How Is Charge Transport Different in Ionic Liquids and Electrolyte Solutions?

Hemant K. Kashyap,[†] Harsha V. R. Annapureddy,[†] Fernando O. Raineri,[‡] and Claudio J. Margulis*,[†]

[†]Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, United States

[‡]Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794, United States

ABSTRACT: In this article we show that, analyzed in a barycentric reference frame, the deviation in conductivity measured directly from impedance experiments with respect to that estimated indirectly from NMR diffusion experiments has different origins in electrolyte solutions and pure salts. In the case of electrolyte solutions, the momentum conservation law is satisfied by solvent + ions. Instead, in a molten salt or ionic liquid momentum conservation must be satisfied solely by the ions. This has significant implications. While positively correlated motion of ions of opposite charge is a well justified explanation for the reduction in impedance conductivity in the case of electrolyte solutions, it is not so in the case of ionic liquids and molten salts. This work presents a set of equations that in the case of ionic liquids and molten salts can be used to obtain from direct measurements of impedance and NMR the distinct part of the diffusion coefficient matrix in the barycentric reference frame. In other words, by using experimentally measurable quantities, these equations allow us to access the motional coupling between ions for which there is no single direct experimental measurement technique. While equations of this type have been proposed before, the ones presented here can be easily derived from the momentum conservation law and linear response theory. Our results indicate that the decrease in the impedance conductivity with respect to NMR conductivity in ionic liquids and molten salts is due to anticorrelated motion of ions of same charge. This scenario is different in electrolyte solutions, where the positively correlated motion of ions of opposite charge makes a significant contribution to the decrease in the impedance conductivity. In contrast, in a system comprising a single binary salt (a room temperature ionic liquid or a molten salt), the cation—anion distinct diffusion coefficient is negative definite and opposes the contribution from the cation—cation and anion—anion distinct diffusion coefficients. This property of the cation—anion distinct diffusion coefficient in systems comprising just two ion-constituents holds true not just in the barycentric reference frame but also in any of the internal reference frames of nonequilibrium thermodynamics.
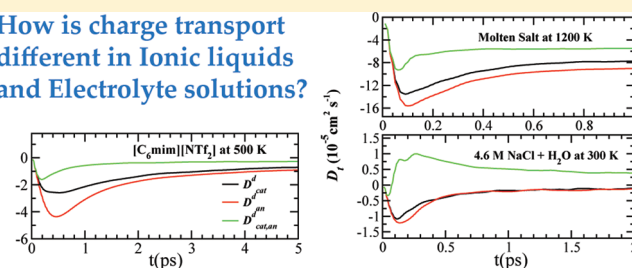
1. INTRODUCTION

Modern ionic liquids (ILs) are composed of organic cations and organic or inorganic anions that are liquid at room temperature. Much has been learnt in the last 10 years about these systems, but a significant number of problems still remain unresolved.[1−3] One such challenge is the understanding of motional correlation between ions and how this affects transport properties. This is very important in order to better understand their applicability to energy related problems of electrochemical nature.

It is well established that for room-temperature ionic liquids (RTILs), molten salts, and electrolyte solutions the ratio of impedance vs NMR derived conductivities is $\Lambda_{imp}/\Lambda_{NMR} \leq 1$.[4−20]

The deviation of impedance measurements from NMR derived conductivities is often described by a parameter Δ, defined as $\Delta = 1 - (\Lambda_{imp}/\Lambda_{NMR})$. The parameter Δ has often been used to describe the degree of so-called ion pairing.[5−7,21,22] For ILs Δ is always *positive* (i.e., $\Lambda_{imp} < \Lambda_{NMR}$) and in the range 0.3−0.5. While a number of measurements[5−11,15,16] and computer simulations[21,23−47] have agreed on these findings, what is still missing is a clear physical understanding of charge transport.[1,2] What we show in subsequent sections is that the origin of this phenomenon is different in electrolyte solutions and pure salts.

