimidazole at 65 °C under a nitrogen atmosphere with a condenser to prevent any evaporation. The reaction was allowed to proceed for 48 hours. After the reaction was complete, the 1-n-hexyl-3-methylimidazolium bromide was diluted in water and mixed with $LiNTf_2$ where an ion exchange took place to form LiBr and $[C_6mim][NTf_2]$. The $[C_6mim][Br]$ was washed with ethyl acetate to remove excess hexylbromide and $[C_6mim][NTf_2]$ was washed with water to remove excess LiBr. The final sample was dried under vacuum (< 15 mbar) at 60 °C for at least 48 hours to remove any residual water before use. The purity of $[C_6mim][NTf_2]$ was estimated to be 99%. The G4 was purchased from Sigma Aldrich (99% purity) and used without further purification.

The IL/G4 mixtures were prepared in a controlled nitrogen atmosphere glove box to prevent any absorption of water during the sample preparation. The water contents in all IL/G4 mixtures were found to be less than 500 ppm using a Karl Fischer coulometric titration procedure. Note that the water contents may increase after the density and viscosity measurements. The densities of the mixtures were determined using a DMA 4500 Anton Parr densitometer between 22-60 °C. The densitometer requires about 1.5 mL of sample and reports the density to an accuracy of 1×10^{-3} g/cm³.

IL, G4, and IL/G4 mixture viscosities were measured with an Anton Parr AMVn falling ball viscometer. The viscosities were measured in either a 1.6 mm capillary that has a viscosity range of 0.3 - 10 cP and requires 0.4 mL of sample or a 1.8 mm capillary that has a viscosity range of 2.5 - 70 cP requiring 0.6 mL of sample. The 1.6 mm and 1.8 mm capillaries were calibrated using the S3 Cannon oil certified standard (purchased from Cannon Instrument Company) and the APN26 oil standard (provided by Anton Paar) respectively at angles between 20 and 70 degrees and temperatures between 20 and 60 °C. The angle is the angle at which the arm rotates to, allowing the ball to fall. The smaller the angle, the slower the ball will fall. The calibration constant was determined using the following equation:

$$K_1 = \frac{\eta_{standard}}{t_1(\rho_{steelball} - \rho_{standard})} \quad (1)$$

where t_1 is the time it takes for the ball to roll, the density of the steel ball is $\rho_{steelball} = 7.95 \text{ g/cm}^3$ and the density and viscosity of the standards are known. The 1.6 mm capillary calibration constant was found for every angle. The capillary calibration was verified with multiple low viscosity solvents including H₂O, dodecane, and tetradecane, while the 1.8 mm capillary calibration was verified with the S6 Cannon oil certified solvent and diglycolamine (DGA). The viscosities of the calibration solvents did not deviate more than 3% from literature values. It was found that the ideal ball fall time should be greater than 20 seconds. If the ball falls too fast (< 20 seconds fall time) the uncertainty in the experimental values increase. Therefore, for each sample the angle was modified to assure that the fall time was at least 30 seconds. For each sample, the measurements were repeated three times and the temperature was controlled to ± 0.1 °C with an equipped Pt100 probe. Equation 1 was rearranged to determine the unknown kinematic viscosity once the calibration constant was known. The fluid density was then used to determine the dynamic viscosity (η) in cP.

Measurements of ionic conductivities were obtained in the temperature range of 10 to 80 °C using an electrochemical impedance spectroscopy (EIS) system composed of a Solatron SI 1260 impedance/gain-phase analyzer and a Solatron 1287 electrochemical interface. The uncertainty in the measurements is approximately $\pm 3\%$. The mixtures were kept in a Binder

refrigerated incubator KB53 (E3.1) and allowed more than 45 minutes at each temperature to reach equilibrium.

