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Dilute or Concentrated Electrolyte Solutions? Insight from Ionic Liquid/Water Electrolytes

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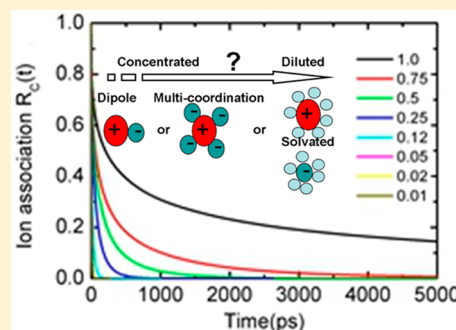
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Supporting Information

ABSTRACT: When room-temperature ionic liquids (IL) are used as an electrolyte, their transport behaviors are still under heavy debate due to their complicated ion-associations. In this article, we conducted molecular dynamics simulations to study the molecular scale ion associations from the very dilute 1-butyl-3-methylimidazolium iodide/water solution to the pure IL. It revealed that ions are localized in a multicoordinated ion cage structure with nanoseconds in concentrated IL solutions. Dynamics analyses indicate that the transport of this solution can be depicted by the Debye–Hückel model only in dilute IL/water electrolyte. The velocity and rotational correlation functions showed that the lifetime of translational and rotational motions are at the level of picoseconds and nanoseconds, respectively, because of the ion cage effect. The lifetime of ion association demonstrated that the recombination of association ions was prevalent in IL solutions. It means that the dipolar or stable contact ion-pairs model may not be suitable for depicting the IL transport.



Room-temperature ionic liquids (RTILs),¹ which are nonvolatile solvents and promising electrolytes, have already attracted much attention and increasing research interest. Given their good conductivities, large electrochemical windows, excellent thermal stabilities, and long cycle life, ionic liquids electrolytes are widely applied in many fields, including electrochemistry, lithium ions cells, supercapacitors, and dye-sensitive solar cells.^{2–6} Ionic liquids are composed of cations and anions and can be generally considered as a concentrated ion electrolyte system. Hence, describing their transport behaviors by custom Debye–Hückel models,⁷ which are based on the dilute-solution electrolytes approximation, is difficult. Moreover, similar to traditional salts (such as alkali-halides), ionic liquids show a strong Coulomb interaction and more complicated van der Waals interactions. These long-range electrostatic interactions and short-range dispersion forces finally resulted in local aggregation of the nonpolar region and ionic associations.

Recently, many experiments and simulations have confirmed that the structural heterogeneity of ionic channels and nonpolar domains in ionic liquids may affect ion diffusion and ionic conductivity.^{8–12} The strong cation–anion associations yield neutral ion pairs or dipoles, which may reduce the amounts of free-moving ions and charge transport. Therefore, a deeper understanding of how the structural heterogeneity and ion associations affect ionic transport properties is of great significance. Regarding structural heterogeneity, Urahata and Ribeiro¹³ first found microheterogeneity in long alkyl chain ILs. Wang et al.¹⁴ found nanostructural organization in a polar and

water network in ionic liquid water solutions. Chen et al.¹⁵ discussed the possible cluster self-assembly in ionic liquids and ionic liquids solutions. Hu and Margulis¹⁶ also revealed that the slow transport dynamics in ionic liquids is due to structural heterogeneity. Zheng et al.¹⁷ recently suggested that aside from structural heterogeneity, dynamic heterogeneity also commonly exists in ionic liquids. Among the features of ion associations, the long-lived association of ions in ionic liquid electrolyte has been discussed at length by researchers. The intense hydrogen bonds and the large binding energy between the cations and anions result in slow ion dynamics and ionic associations. This ionic association is supported by the fact that the diffusion coefficients of cations and anions are always in the same order of magnitude even in an ionic liquid with an asymmetric ions volume. However, questions about the origin of this association remained unanswered, that is, whether or not stable ion pairs contribute in this association and finally affect the transport dynamics. Indeed, both in experiments^{18,19} and in molecular simulations,²⁰ ion associations were discovered to exist in dilute solutions of ionic liquids. Stassen et al. further speculated that the multi-ion association or loose ion pairs structure may be present in the IL solutions.²¹ Zhao et al.²² used molecular dynamics simulations and found that ion associations are multicoordinated association in the bulk ionic liquid BmimPF₆, but its lifetime is just at the nanosecond level. However, recent