In this article we present theory and computational results that in comparison with experiments address the physical origin of the observed values of Δ. We focus in particular on ion transport in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_n mim][NTf_2]$ with $n = 6$ at 500 K, a prototypical high temperature molten salt at 1200 K and 4.6 M NaCl aqueous solution at ambient conditions.

The quantity Δ can be interpreted in terms of self and distinct diffusion coefficients.[19,48−57] Whereas the self-diffusion coefficients are reference frame independent, the distinct diffusion coefficients are not and one can choose to "open" or split Δ for interpretation in different frames of reference. In this article we choose the barycentric reference frame where energy is conserved and the total momentum of the system is zero. In the Appendix we show that some of the key results of this article turn out to be reference frame independent.

In the case of ionic liquids and molten salts we develop a theoretical method to calculate the distinct diffusion coefficients

in the barycentric reference frame from the self-diffusion coefficients of the ions and the macroscopic conductivity. The simple theoretical expressions derived here should be useful to experimentalists with access to independent conductivity and NMR measurements. These equations are general and can be applied to any kind of binary ionic liquids or molten salts. A similar set of equations has been previously derived from a phenomenological perspective by Schönert.[58] These equations have been used in recent years to describe coupling between ions in some ionic liquids.[8−11]

2. SIMULATIONS METHODS

Molecular dynamics simulations were carried out using the GROMACS software.[59,60] We used OPLS-AA force field[61,62] for the cation with the partial charges derived from Pádua and co-workers.[63] The potential energy parameters for the anion are taken from the work of Lopes and Pádua.[64] A cubic box of 300 ion pairs was first equilibrated for several nanoseconds during which we lowered and raised the temperature and partial charges until convergence of the density for the fully charged system was achieved at 500 K. At this point, the system was further equilibrated in the isothermal−isobaric canonical (NPT) ensemble with full charges at 500 K for at least 3 ns. The pressure was kept at 1 bar. Equations of motion were integrated using the leapfrog algorithm[59,60] with 1 fs time step and with proper periodic boundary conditions as coded in GROMACS. Temperature and pressure were regulated using the Nosé−Hoover thermostat[65,66] and Parrinello−Rahman barostat.[67] The Lennard-Jones interactions were cutoff at 15 Å. Electrostatic interactions were calculated using the Particle Mesh Ewald (PME) summation algorithm with a real space cutoff of 15 Å.[68,69] The equilibrated system was used for a production run in the microcanonical (NVE) ensemble with zero center of mass velocity. Velocities were stored every 20 fs during our 10 ns long production run. Though RTILs are in general viscous, 10 ns at 500 K was sufficient to properly converge velocity correlation functions.

To model a generic monovalent molten salt, we equilibrated 343 ion pairs at 1200 K in the NPT ensemble for 1 ns. Production runs in the NVE ensemble with zero center of mass velocity were 6 ns in duration. OPLS-AA[61,70,71] force-field parameters for Na^+ and Cl^- ions were chosen to model the molten salt. While other more sophisticated potentials[72,73] exist to model this system that accurately predict the structure and density of NaCl, our purpose here is simply to model a prototypical monovalent salt in the liquid phase for which the model chosen is sufficient. Velocities for each ion were stored every 10 fs.

We also modeled a concentrated (4.6 M) aqueous NaCl solution using OPLS-AA parameters for the ions and the TIP5P water model[74] of Mahoney and co-workers. Equilibration of this system was carried out in the NPT ensemble at 300 K and 1 bar for 2 ns followed by a production run in the NVE ensemble with zero center of mass velocity of 16 ns in duration. 100 pairs of Na^+ and Cl^- were dissolved in a box of 1200 water molecules. Velocities were stored every 10 fs for further analysis.