3 Simulation Procedure

Equilibrium molecular dynamics (MD) simulations were carried out using the package LAMMPS.⁴⁰ Systems consisting of pure $[C_6mim][NTf_2]$, pure G4 as well as mixtures with G4 mole fractions of 10%, 20%, 30%, 40% and 50% were considered. For each system, the simulation box was built up by putting a total of 300 molecules (sum of ion pairs and G4 molecules) randomly in a cubic box using the package Packmol.^{41,42} Following a quick structure minimization, the simulation boxes were equilibrated for 2 ns in the isothermal-isobaric (NPT) ensemble at a pressure of one atmosphere in order to determine density. Production runs were then generated in the canonical (NVT) ensemble at the equilibrium density. Production runs were 20 ns long at each temperature. These trajectories were used to compute self-diffusion coefficients, ideal ionic conductivities and the liquid structure. The Nosé-Hoover thermostat⁴³ and the extended Lagrangian approach⁴⁴ were applied to control the temperature and pressure. Periodic boundary conditions were applied in all simulations and a time step of 1 fs was used.

The united atom force field developed previously by Zhong and co-workers was used to describe $[C_6mim][NTf_2]$.⁴⁵ For G4, intermolecular parameters as well as intramolecular angle and dihedral parameters were taken from the TraPPE force field.⁴⁶ TraPPE is a rigid bond model, so to be consistent with the fully flexible $[C_6mim][NTf_2]$, bond stretching parameters from the general Amber force field (GAFF)⁴⁷ were adopted for G4. To account for the effect of charge transfer and polarizability in the condensed phase, the charges of IL atoms were scaled uniformly by a factor of 0.8, which was found previously to yield more reliable dynamic properties for similar ILs.⁴⁸ The point charges of G4 atoms were not scaled. Long-range electrostatic interactions were calculated using the particle-particle particle-mesh (PPPM) method.⁴⁹

The shear viscosity of each system was calculated using the time-decomposition method.⁵⁰ For each system, 50 independent 10 ns NVT trajectories were generated. For each trajectory, the stress tensor was saved every 5 fs. The first 1 ns of each trajectory was considered equilibration and discarded. The remaining 9 ns of each trajectory was used to calculate the viscosity from the time integral of the stress tensor autocorrelation function following the Green-Kubo relation

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \tau_{\alpha\beta}(t) \cdot \tau_{\alpha\beta}(0) \rangle dt \quad (2)$$

where V is the system volume, k_B is the Boltzmann constant, and $\tau_{\alpha\beta}$ denotes the $\alpha\beta$ -component of the stress tensor. The average running integral over 50 trajectories was fit to a double exponential function of the following form

$$\eta(t) = A\alpha\tau_1(1 - e^{-t/\tau_1}) + A(1 - \alpha)\tau_2(1 - e^{-t/\tau_2}) \quad (3)$$

with a weighting function derived from the corresponding time-dependent standard deviation of the running integrals

$$\sigma(t) = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (\eta(t)_i - \langle \eta(t) \rangle)^2} \quad (4)$$

where N is the number of independent trajectories.⁵⁰ In Eq. 3, A , α , τ_1 and τ_2 are fitting parameters. The value at the long time limit of the fitting results was taken as the viscosity of each system.

4 Results and Discussion

4.1 Density and Thermal Expansion Coefficient

The densities of pure $[C_6mim][NTf_2]$, pure G4 and the mixtures of the two with G4 mole fraction of 10%, 20%, 30% and 50% were measured between 298 and 353 K. The results are shown in Figure 1 as lines; numerical data are provided in the Supplementary Material. For pure $[C_6mim][NTf_2]$ and G4, the results agree very well with previous experiments.^{51–56} As expected, as the mole fraction of G4 increases, the density of the mixture decreases. The

Figure 1: The density of $[C_6mim][NTf_2]/G4$ mixture as a function of temperature from experiments (solid lines) and MD simulations (symbols). The deviation in the calculated density from experiments is less than 1% for pure IL and all mixtures. The density of pure G4 has slightly larger deviation, but is still less than 2.5%.

densities calculated from MD simulations over the same temperature range are also shown in Figure 1 as symbols. The calculated densities are consistently larger than the experimental densities, but by only about 1% for most systems. The largest deviations are for pure G4, but still the differences are less than 2.5%. The calculated densities follow the experimental trend as functions of temperature and concentration very well. Figure 2 shows the experimental and computed coefficient of thermal expansion as a function of G4 concentration. For the experiments, the expansivity was computed from the slope of the density versus temperature data from 298 to 353 K. A similar procedure was used to compute the simulated expansivity of the pure IL and the mixtures, except the full simulation temperature range (298 to 500 K) was used to improve statistics. For G4, however, since the density of G4 varies non-linearly with temperature over this range, we only used the simulation results from 298 to 353 K. All numerical results are provided in the Supplementary Material. The agreement between simulations and experimental measurements is good, suggesting that the force field can at least capture volumetric properties reasonably well.