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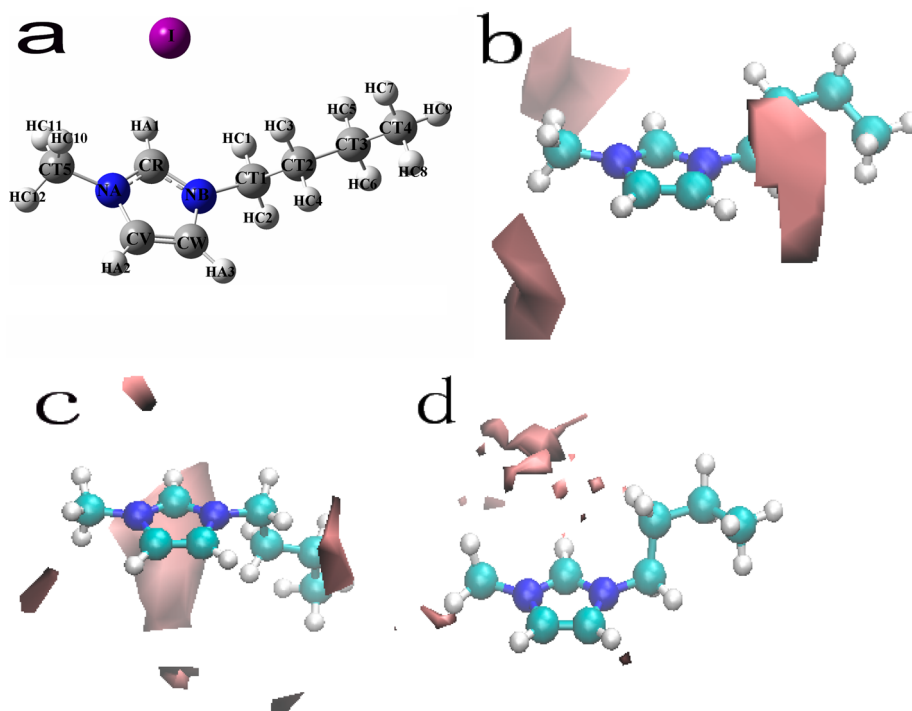


Figure 1. Molecular structure of BmimI and the spatial distribution functions of anion around cation as a function of IL mole fractions. The isosurface value is $0.01/\text{\AA}^3$. (a) Molecular structure with atomic labels. Mole fractions: (b) 0.5, (c) 0.125, and (d) 0.05.

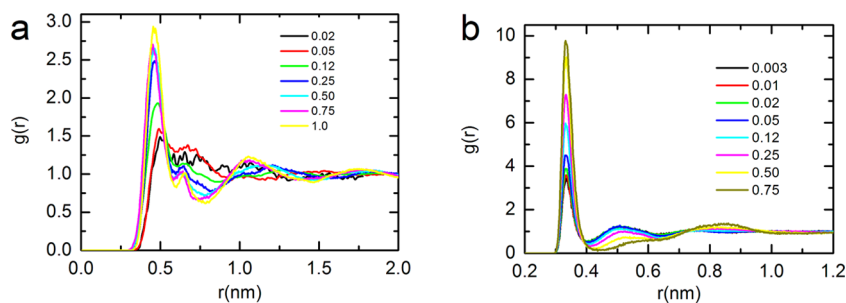


Figure 2. Mass-center radial distribution functions of cation–anion and anion–water as a function of IL mole fractions. (a) cation–anion and (b) anion–water.

surface force balance experiments²³ demonstrated that most ions in ionic liquids are bound as ion pairs and behave effectively as dipoles. Hence, ionic liquids only have a low concentration of free ions with long-lived ion pairs and behave as dilute electrolytes. This transport model of ionic liquids was very different from previous ionic liquid electrolyte transport models and has since caused conflicting results.^{24–26} Lee et al.²⁶ used a mean field model to suggest that ion pairs in ionic liquids have a short lifetime comparable to the time scale for diffusion. From their results, bulk ionic liquids can be seen as concentrated rather than dilute electrolytes. Holl  czki et al.²⁷ pointed out the charge transfer between the cation and the anion may suppress the producing of ion pairs. Previous simulations^{28,29} also displayed that although the interaction energy between the ion pairs is very strong, the lifetime of ion pairs is short because of the strong competing and screening interactions of surrounding ions. In summary, to settle these debates and contradicting conclusions, further investigation on the details of the ions structure images, ion transport properties, and mechanism at the molecular level is needed.