3. THEORY FRAMEWORK

The expression of the conductivity in terms of the microscopic charge current time autocorrelation (CACF) function in the linear response Green−Kubo formulation is given by[75]

$$\sigma_{CACF} = \frac{1}{3k_B T V} \int_0^\infty \left\langle \vec{J}(t) \cdot \vec{J}(t=0) \right\rangle dt \qquad (1)$$

where k_B is the Boltzmann constant, T is the temperature, and V is the volume of the system. Furthermore, $\vec{J}(t)$ is the microscopic charge current, defined as

$$\vec{J}(t) = e \sum_{i=1}^{N} z_i \vec{v}_i(t)$$

$$= e \sum_{i_{cat}=1}^{N_{cat}} z_{cat} \vec{v}_{i_{cat}}(t) + e \sum_{i_{an}=1}^{N_{an}} z_{an} \vec{v}_{i_{an}}(t) \qquad (2)$$

where e is the protonic charge, z_{cat} and z_{an} are, respectively, the charge numbers of the cationic and anionic species, $\vec{v}_i(t)$ is the center-of-mass velocity of the ith ion at time t with respect to a reference velocity (in this study this reference velocity is taken as the velocity of the center of mass of the system which is set to zero) and $N = N_{cat} + N_{an}$ is total number of ions. In the second equality we have separated the contributions from the cationic and anionic species to the microscopic charge current; in this work we restrict the discussion to systems comprising a single binary salt or a single binary salt dissolved in a molecular solvent.

Inserting the expression in eq 2 for the microscopic charge current into the Green−Kubo formula for the electrical conductivity, eq 1, and carrying out some algebra we obtain eq 3 (see Appendix A)

$$\sigma_{CACF} = \frac{\rho e^2}{k_B T}[x_{cat} z_{cat}^2 D_{cat}^s + x_{an} z_{an}^2 D_{an}^s + x_{cat}^2 z_{cat}^2 D_{cat}^d$$

$$+ x_{an}^2 z_{an}^2 D_{an}^d + 2x_{cat} x_{an} z_{cat} z_{an} D_{cat, an}^d] \qquad (3)$$

where $\rho = N/V$ is number density of the ions, and where x_{cat} and x_{an} are mole fractions of the cationic and anionic species defined with respect to total number of ions. In this expression for the electrical conductivity D_{cat}^s and D_{an}^s are the self-diffusion coefficients of the cationic and anionic species, respectively. Furthermore, D_{cat}^d, D_{an}^d, and $D_{cat,an}^d$ (defined in eqs A6−A10 of Appendix A) are the three relevant distinct diffusion coefficients in a system comprising just a single binary salt.

Unlike the self-diffusion coefficients[76] and the electrical conductivity,[77] which are independent of the reference frame (see also Appendix D), the distinct diffusion coefficients must be expressed in terms of the velocities of the ions relative to a microscopic reference velocity $\vec{w}_R(t)$.[51,78,79] Subtracting a reference velocity from the velocity of the ions, which makes the distinct diffusion coefficients to depend on the choice of the internal reference frame in an essential way, is required so that the time-integrals in eqs A8−A10 converge.[51] In this study the microscopic reference velocity is taken as the velocity of the center of mass of the system, $\vec{w}_M(t)$, leading to distinct diffusion coefficients defined in the barycentric reference frame. Moreover, in our NVE simulations $\vec{w}_M(t)$ is set to zero. It is shown in ref 50 that eqs A8−A10 also apply more generally in a thermal equilibrium ensemble with fluctuating $\vec{w}_M(t)$.

After rearranging the terms in eq 3, a convenient representation of the electrical conductivity is given by the expression[75]

$$\sigma_{CACF} = \frac{\rho e^2}{k_B T}[x_{cat} z_{cat}^2 D_{cat}^s + x_{an} z_{an}^2 D_{an}^s] \times [1 - \Delta] \qquad (4)$$

where

$$\Delta = -\frac{[x_{cat}^2 z_{cat}^2 D_{cat}^d + x_{an}^2 z_{an}^2 D_{an}^d + 2x_{cat} x_{an} z_{cat} z_{an} D_{cat, an}^d]}{[x_{cat} z_{cat}^2 D_{cat}^s + x_{an} z_{an}^2 D_{an}^s]}$$

$$(5)$$

The Nernst–Einstein (NE) conductivity obtained from NMR self-diffusion experiments corresponds to the special case when $\Delta = 0$ in eq 4:

$$\sigma_{NE} = \frac{\rho e^2}{k_B T} [x_{cat} z_{cat}^2 D_{cat}^s + x_{an} z_{an}^2 D_{an}^s] \qquad (6)$$