Figure 2: The calculated coefficients of thermal expansion of the $[C_6mim][NTf_2]/G4$ mixtures as a function of G4 concentration. For experiments, the expansivity was computed using the density data from 298 to 353 K. The expansivity from MD simulation was computed using the density data from 298 to 500 K for pure IL and IL/G4 mixtures; for pure G4, since the density varies non-linearly at high temperatures, the data from 298 to 350 K were used.

4.2 Viscosity and Liquid Structure

For the pure compounds and mixtures, the viscosities between 298 and 350 K were measured experimentally. The results as a function of inverse temperature are shown in Figure 3, with numerical values given in the Supplementary Material. For pure $[C_6mim][NTf_2]$ and G4, the results agree with previous measurements very well.^{51–57} As shown in the figure, the shear viscosities in each system decrease with increasing temperature and increasing G4 concentration. The data were fit to the Vogel-Tamman-Fulcher (VTF) equation⁵⁸

$$\eta = A \exp(B/(T - T_0)) \quad (5)$$

where A , B and T_0 are fitting parameters. The fitting results are summarized in Table 1. The T_0 parameter is approximately equal to the glass transition temperature (T_g) for fragile liquids, and is lower than T_g for strong liquids.⁵⁹ In the current work, T_0 was found to be between 160 and 184 K, similar to values reported previously for other ILs^{54, 60–62} and close to the experimentally measured T_g .⁶³

Table 1: The parameters fit to the VTF equation (Eq. 5) for the viscosities from experiments (Exp.) and MD simulations (Calc.)

G4 fraction (%)	Exp.			Calc.		
	A (cP)	B (K)	T_0 (K)	A (cP)	B (K)	T_0 (K)
0	0.302	620.7	183.9	0.200	590.0	221.0
10	0.308	593.9	184.0	0.155	645.6	213.4
20	0.124	793.6	160.0	0.093	830.3	192.4
30	0.130	763.0	163.4	0.106	773.3	192.2
40	-	-	-	0.089	796.5	190.7
50	0.120	702.5	164.2	0.089	739.8	199.7
100	0.170	356.3	178.5	0.029	772.2	191.3

Due to the fact that the dynamics of these systems are sluggish at low temperature and thus sampling is difficult, MD simulations were carried out at higher temperatures between

Figure 3: The viscosity of $[C_6mim][NTf_2]/G4$ mixture as a function of inverse temperature from experiments (solid lines) and MD simulations (dashed lines). Lines are added to guide the eye.

350 and 500 K in 25 K intervals. Viscosities were calculated at each temperature using the time-decomposition method.⁵⁰ The results are included in Figure 3 and extrapolation enables a comparison with the experimental results at lower temperatures. As shown in the figure, the calculations overestimate the viscosities, but capture the experimental trend as a function of both temperature and G4 composition. It is well known that the use of fixed charge models tends to lead to an underestimation of the dynamics of ionic liquids,^{64,65} though trends in dynamics are usually accurate. The current results are consistent with this finding. The calculated viscosities were fit to the VTF equation and the fitting parameters are provided in Table 1. As can be seen in the table, except for pure G4, the B parameters derived from the calculated viscosities agree with those from the experimental viscosities very well, indicating that the temperature dependence of the viscosity is captured by the simulations. For pure G4, the experimental B parameter is less than half the simulated B parameter, suggesting that the calculations overestimate the viscosity change as a function of temperature for pure G4, as can be seen in Figure 3. The T_0 parameters from the fitting of the calculated viscosities have values between 190 and 220K, close to those derived from experimental viscosities with a systematic overestimation of around 30 K.