In this study, we used molecular dynamics simulation to study the microstructure and lifetime of ion associations and ion transport dynamics from bulk phase ionic liquid to the dilute solution. The choice from pure state to a dilute electrolyte solutions was not only a practical need to mix ionic liquids electrolytes with other compounds as a cosolvent but also provided new insight into how custom dilute-solution theory works and how the Debye–H  ckel models are slowly changed in real ionic liquids transport models. Considering the fact that water/ionic liquids dilute-solutions have been studied in experiments and that they follow the typical Debye–H  ckel model,^{30,31} the mixtures of BmimI and water solutions over the full concentration range ($0 < x < 1$) were studied via molecular dynamics simulation, in which x is the mole fraction and can be defined as $x = N_{\text{BmimI}}/(N_{\text{BmimI}} + N_{\text{water}})$, N_{BmimI} and N_{water} are the number of BmimI and water molecules, respectively. In our work, a series of structure and dynamics properties of ion associations, including structure, formation of ion and water networks, the lifetime of ion associations, transport properties, and ion–ion and ion–water interactions, were analyzed in detail. These studies will help determine changes in the real

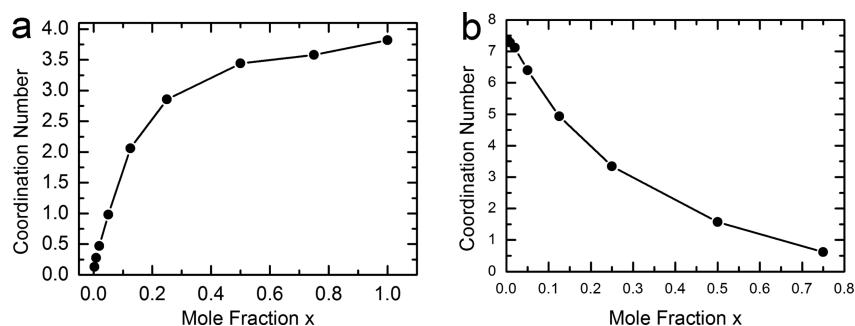


Figure 3. Coordination number of shell in cation–anion and anion–water as a function of IL mole fractions. (a) Anion around cation. (b) Water around anion.

mechanism from dilute electrolytes to real ionic liquids electrolytes, understand the electrolyte transport properties of ionic liquids at a molecular level and provide a theoretical basis for constructing a new electrolyte model of ionic liquids.

The first direct analysis of the electrolyte mixture structures is the spatial distribution functions (SDF) of cation–anion (see Figure 1). The SDF can provide a clear probability density to find an ion around another ion. In Figure 1, three large probability density regions are found around the cation. The most prominent region to find an anion is above and below the imidazolium ring, and the probability is high in HA1. This spatial association structure of anion–cation is a multisite association structure. Actually, finding any isolated ion pair structure or dipole in pure ionic liquids is difficult. This result is similar to previous simulations of other imidazolium-based ionic liquids.^{22,32} Following the mixture of water into the ionic liquid, the probability density of anion around the cation is continuously decreased. In the low ionic liquid mole fraction of 0.05, the cation–anion association spatial structure remains patch of probability distributions. Actually the association structure of cation–anion vanishes last in our lowest IL mole fraction of 0.003. This cation–anion association network was completely replaced by the anion–water network in an IL dilute-solution. The disassociation ion pairs in very dilute-solution is consistent with the recent experiment and simulations.^{33,34} These results can also be confirmed by the radial distribution functions (RDF) of cation–anion and anion–water. Figure 2 shows a clear maximum peak of 0.47 nm and long-range spatial correlations in cation–anion mass of center RDF for pure ionic liquid. These features can be retained even at a low ionic liquid mole fraction of 0.2. At mole fractions below 0.2, the peak height rapidly decreased, followed by a broadening of the peak width and a shifting of the peak position. This result suggested that the strong cation–anion association was rapidly weakened by water molecules at low ionic liquid mole fractions. This result also coincided with the previous SDF of cation–anion structures at low ionic liquid mole fractions. To obtain a spatial correlation of ion–water, we also calculated the anion–water RDF for different ionic liquid mole fraction mixtures. These RDFs exhibited distinct peaks in all the mixtures, thereby showing that the water molecules are present in the solvation structures around the anion at all concentrations. The heights of peaks significantly increase following with the increase of water concentrations, thereby indicating strong water–anion interactions in ionic liquid–water mixture solutions. These anion–water interactions are much stronger than cation–water interactions and even stronger than the cation–anion interaction, which can be confirmed by the

interaction energies analysis (see Supporting Information Figure S4) and previous experiments and simulations.^{35–38}