The molar conductivity is calculated as $\Lambda_x = \sigma_x/c$, where the subscript x refers either to CACF or NE, and where c is the molar concentration of the salt.

From the fact that the electrical conductivities in eqs 4 and 6 are both independent of the internal reference frame[76,77] (also see Appendix D) it follows that Δ defined in eq 5 must also share this property. Consequently, even though the distinct diffusion coefficients depend on the reference frame,[19,49−53] the linear combination of these coefficients in the numerator of eq 5 is not. For the most part, the results in subsection 3.1 are specific to the barycentric reference frame, for which the center of mass velocity of the system $\vec{w}_M(t)$ is zero. In Appendix D, however, we demonstrate that, in the case of ionic liquids and molten salts, some of the key results in subsection 3.1 are general in any proper reference frame.

3.1. Momentum Conservation Law. In the case of electrolyte solutions, momentum conservation for the system must be jointly satisfied by the ions and the solvent. The case of molten salts and room temperature ionic liquids is very different. While positively correlated motion of ions of opposite charge, as measured by the time integral from zero to infinity of the cation–anion distinct velocity correlation function, is definitively present in the case of electrolyte solutions (see subsequent sections), the momentum conservation law forbids this in the case of ionic liquids and molten salts. Below we derive a set of equations that liquids composed only of ions must satisfy in the molecular dynamics ensemble, in which $\vec{w}_M(t) = 0$. Consequences of these equations carry to velocity correlation functions from which electrical conductivity is derived.

From the law of conservation of total momentum we must have[50,51]

$$m_{cat} \sum_{j_{cat}=1}^{N_{cat}} \vec{v}_{j_{cat}} = -m_{an} \sum_{j_{an}=1}^{N_{an}} \vec{v}_{j_{an}} \qquad (7)$$

where m_{cat} and m_{an} are the masses of cations and anions, respectively. In Appendix B we show that eq 7 in combination with the definitions of self and distinct diffusion coefficients lead to the following relations:

$$m_{cat}[D_{cat}^s + x_{cat} D_{cat}^d] = -m_{an} x_{an} D_{cat, an}^d \qquad (8a)$$

$$m_{an}[D_{an}^s + x_{an} D_{an}^d] = -m_{cat} x_{cat} D_{cat, an}^d \qquad (8b)$$

Equations 8 are valid in the barycentric reference frame, and are a particular case of the more general expressions derived in ref 51 for any of the reference frames used in nonequilibrium thermodynamics for the treatment of mass transport in multicomponent systems.[77−80]

We observe that the assumption of concurrent negligible ion– ion (cation–cation, anion–anion, and cation–anion) distinct correlated motions in the case of ILs or molten salts is physically impossible, as these coefficients must satisfy eqs 8 (or, more generally, eqs 3.6 and 3.7 of ref 51). It is simply impossible to have all distinct diffusion coefficients equal to zero or negligible simultaneously when the self-diffusion coefficients of cations and anions are non-negligible. This is a key issue to be reckoned with when discussing how or when the Nernst–Einstein approximation can be applied to ionic systems. In other words, when discussing the suitability of the NE equation in the context of ionic liquids one should not think in terms of lack of ionic dynamic correlations, but instead in

terms of distinct or cross couplings that are balanced such that

$$x_{cat}^2 z_{cat}^2 D_{cat}^d + x_{an}^2 z_{an}^2 D_{an}^d + 2 x_{cat} x_{an} z_{cat} z_{an} D_{cat, an}^d = 0 \qquad (9)$$

In contrast with molten salts or ionic liquids, in an electrolyte solution all the ion–ion distinct diffusion coefficients may vanish (as is certainly the case in solutions at extremely low concentrations) or may be negligible simultaneously, as the momentum balance is partly accomplished by the solvent.