The viscosity results of each system from both experiments and MD simulation are also plotted as a function of G4 mole fraction in Figure 4. For the results at 350 K, the calculated viscosities from MD simulations are systematically higher than those from experiments by a factor of around two. Similar behavior is expected for the results at other temperatures as well. As shown in the plot, the trend in viscosity as a function of G4 concentration observed in the experiments is successfully captured in the simulations; the viscosity of the liquid decreases significantly when G4 is added to the IL.

Based on both the experimental and the calculated viscosities, the ratio between the actual and ideal viscosities of the mixture was calculated using the empirical Grunberg-Nissan equation^{28,66}

$$\ln(\eta/\eta^{id}) = \ln \eta - \sum x_i \ln \eta_i \quad (6)$$

where η is the viscosity of the mixture, η_i is the viscosity of the pure component i , and x_i is the mole fraction of component i in the mixture. The results are shown in Figure 5. As shown in the figure, all the $\ln(\eta/\eta^{id})$ results have positive values between 0 - 0.45 in the studied range of composition, suggesting that the viscosities in the mixtures are higher than the prediction from an ideal mixing model. The experimental results show an almost ideal mixing with 20% G4 which is not captured in the simulated viscosities. Other than that, both experimental and simulation results behave similarly and show increased deviation from an ideal mixing model with increasing G4 concentration.

It is clear that adding low viscosity diluents to a high viscosity IL is an effective strategy for lowering the mixture viscosity, but it is difficult to predict how much the viscosity will be lowered by a given type of diluent and at a particular concentration. It is therefore important to understand the mechanism by which the viscosity is reduced. Lopes and co-workers have suggested that the viscosity of IL diluted by molecular solvents is related to two factors.²⁸ The first is that diluents can increase the free volume of the mixture, thereby reducing viscosity. The second is that diluents solvate the ions, which reduces the electrostatic interactions between the ions and speeds the dynamics. Lopes and co-workers found that the free volume change, as determined by the excess volume of mixing, tends to

Figure 4: The viscosity of $[C_6mim][NTf_2]/G4$ mixture as a function of G4 mole fraction from experiments (upper panel) and MD simulations (lower panel). The uncertainties in the viscosities are smaller than the symbols. Note the different scale in Y-axis. The same trend that the viscosity decreases with increasing G4 concentration fraction was observed by both experiments and simulation. At 350 K, the calculated viscosities are about twice as high as the corresponding experimental results. Lines are added to guide the eye.

Figure 5: The calculated ratio between the actual and ideal viscosities for $[C_6mim][NTf_2]/G4$ mixtures using Eq. 6. The uncertainties in the ratio for both experimental and computational results were estimated to be around ± 0.03 . All values are positive, suggesting that the mixture viscosity is higher than that expected for ideal mixing. Experimental and simulation results show a similar trend that the deviation from ideal mixing increases with increasing G4 concentration.

be very small and thus has a minor effect on the viscosity. Our results confirm this finding; we observed very small excess volumes of mixing, which suggests that free volume effects are minimal. On the other hand, we do observe that G4 solvates the ions and reduces the interactions. This can be seen by the center of mass radial distribution functions (RDFs), which are shown in Figure 6 at 350 K. As the concentration of G4 increases, the peak positions in the cation-anion and anion-anion RDFs shift slightly to longer distances and the peak heights decrease. This suggests that G4 weakens the interaction between the cation and anion.

The peak positions in the cation-cation RDFs also shift to longer distances and the shift is more significant than those in cation-anion and anion-anion RDFs. Unlike the cation-anion and anion-anion RDFs, the peak heights in the cation-cation RDFs actually increase with increasing concentration of G4, suggesting that the G4 is changing the local environment around the cations and anions. On the other hand, with more G4 added to the mixture, the peak height of all RDFs related to G4 molecules increase, accompanied by a slight shift of the peak position to shorter distances. This indicates that the interaction between G4 and all species in the liquid gets stronger as the G4 concentration increases.