The RDFs can also determine the coordination number for ions or solvation shells in different mixture systems. By integrating $g(r)$ out to the location of the first minimum, the coordination number of the first shell, N , can be calculated via the following equation: $N = \int_0^{r_{\text{shell}}} \rho g(r) 4\pi r^2 dr$ where ρ is the number density and r_{shell} is the first minimum in $g(r)$. At $r_{\text{shell}} = 0.59$ nm, corresponding a minimum in $g(r)$ of cation–anion, the calculated coordination numbers of different ionic liquid mole fractions for the cation–anion first shell are shown in Figure 3a. At ionic liquid mole fractions higher than 0.25, the coordination number of the shell retains a relatively stable value such that each cation is surrounded by nearly three to four anions. Thus, the cation–anion retains its multisite association structure even at a low IL mole fraction. Hence, the common isolated ion-pair or dipole structure may not be suitable in depicting the ionic liquid system even at a relatively low concentration. However, the shell coordination numbers rapidly declines to a very small value at dilute solutions. For example, the value is less than 1.0 in very dilute IL solutions, thereby indicating that a stronger hydrated solvation shell structure starts to dominate the shell around the ions. This result can be validated by the anion–water coordination numbers for different ionic liquid mole fractions in the first shell, as shown in Figure 3b. When the water concentration is increased, the anions are gradually hydrated, exceeding seven water molecules in the anion coordination shell for very dilute IL solutions. This result means that the cation–anion network structure was destroyed in very dilute ionic liquid solutions. The slow disappearance of the cation–anion network structure and the formation of an ion-hydrated structure was confirmed by the snapshots of different IL mole fractions (see Figure S2 in the Supporting Information). This result is very different from those of ionic liquid/naphthalene dilute solutions,²⁰ in which the sizable fraction of ions condense into dipolar chains at low IL concentration solutions. The reason for this difference is that water is a polar solvent and has a strong hydration capability and interaction to inorganic ions compared with nonpolar naphthalene, which is an organic solvent.

To understand the ion dynamics and the hydration effect, the self-diffusion coefficients and conductivities were calculated at different IL mole fractions. The diffusions and conductivities govern mass transfer behavior and are crucial in determining the transport performance of IL electrolytes in electrochemical applications. Figure 4 shows the self-diffusion coefficients of cation, anion and water as functions of IL mole fractions. In the pure IL, the diffusion coefficients of cation and anion in our

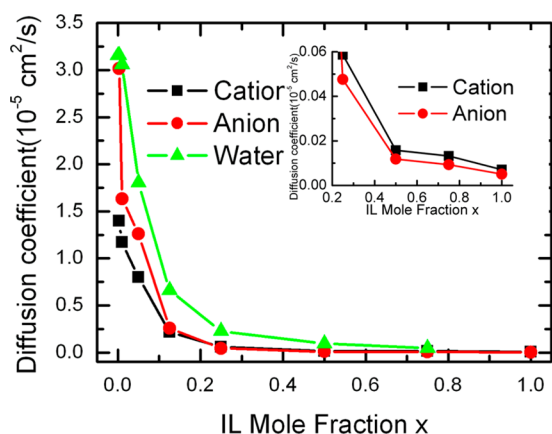


Figure 4. Diffusion coefficients of cation, anion and water as a function of IL mole fractions. The inset is an enlarged version for the diffusion coefficients of cation and anion in high IL mole fractions.

simulation are both at the order of $10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$, which are fairly close to the experimental results of imidazolium-based ILs.^{39,40} The values were similar to the self-diffusion coefficients for cations and anions at IL mole fractions larger than 0.25. This result indicated a strong associated ion motion in the concentrated IL electrolyte solutions. In concentrated IL solutions, the smaller amounts of water molecules was confined to resemble a water cluster in a large ion cage (see Figure S2 in Supporting Information). Hence, breaking up this cation–anion correlation motion is difficult. When water concentration increases, the strong ion–water interactions will eventually convert these ion correlations into ion hydration, thereby inducing a large increase in the self-diffusion coefficient at IL dilute solutions, especially for the anion. The anion nearly had a similar value of diffusion coefficient with that of water molecules at the lowest IL mole fraction, and the value was about twice as that of the diffusion coefficient of the cation. This result showed a complete hydration effect.