3.2. Distinct Diffusion Coefficients can be Directly Obtained from Experimental Conductivity and Self Diffusion Coefficients. While there is no way to directly measure distinct diffusion coefficients, the combination of self-diffusion and impedance experiments yields enough information to mathematically derive them.[8] In this section we present a set of rigorous general expressions derived from linear response and conservation laws that apply to arbitrary binary ionic liquids of symmetric and asymmetric charge.

Let us define a quantity that may be calculated from NMR and impedance conductivity measurements

$$\Delta' = \frac{\Lambda_{imp} - \Lambda_{NMR}}{\rho e^2/c k_B T} \qquad (10)$$

Note also that we have, from eqs 3 and 6, that

$$\Delta' = x_{cat}^2 z_{cat}^2 D_{cat}^d + x_{an}^2 z_{an}^2 D_{an}^d + 2 x_{cat} x_{an} z_{cat} z_{an} D_{cat, an}^d \qquad (11)$$

Using eq 11 in conjunction with eqs 8, we demonstrate in Appendix C that

$$D_{cat, an}^d = -\frac{m_{cat} m_{an} \Lambda_{imp}}{(\rho e^2/c k_B T) x_{cat} x_{an} [z_{cat} m_{an} - z_{an} m_{cat}]^2} \qquad (12a)$$

$$D_{cat}^d = -\left[\frac{D_{cat}^s}{x_{cat}} - \frac{m_{an}^2 \Lambda_{imp}}{(\rho e^2/c k_B T) x_{cat}^2 [z_{cat} m_{an} - z_{an} m_{cat}]^2} \right] \qquad (12b)$$

$$D_{an}^d = -\left[\frac{D_{an}^s}{x_{an}} - \frac{m_{cat}^2 \Lambda_{imp}}{(\rho e^2/c k_B T) x_{an}^2 [z_{cat} m_{an} - z_{an} m_{cat}]^2} \right] \qquad (12c)$$

All quantities on the right-hand side of eqs 12a−c are experimentally known.

Note from the above equations that $D_{cat,an}^d$ is always *negative*, and therefore, it is clear that the term involving this coefficient in eq 3 *will always increase the conductivity*. In other words, on average, in an ionic liquid motion of species of different charge must be anticorrelated! In Appendix D we prove that $D_{cat,an}^d$ is negative not just in the barycentric reference frame but in all proper internal reference frames. This means that the interpretation of $D_{cat,an}^d$ as a signature of anticorrelated motion of cations and anions is quite general and independent of the reference frame. Since Δ (the deviation between impedance and NMR measured conductivities) is always positive and independent of reference frame, eq 5 implies that $x_{cat}^2 z_{cat}^2 D_{cat}^d + x_{an}^2 z_{an}^2 D_{an}^d$ must always be negative and larger in magnitude than $2 x_{cat} x_{an} z_{cat} z_{an} D_{cat,an}^d$. Hence the motion of ions of the same charge is also overall anticorrelated.