Coordination numbers in the first solvation shell of each species were calculated from the RDFs. The first solvation shell was defined as the location of the minimum between the first and second maximum in the corresponding RDF. The results are shown in Figure 7. As expected, the coordination numbers between cation-anion, anion-anion, G4-cation and G4-anion all decrease with increasing G4 concentration. This is essentially a dilution effect; more cations and anions have G4 in their first solvation shell as G4 concentrations increase, which is why the cation-G4 and anion-G4 coordination numbers increase with increasing G4 concentration. It is interesting that the number of cations in the first solvation shell of other cations increases when more G4 molecules are available in the mixture. This is due to the fact that the distance that defines the first solvation shell for cation-cation interactions is large and increases from 13.5 Å in pure IL to 17.2 Å in the mixture with G4 mole fraction of 50%. At longer distances there are simply more cations around that can be included

Figure 6: The center of mass radial distribution functions (RDFs) from MD simulations at 350 K. The cation-G4 RDF shows a peak at a shorter distance than that in cation-anion RDF, suggesting stronger cation-G4 interaction than that of cation-anion due to the chelate effect of G4 molecules. Results at other temperatures show similar behavior.

in the first solvation shell, but at such large distances the cations will not have significant association energies.

The first peak positions in the cation-G4 RDFs are at much shorter distances than those in the cation-anion RDFs, whereas the first peak positions of the anion-G4 RDFs are at longer distances than the first peak positions of cation-anion RDFs. This suggests that G4 preferentially solvates cations. This behavior can be seen most clearly from the spatial distribution functions (SDFs) in Figure 8, which show the most probable locations of anions and G4 molecules about a central cation. Consider first the results in Figure 8 for 10% G4. There are three preferred sites for the anions near the C2, C4 and C5 carbon atoms of the imidazolium ring. This is typical behavior observed for pure ILs.^{18,67} Consistent with the RDFs, G4 molecules localize in two areas “inside” the anions: near the C2 position and between the C4 and C5 positions. As the G4 concentration increases, the anion distribution around the C5 position stays about the same, but the distributions around C2 and C4 becomes smaller, with the C4 location finally vanishing at a G4 mole fraction of 50%. Figure 9 shows the distribution of cations and G4 molecules about a central anion. The three distinct regions “above” the anion are areas of largest negative charge. Cations locate closest to the anion in these regions, but G4 molecules (which are solvating the cations) locate adjacent to these regions. “Below” the anion is the area with the smallest negative charge, and this is where additional G4 molecules are found. Taken together, these results show that as G4 concentration increases, G4 more effectively solvates the cation and decreases the interaction between the cation and anion.

Similar behavior has been observed when glymes are added to ILs containing metal ions.^{29,30,34–36,68} In these studies, glyme molecules were found to chelate metal ions (usually Li^+ or Mg^{2+}) via their oxygen atoms, thereby breaking the close association between the metal cations and anions. This chelation effect was believed to be one of the reasons that these “solvate ILs” have better battery performance than other electrolyte systems.^{31,36,68} This is exactly what is observed in Figure 7, where the addition of G4 decrease the coordination number between cations and anions significantly. The change in the coordination

Figure 7: The calculated coordination numbers in the first solvation shell using the RDFs shown in Figure 6. The first solvation shell is defined by the minimum between the first and second maximum in the corresponding RDF. Both “A-B” (B surrounding A) and “B-A” coordination numbers are provided when they are different.

Figure 8: The calculated spatial distribution functions for anions and G4 about a central cation at 350 K. Iso-density surfaces are drawn at 6 times the bulk density. Consistent with the RDF results shown in Figure 6, the distribution of the G4 molecules is closer to the central cation than the anions for all mixtures. Results at other temperatures show similar behavior.

Figure 9: The calculated spatial distribution functions for cations and G4 about a central anion at 350 K. Iso-density surfaces are drawn at 2.5 times the bulk density. Consistent with the RDF results shown in Figure 6, the distribution of the cations is closer to the central anions than the G4 molecules for all mixtures.

structure in the liquid phase and the associated interaction between the cations and G4 molecules are likely to be the main reason that the viscosity decreases with increasing concentration of G4.