Electrical conductivity (Λ) is an important transport property of ionic liquids in practical applications. The Nernst–Einstein (N–E) approximation was typically used to calculate the conductivity. The N–E method neglects the contributions of cross-correlations among ions, and generally overestimates the electrical conductivity. In concentrated IL solutions, the ions may be strongly associated and this gives rise to correlated ionic motions. In order to consider the correlated ionic motion, the electrical conductivity was also calculated as the time integral of the electrical current autocorrelation

function (ECACF, the detail calculations see Supporting Information). The calculated ratios $\Delta = 1 - ((\Lambda_{\text{ECACF}})/(\Lambda_{\text{N-E}}))$ are usually larger than 0, and can represent the degree of the ion associations. In our simulations, the ratio is 0.45 in pure IL and decreases largely with the reduced IL mole fractions. The association degree becomes negligible in dilute solutions, for example, only 0.075 in IL mole fraction 0.12. Figure 5a shows the calculated conductivity by two methods as a function of different IL molar concentrations. In contrast to the large conductivity values (about $10^2 \text{ S} \cdot \text{cm}^{-1}$) and low association ratios in dilute solutions, the differences of the conductivity by two methods (less than $1 \text{ S} \cdot \text{cm}^{-1}$) in concentrated IL solutions are relatively small. Hence, the calculated conductivity curves by two methods in Figure 5a looks almost the same. The conductivity shows a prominent increase of about 2 orders of magnitude when the IL mole fraction was decreased to $x = 0.05$ because the swiftly transferred hydrated ions overcompensated for the decrease in the carrier density. Due to the conductivity is just the ions diffusion with a density prefactor, the hydrated ions diffusion rate may increase by almost 3 orders of magnitude compared with the ions in pure IL. A low mole fraction of 0.05 corresponded to a molar concentration of about 1.8 mol/L, which was a high value for molar concentrations. This conductivity trend in water solutions is similar to other experimental^{30,31} and simulation results⁴¹ but is very different to the conductivity trend in IL–nonpolar solvent solutions. Del Popolo²⁰ only reported a slight increase in the conductivity in IL BmimPF₆/naphthalene electrolytes, thereby indicating that nonpolar solvents hardly solvate the IL ions into isolated solvent ions.

Gebbie²⁴ tried to define IL as dilute electrolytes, which would mean that the transport behavior adheres to the Debye–Hückel models. The molar conductivities of water solutions would also be the square root of the IL concentration. Hence, we calculated the molar conductivity as a function of molar concentrations in Figure 6 (the conductivity of mole fraction is shown in Supporting Information Figure S5). The molar conductivity was in good agreement with the Debye–Hückel models at low concentrations, that is, molar concentrations below 4 mol/L, and the molar conductivity corresponded to a mole fraction of about 0.25. This mole fraction was exactly the concentration that the ions–water interaction energies become stronger than the cation–anion interaction energy (see Figure S4 in Supporting Information). This will result in a transition from an ion cage structure to a hydrated ion structure. At mole fractions higher than 0.25, the IL solutions showed a different

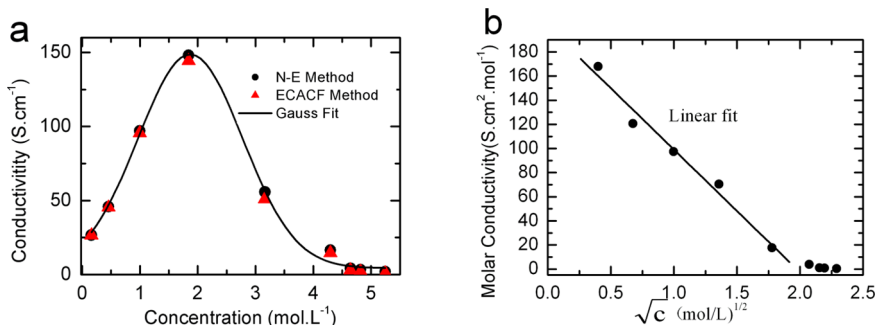


Figure 5. (a) Conductivities as a function of IL mole concentrations. (b) Molar conductivities as a function of the square root of IL mole concentrations.