While experiments may be restricted to the measurement of the infinite time (zero frequency) transport properties, eqs 12 are valid at any intermediate time so long as Λ_{imp} and diffusion coefficients are also taken as time dependent. We have verified the validity of eqs 12 by contrasting them against direct computation of the time dependent distinct diffusion coefficients (for which the time integrals of the corresponding velocity time
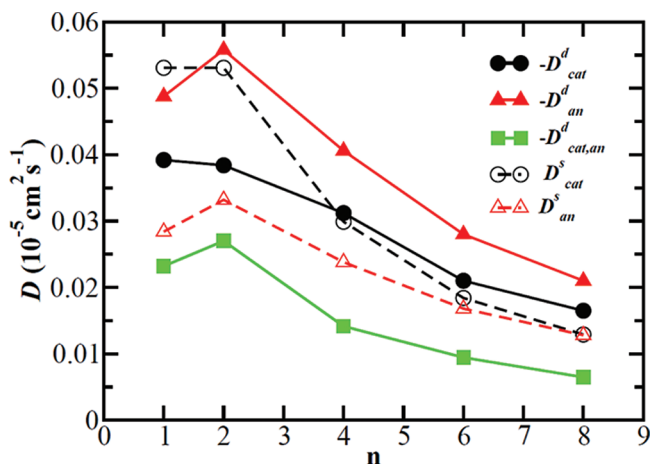
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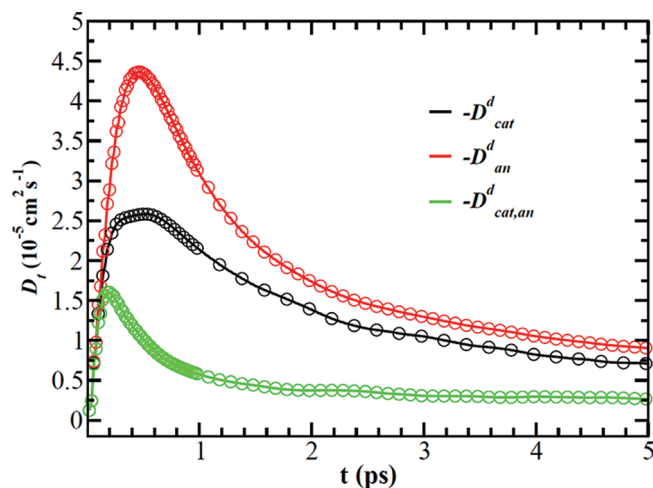
Figure 1. Comparison of the time dependent ion−ion distinct diffusion coefficients from eqs 12a−c (—) and those independently obtained from simulation by computing distinct velocity correlation functions (◯) in the case of $[C_6mim][NTf_2]$ at 500 K.

Figure 2. Experimental self diffusion coefficients (---) for the family $[C_nmim][NTf_2]$ at 300 K represented as a function of the alkyl chain length n. Negative of the distinct diffusion coefficients (—) obtained using eqs 12 from self diffusion coefficients and conductivity measurements from the work of Tokuda et al.[6]

correlation functions extend up to a variable time t) from simulation. Figure 1 compares the time dependent distinct diffusion coefficients calculated from (a) the charge current autocorrelation function (that determines the impedance conductivity) and the velocity autocorrelation functions of the ions (that determine the self-diffusion coefficients), and (b) the time dependent versions of eqs A8−A10. The figure shows that indeed both methods are equivalent. The (long time) asymptotic value of the curves corresponds to the macroscopic transport property.

Notice that even if Δ' in eqs 10 and 11 is zero (this is the case when the NE approximation is strictly valid by cancellation of terms) and conductivities derived from NMR and impedance measurements are the same, eqs 12a−c can still be used to derive the distinct diffusion coefficients, that because of eqs 8 will be different from zero.