4.3 Self-Diffusivity and Ionic Conductivity

The ideal ionic conductivities and self-diffusion coefficients of the IL/G4 systems were also computed from the MD simulations. The ideal ionic conductivities were computed using the Nernst-Einstein (NE) equation

$$\sigma_{NE} = \frac{N_{pair}}{Vk_B T} (q_+^2 D_+ + q_-^2 D_-) \quad (7)$$

where σ_{NE} is the ideal ionic conductivity, N_{pair} is the number of ion pairs in a given volume V , q_+ and q_- are the total charges on the cation and anion, and D_+ and D_- are the self-diffusion coefficients of the cation and anion, respectively. The self-diffusion coefficients D_+ and D_- , as well as the self-diffusion coefficient of G4, were computed from the mean-square displacements (MSDs) using the Einstein relation

$$D_s = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle (r_i(t) - r_i(0))^2 \rangle \quad (8)$$

where $r_i(t)$ is the position of the center of mass of species i at time t and the angle brackets indicate an average over all species. The computed self-diffusion coefficients at 350 and 500 K are shown in Figure 10. The self-diffusion coefficients tend to be higher for systems with lower viscosity, consistent with the empirical Stokes-Einstein relation. The calculated ideal ionic conductivities are shown in Figure 11.

At 350 K, the self-diffusion coefficients of the anions and G4 molecules increase with increasing concentration of G4, whereas the cation self-diffusivity remains more or less constant. There is a crossover in which the cations diffuse faster than the anions in the pure IL, but at 50% G4 the anions actually diffuse faster than the cations. The same phenomenon is observed at 500 K, although here the self-diffusivities of all species increase with increasing G4 concentration. In addition, the self-diffusivities are all much larger at 500 K. These results

Figure 10: The calculated self-diffusion coefficients using the Einstein equation (Eq. 8) from MD simulations at 350 K (upper panel) and 500 K (lower panel). The uncertainties in the results are about the size of the symbol or smaller.

are consistent with the structural results discussed in the previous section. G4 preferentially solvates the cations, which weakens the association of the anions with the cations, thereby enhancing the mobility of the anions. The cation mobility is somewhat more hindered than anion mobility because of the formation of these G4-cation chelation complexes.

As suggested in Eq 7, as the ion self-diffusivity increases, the ionic conductivity of the mixture increases. At the same time, the ionic conductivity will go down as the concentration of the charge carrying species is reduced through the addition of G4. There is a competition between these two effects, which leads to a maximum in the ideal ionic conductivity at intermediate G4 concentrations, as shown in Figure 11. At 350 K, this maximum appears to occur at around 20% G4, though the ideal ionic conductivity is fairly flat at low G4 concentration. As the concentration of G4 increases further, the ideal ionic conductivity drops rapidly. Similar behavior was observed for the calculated ideal ionic conductivities at 500 K except that the maximum ideal ionic conductivity is more clearly seen at a G4 mole fraction of 10%. It is worth noting that the ideal ionic conductivity calculated from the NE relation assumes no correlation between the cations and anions.^{69–71} This is technically only true for very dilute electrolytes; the actual conductivity in liquids with high IL concentrations will be lower than the ideal ionic conductivity. When the G4 fraction is increased in the liquid, however, the assumption that the cations and anions are not correlated becomes better. Therefore, the maximum in the actual ionic conductivity should appear at higher G4 fraction. The actual ionic conductivities measured experimentally are shown in Figure 12. The maximum is observed at around 40% G4, consistent with the above discussion. With the same G4 fraction, the experimentally measured actual ionic conductivity was found to be higher than the calculated ideal ionic conductivity due to the slower dynamics in the simulation, consistent with the viscosity results (see Figure 4).

4.4 Distribution of Mobilities from the van Hove Function

In the above discussion, the calculated MSD is the average distance that a component moves within a time t . In order to have a better understanding of the dynamic properties, the

Figure 11: The calculated ideal ionic conductivity as a function of G4 mole fraction at 350 K (upper panel) and 500 K (lower panel) using the Nernst-Einstein relation (Eq. 7). A maximum value was observed at low G4 concentrations at both temperatures as a result of the competition between enhanced ionic diffusivity and ion dilution with increasing concentration of G4. The uncertainty was calculated for a mixture of 30% G4 based on three independent NVT trajectories at each temperature. The uncertainties at other concentrations were estimated based on the same ratio as that in 30% G4 mixture. Due to the different number of ions in the mixture, the uncertainty in the low G4 concentration mixtures (therefore high IL concentration) is likely lower than that shown in the plot and that in the high G4 concentration mixtures is likely higher.