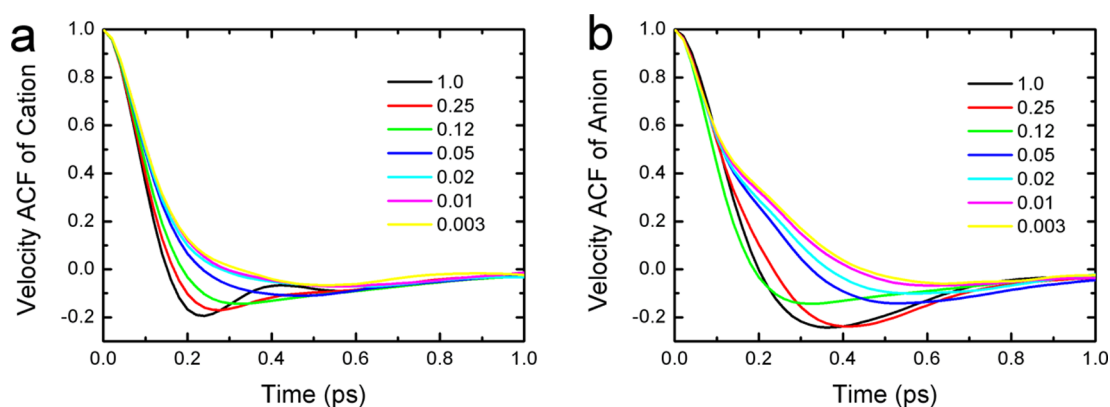


Figure 6. Velocity autocorrelation functions of cation and anion as a function of IL mole fractions. (a) Cation. (b) Anion.

molecular image compared with the ion atmosphere of the Debye–Hückel models. Concentrated IL solutions were filled with ion associations and ion cage formation rather than simple isolated ion pairs and free ions. Hence, in a pure IL or concentrated IL solutions, ion association and the ion cage effect may produce many recombinations and reorientations in ion transport, which determines the basic transport properties of IL systems.

Microscopical dynamics are crucial to pure IL or IL solutions because many microscopical dynamic behaviors may affect the efficiency of ion transport. One insight about microscopical dynamic behaviors can be obtained from the center-of-mass velocity autocorrelation functions (ACF). In general, the velocity ACF can be written as $C(t) = \langle v(t) \cdot v(0) \rangle$, where $v(t)$ is the velocity of the center of mass of the molecule. The self-diffusion coefficients can be calculated by integrating the velocity ACF as $D = (1/(3N)) \int_0^\infty \sum_{i=1}^N C_i(t) dt$, where the sum term considers all of the number of ions. Hence, the transport behaviors are directly affected. Figure 6 shows the velocity ACFs of cations and anions as functions of IL mole fractions. The velocity ACFs for pure IL decayed quickly and reached a zero value at about 0.15 ps for cation and 0.2 ps for anion. The velocity ACFs in pure IL or concentrated IL solutions also showed a negative asymptotic plateau, which may be attributed to backscattering. The backscattering refers to the phenomenon of ions' collision and bouncing back and forth within an ion cage. The cation not only was confined to an ion cage but also formed an aggregation of alkyl chains. Hence, its velocity quickly decreased. When the water concentration increased, the VACF decays just to zero and shows no negative plateau for dilute IL solutions, thereby showing that the ion cage was gradually replaced by a hydration shell. This negative plateau slowly disappeared in the IL dilute-solution because a lighter hydration shell did not produce a negative collision velocity, such as the case in a rigid, long-lived ion cage.

To obtain a reorientation dynamics of ions, we calculated the rotational ACF $C(t)$ as a function of IL mole fractions in Figure 7, where $C(t) = \langle \vec{u}(t) \cdot \vec{u}(0) \rangle$, and \vec{u} is a unit vector representing the perpendicular direction in a cation imidazolium ring. The rotational motion of the cation slowly decayed unlike the velocity ACFs. This slow decay was expected because of the strong ion cage that hindered the rotational motion of ions. When the water fraction was increased, the decay time of these ACFs obviously decreased. The constant of the rotational motion can be estimated by integrating the rotational ACF $C(t)$ as $\tau = \int_0^\infty C(t) dt \approx (\int_0^{t_0} C(t) dt) / (1 - C(t_0))$, where we assumed that $C(t)$ decayed as a pure exponential beyond time $t = t_0$. For

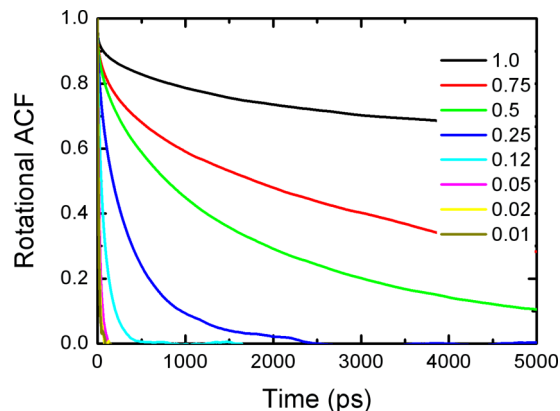


Figure 7. Rotational autocorrelation function of perpendicular line in imidazolium ring as a function of IL mole fractions.