4. RESULTS AND DISCUSSION

With the help of eqs 12, we can use experimental data instead of computer simulations to directly address the role of interionic motional coupling in conductivity. The first thing one notices by analyzing Figure 1 is that, at all times, all distinct diffusion coefficients are *negative*. The exact same thing can be derived using eqs 12 from the experiments of Tokuda et al.[6] and also the results in ref 9. Experimentally measured self-diffusion coefficients and distinct diffusion coefficients derived using eqs 12 are shown in Figure 2 for the family of $[C_nmim][NTf_2]$ RTILs at 300 K. Figures 1 and 2 indicate that, on average, independent of whether ions are of the same or opposite charge, their motion is anticorrelated. This point requires further clarification. It is not that any particular pair of ions has anticorrelated motion; instead, the motion of any given positive or negative ion is on average anticorrelated with respect to the overall motion of all other cations and anions. Equations 8a and 8b predict that distinct diffusion coefficients can never be simultaneously negligible. Figure 2 confirms that the distinct diffusion coefficients in the case of $[C_nmim][NTf_2]$ at 300 K are of the same order of magnitude as the corresponding self diffusion coefficients. This has important implications in our understanding of the validity of the NE approximation. As discussed in section 3.1 in the case of ionic liquids and molten salts, the NE approximation can only hold true in the case of cancellations in eq 9 but never because
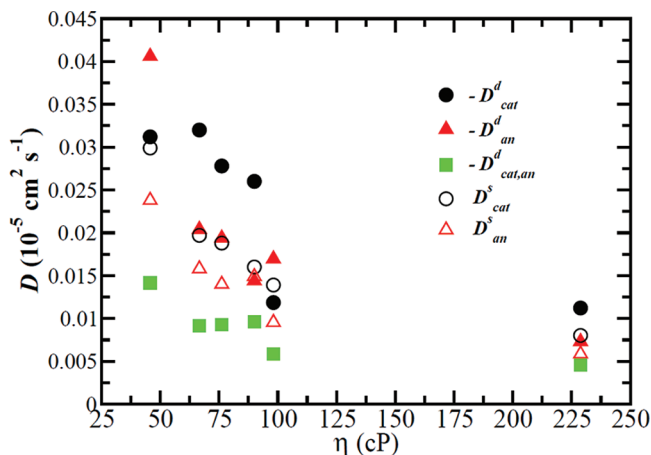

Figure 3. Self -and distinct diffusion coefficients for $[C_4mim][X]$ at 300 K vs the shear viscosity of each ionic liquid. The anions from left (lowest viscosity) to right (highest viscosity) are X = NTf_2^-, $CF_3CO_2^-$, $CF_3SO_3^-$, BF_4^-, $(C_2F_5SO_2)_2N^-$, and PF_6^-.

of negligible coupling between ions. We show in section 4.1 that because of the momentum buffering ability of the solvent in an electrolyte solution, $D_{cat,an}^d$ does not need to be negative.

Figure 3 shows distinct diffusion coefficients derived using eqs 12 from the experimental data of Tokuda et al.[5] for the family of $[C_4mim][X]$ ionic liquids. Just as in the case of Figure 2, here also distinct diffusion coefficients are negative and scale with viscosity. Perhaps the most interesting question that should be posed from a technological perspective is which RTILs will be the ones with highest conductivity. The answer to this question is not simple, but one can start by noticing that in the case of typical monovalent RTILs eq 11 predicts that maximum conductivity, which occurs when $\Delta' = 0$, will happen when the cation−anion distinct diffusion coefficient is equal to the average of the cation−cation and anion−anion distinct diffusion coefficients. In all cases shown in Figures 2 and 3, we see that cation−anion distinct diffusion coefficients are significantly below the semisum of the cation−cation and anion−anion distinct diffusion coefficients.