Figure 12: The experimental ionic conductivity as a function of G4 mole fraction at 350 K. A maximum value was observed at higher G4 concentrations than that seen in the calculated ideal ionic conductivity (see Figure 11). The uncertainty was estimated to be less than 3%. The original data at multiple temperatures are provided in the Supplemental Material.

distribution of the displacements was studied by computing the self-part of the van Hove function^{72–74}

$$G_s(r, t) = \frac{1}{N} \sum_{i=1}^N \langle \delta(r - |\vec{r}_i(t) - \vec{r}_i(0)|) \rangle \quad (9)$$

where $4\pi r^2 G_s(r, t)$ is the probability that a particle has moved a distance r within the time t . Normalized van Hove functions ($4\pi r^2 G_s(r, t)$) at 350 and 500 K are shown in Figure 13. In each plot, the peak position moves to the right as time increases, consistent with diffusive motion. All the van Hove functions shown in the figure have a single peak, suggesting that the diffusion is a continuous process in these systems. At 350 K, the van Hove functions of the cations in each mixture almost overlap each other at 30 ps. At 1 ns, the curves with different G4 concentrations show some differences, but are still very similar. As noted above, the G4 molecules prefer to coordinate with cations in the liquid. Therefore, even though the addition of G4 reduces cation-anion association, because of the chelation effect of the G4, the diffusivity of the cations remains about the same and the van Hove functions are essentially independent of the G4 concentration.

Figure 13: The self-part of the van Hove function at different times based on MD simulations at 350 K (left column) and 500 K (right column). Note the different time scale at different temperatures.

A slightly larger dependence on the mixture composition was observed in the G4 van Hove functions. However, except for the mixture with 50% G4, the G4 curves are very similar to one another. At relatively high mole fraction (50%), some of the G4 molecules are free of cation association³⁴ so that the van Hove function starts to deviate from the low concentration curves.

The van Hove functions for the anions, on the other hand, show clear dependence on the G4 mole fraction. As the concentration of G4 increases, the van Hove functions become broader, suggesting that the addition of G4 causes a larger distribution of anion displacements. In other words, at high G4 concentrations, some anions move much faster than others. This is particularly clear at 300 ps and 1 ns. As shown above, this is due to the fact that G4 solvates the cations, thereby “freeing” some of the anions from their cation pair and enabling greater mobility since they are not bound strongly to G4. All These results are consistent with the self-diffusion coefficients shown in Figure 10.

At 500 K, all species in the liquid move faster but the van Hove functions show similar behavior as those at 350 K. Due to the enhanced kinetic energy, it is easier for each species to overcome intermolecular interactions and move relatively freely. As a result, the van Hove functions of all species show stronger G4 mole fraction dependence. However, the dependence on G4 concentration for the cations is still weaker than that of the G4 molecules, and the anions have the strongest dependence on G4 concentration.

4.5 Effect of Charge Localization

It is clear from the above discussion that the chelation effect of G4 plays an important role in governing the liquid structure and transport properties of IL/G4 mixtures. To get a better understanding of this effect, a computer experiment was carried out. In this experiment, a model G4 molecule was created in which the charges on the G4 atoms switch their sign from the original model so that the oxygen sites have positive charges and the carbon sites have negative charges. The charge magnitudes were kept the same. This reversed charge model will be referred to as -G4. MD simulations were carried out for the mixture of

Table 2: Comparison of the calculated self-diffusion coefficients ($10^{-12}m^2/s$) using Eq. 8 for mixtures with G4 or -G4 molar fraction of 30% at 350 K.

	D_+	D_-	D_{G4}
G4	74.52	74.19	64.75
-G4	86.48	58.50	65.85

[*C₆mim*][*NTf₂*] IL and -G4 molecules with a -G4 mole fraction of 30% at 350 K following the same procedures described above. The RDFs were calculated and compared to those of the original G4 mixtures in Figure 14. Most RDFs are similar and independent of the charge distribution on G4. However, the RDFs involving ions and the -G4 or G4 model show clear differences. Comparing to the original G4 case, the first peak in the cation-(-G4) RDF shifts to a longer distance and the anion-(-G4) first peak shifts to a shorter distance, suggesting that the -G4 molecules coordinate with the anion more strongly than with the cation. This is opposite to the behavior in the original G4 mixture. The preferred interaction between -G4 and the anions can also be seen in the SDFs shown in Figure 15. The self-diffusion coefficients were also calculated for the species in the -G4 mixture. The results are compared with those of the corresponding G4 mixture in Table 2. As expected, comparing to G4 model, the cations diffuse faster and anions diffuse slower in the -G4 mixture. The G4 self-diffusion coefficient stays about the same. These observations are consistent with the liquid structure in the mixtures.