pure IL, the rotational constant was about 14.2 ns, which was slightly larger than those reported for imidazolium-based ionic liquids.^{40,41} In dilute IL water solutions, the rotational constants fall into the level of picoseconds, that is, 12.9 ps in the lowest mole fraction of 0.01. This result demonstrated that the water molecules greatly affected the rotational motion of ions. In pure or concentrated IL solutions, the rigid ion cage may hinder the freedom of ions rotation. However, in dilute solutions, the ions underwent a diminished caging effect of counterions by the replacement of the cage with a flexible solvation shell. Thus, the ions rotated more freely. Based on the Stokes–Einstein and Stokes–Einstein–Debye relationships,^{42,43} the inverse of the rotational constant was proportional to the translational diffusion coefficient, that is, $\tau^{-1} \propto D$. Hence, a long rotational motion would correspond to a slow translational diffusion. For our IL system, this ion cage effect may decrease the ion translation motion within picoseconds based on the velocity ACFs and may hinder the ions rotation up to the nanosecond level. The ion cage effect may not result in a lifetime of more than a few nanoseconds with stable ion association.

Strong ion associations in pure or concentrated IL solutions resulted in the formation of an ion cage and affected ion dynamics properties. Hence, the ion association dynamics need to be studied. However, it is also controversial to explain the association formation, that is, which model is suitable to depict the ion association a stable ion-pair, a long-lived ion cage, or only short-lived association effect. To answer this question, we calculated the ion association dynamics via the time autocorrelation function, which is defined as $R(t) = (1/$

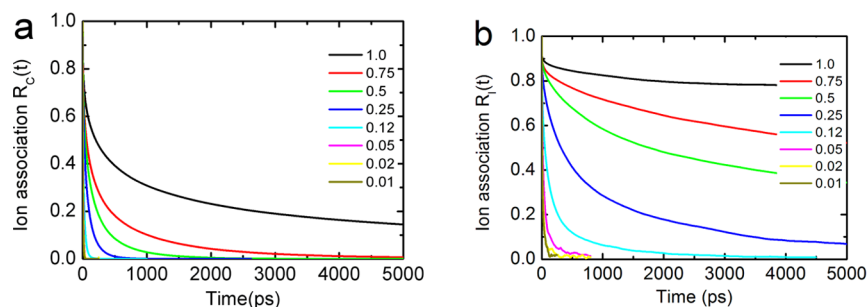


Figure 8. Time correlation function of ion association as a function of IL mole fractions. (a) Consistent associations. (b) Inconsistent associations.

$(N_c N_a) \sum_{i=1}^{N_c} \sum_{j=1}^{N_a} \langle \theta(r_{ij}, 0) \theta(r_{ij}, t) \rangle$ where the $\theta(r, t)$ is the heaviside step function. It has a value of 1 when the cation and anion are combined and is zero when the two ions depart. N_c is the number of cations, and N_a is the number of anions that are bound to cation. In this study, we defined the ion association if the distance is within the first coordination shell minimum of mass-center RDF of cation–anion. Two types of $R(t)$ are shown in Figure 8. $R_c(t)$ does not allow for temporary dissociation, and $R_i(t)$ allow for the breaking and recombination of ion associations.

In both $R_c(t)$ and $R_i(t)$, the lifetimes of ion associations rapidly decreases by decreasing the IL mole fractions, thereby showing that the water molecules have a huge effect on the ion association lifetime. Actually, the hydration effect of ions and ion associations compete with each other and achieve a balance in IL/water solutions. Even in dilute solutions, ion associations remain. However, this ion association seems very transient, unlike the nanosecond lifetime in pure IL. The ion-associations in dilute solutions only have a lifetime of several picoseconds. Another distinct property shown in Figure 8 is that the ion association recombination is prevalent in IL solutions, especially in concentrated IL solutions. Thus, associated ions hardly break off the ion cage and always recombine into previous association structures. This recombination behavior was much more apparent in pure IL or concentrated IL solutions because the strong ion cage induced ionic recombination. We can calculate the lifetime of associations by $\tau = \int_0^\infty R(t) dt$. In pure IL, the lifetimes of association for $R_c(t)$ and $R_i(t)$ were about 3.5 and 23.5 ns, respectively. For dilute IL solution, at a mole fraction of 0.01, the values of $R_c(t)$ and $R_i(t)$ were about 4 and 19 ps, respectively. Thus, ion associations and recombination became transient and insignificant in very dilute solutions. At the lowest IL mole fraction of 0.003, the ions were completely surrounded by the hydration shell, and no ion association structure was found at this concentration. Even in pure IL, the longest lifetime of the recombination ion association was only at the nanosecond level, which was not large enough to form a stable, long-lived ion-pair or dipole and may influence macroscopic diffusion behavior. Hence, the argument of the dilute electrolytes model for IL with stable ion-pairs or dipole^{23–25} may not be true. Combined with the previous spatial distribution function, radial distribution function, and association dynamics results, ion associations in pure IL or concentrated IL solutions are multicoordinated ion associations and only have a lifetime at the level of nanoseconds. We also have found that the linear relation between the inverse of associated lifetime and mole conductivities in concentrated IL solutions (see Supporting Information Figure S6). The relation result agree well with the recent simulation⁴⁴ and indicated that ion cage structures