The united atom model for G4 used in the current work does not have hydrogen atoms and so is comprised of only carbon and oxygen sites.⁴⁶ In the model, all the carbon sites have the same positive charge of 0.25 e and all the oxygen sites have the same negative charge of -0.50 e. The number of carbon atoms is double that of the oxygen atoms in G4 (and all glyme molecules), so the whole molecule is charge neutral. The comparison of results using G4 and -G4 models shows that the sign of charges with the largest magnitude dominates the interaction in the liquid phase. In other words, the more localized charges in the molecular

Figure 14: The calculated center of mass radial distribution functions (RDFs) from MD simulations at 350 K for the mixture with -G4 mole fraction of 30%. The sign on the atomic partial charges for -G4 are the opposite of those for G4. The results for the corresponding G4 mixture are included for comparison. The peak position in the cation-G4 and anion-G4 RDFs changed, suggesting the different interaction in the two model systems due to the different charge localization.

Figure 15: The calculated center of mass spatial distribution functions (SDFs) from MD simulations at 350 K for the mixture with -G4 mole fraction of 30% (red: counterion; blue: G4). As opposed to the results in Figures 8 and 9, the anion distribution is closer to the central cation than that of the -G4 molecules whereas the -G4 distribution is closer to the central anion than that of the cations, suggesting the different interaction in the two model systems due to the different charge localization.

solvent play a larger role in the chelate effect, even for a solvent that is overall charge neutral. This suggests that in order to preferentially solvate anions in order to enhance the mobility of cations, one should use molecular solvents that have a small number of large positive groups. For this reason, glymes may not be the best solvents for use when large cation mobility (e.g. Li^+) is required.

5 Concluding Remarks

ILs have drawn extensive attention during the past decades due to their promising potential in various application areas, including electrolytes for energy storage. Unfortunately, their relatively high viscosity compared to many molecular solvents has been a drawback. Mixing ILs with low viscosity molecular solvents is a potential solution to this problem and has been the focus of many studies in recent years. Understanding how molecular solvents lower mixture viscosity and by how much is therefore an important issue.

In this work, we report new experimental data for the density and viscosity of mix-

tures involving $[C_6mim][NTf_2]$ and the molecular solvent tetraethylene glycol dimethyl ether (tetraglyme or G4) at temperatures ranging from 298 to 353 K and compositions up to 50% G4. We find that both the density and viscosity drop with increasing temperature and G4 concentration. The viscosity does not drop as much as would be predicted by an ideal mixing model. Excess volumes are very small, suggesting that free volume effects do not play a role in the viscosity reduction.

Molecular dynamics simulations were also carried out to compute the density and viscosity as a function of temperature and G4 composition. The agreement between the simulated densities (and volume expansivities) and experiment was excellent. The simulations systematically overestimated the viscosity, but did capture the right trend with temperature and G4 concentration. Self-diffusivities, ideal ionic conductivities and liquid structure were also computed. Detailed analysis of the simulation results suggests that G4 preferentially solvates the cations, thereby weakening the interactions with the anions and resulting in faster dynamics, particularly for the anions. Such behavior was previously observed in electrolyte systems composed of glymes and Li^+ or Mg^{2+} salts,^{29,30,34–36,68} which are sometimes called solvate ionic liquids. Based on the simulation results of a model G4 system, it was further revealed that the localized negative charges on the oxygen atoms of G4 are primarily responsible for the preferential solvation of cations. If G4 (or a similar solvent) instead had large localized positive charges, it would tend to preferentially solvate the anions, resulting in increased cation mobility. This suggests a strategy for selecting molecular solvents that will enhance cation dynamics.

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