determined the lifetimes of ion association and showed a direct correlation with transport properties.

We used molecular dynamics simulations to study the ion structure and dynamic properties of IL BmimI/water electrolyte solutions. These simulations enabled us to establish clear molecular insights into these ion association structures as well as the dynamics of the diffusion, rotation, association at different IL mole fractions. Our simulations revealed that ions are localized in multicoordinated ion cage structures with nanoseconds in pure IL or concentrated IL solutions. Hence, an ion-pair or dipole structure may not be suitable to depict IL systems. The ion cages in pure IL or concentrated IL solutions were gradually replaced by a hydration shell in IL–water dilute electrolytes. Dynamics analyses indicate that the transport of this ionic liquid/water electrolyte can be depicted by the infinite dilution model when the IL mole fractions are below 0.25. The velocity and rotational correlation functions showed that the lifetime of translational and rotational motions are at the level of picoseconds and nanoseconds, respectively, because of the ion cage effect. The lifetime of ion association demonstrated that the recombination of association ions was prevalent in IL solutions. The linear relation between the inverse of associated lifetime and mole conductivities in concentrated IL solutions indicated that ion cage structures determined the lifetimes of ion association and showed a direct correlation with transport properties.

CALCULATION METHODS

The Bmim⁺ cation was treated as a systematic all-atom force field, as developed by Maginn.⁴⁵ This method was successfully used in previous simulations^{44–47} and can reproduce the dynamical properties of imidazolium-based ionic liquids in experiments. The I[−] anion was taken from the OPLS-AA force field.⁴⁸ The SPC/E model was employed to describe the water interactions.⁴⁹ The model system consists of 216 BmimI molecules and different numbers of water molecules placed in a tetragonal box. The cross interactions between unlike atoms were computed according to the Lorentz–Berthelot combination rules. The series of simulations were performed at a fixed temperature of 300 K by using Gromacs 4.6.^{50,51} The simulations were initially equilibrated at an isothermal–isobaric condition (NPT) at 1 atm for 1 ns. The systems were then further equilibrated in a constant volume–temperature (NVT) ensemble for 5 ns. Trajectories of additional 10 ns following equilibration were used for dynamic analysis.

Periodic boundary conditions were applied in all directions. In all simulations, the bond length was constrained with the LINCS algorithm. The cutoff of Lennard-Jones interactions was taken at 12 Å. The long-range coulomb interactions were handled by PME with a cutoff of 12 Å and a grid spacing of 1.2

Å. The Berendsen thermostat and a velocity rescaling thermostat were separately used in the NPT and NVT systems to mimic the weak coupling with a temperature coupling constant of 0.1 ps.

Eight different aqueous-ionic liquid mixtures and a pure ionic liquid system were studied. Six mixture systems contained 216 ion pairs with 72, 216, 648, 1512, 4104, and 10 584 water molecules, which corresponded to ionic liquid mole fractions x of 0.75, 0.50, 0.25, 0.125, 0.05, and 0.02, respectively. The two lowest ionic liquid mole fractions mixtures of 0.01 and 0.003 were simulated with 64 ion pairs and 6336 and 19 136 water molecules, respectively. The lower ionic liquid mole fraction mixtures corresponded to an infinitely dilute ionic liquid electrolyte solution condition; it can provide a clearer molecular insight into ionic liquid electrolytes from infinitely dilute solutions to real concentrated solutions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01513.

Detailed force field parameters, the temperature dependence of ionic liquid density, snapshots of IL solutions, the excess molar volume, the interaction energies, the mole fraction dependence of conductivity and the relation between association lifetime and mole conductivities. (PDF)

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Notes

The authors declare no competing financial interest.

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