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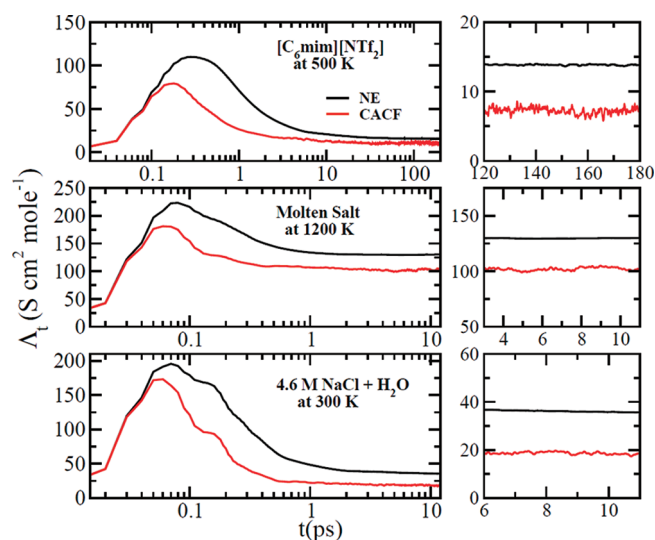
Figure 4. Comparison of the time-dependent molar ionic conductivity obtained from simulations using the Nernst–Einstein equation (equivalent to NMR measurements) and current autocorrelation function (equivalent to impedance measurements) in the case of an ionic liquid, a molten salt, and an electrolyte solution. On the right panels we show the convergence of the molar conductivities at longer times. In all panels black lines correspond to NE, and red lines correspond to CACF.
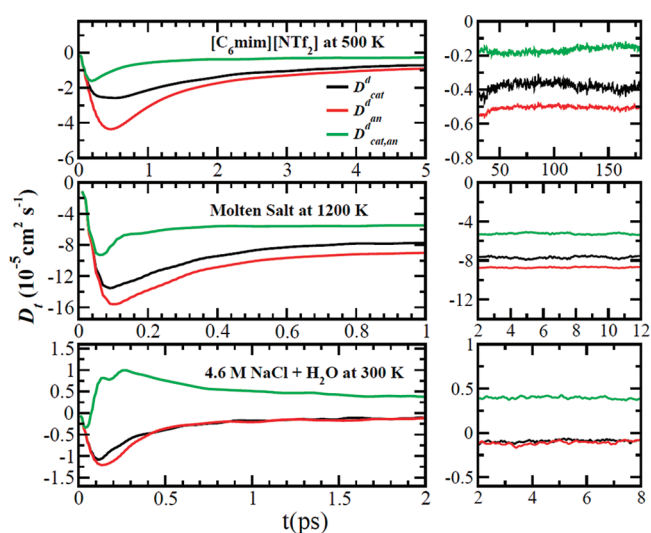

Figure 5. Time dependent distinct diffusion coefficients D_t computed from distinct velocity correlation functions for an ionic liquid, a high temperature molten salt, and an electrolyte solution. On the right panels we show the convergence of the time dependent transport coefficients at long times.

4.1. Physical Origin of the Decrease in Conductivity with Respect to the Nernst–Einstein Equation Is Different in Electrolyte Solutions and Ionic Liquids.

Ionic liquids and molten salts must satisfy momentum balance conditions, and this imposes certain constraints on the motion of the ions. In electrolyte solutions, the situation is different because there is a major third component which can counterbalance ionic motion.

Figure 4 shows that in ionic liquids, molten salts, and electrolyte solutions, NE derived conductivities are always higher than those obtained from direct conductivity calculations (by the same token, NMR derived conductivities are always higher than those obtained from impedance measurements). This seemingly identical phenomenon is of very different origin in electrolyte solutions and pure liquid salts. Whereas $D_{cat,an}^d$ is negative definite (as per eq 12) in the case of ionic liquids and molten salts, Figure 5 clearly shows that this is by no means the case in electrolyte solutions.

In electrolyte solutions, at very short times, $D_{cat,an}^d$ (defined in the barycentric reference frame) appears to be negative but soon after it becomes positive and its long time asymptote is larger than zero. This positively correlated motion is the signature of what one would intuitively understand as short-lived ion-pairing. One expects this correlation to be mostly local since the solvent screens the interaction of ions at long distance. What is peculiar about pure salts is that the cation–anion distinct diffusion coefficient, $D_{cat,an}^d$, is (by eq 12a) always negative, and this implies cation–anion anticorrelated motion.

Figure 5 shows that, in the cases of the electrolyte solution, ionic liquid, and molten salt studied here, anion–anion and cation–cation time dependent distinct diffusion coefficients are always negative. Therefore, in these systems the motion of ions of the same charge is on average anticorrelated.

Anticorrelated motion of ions of the same charge in conjunction with positively correlated cation–anion motion results in a decrease in conductivity in the case of electrolyte solutions. The origin of the decrease in conductivity in ILs and pure molten salts
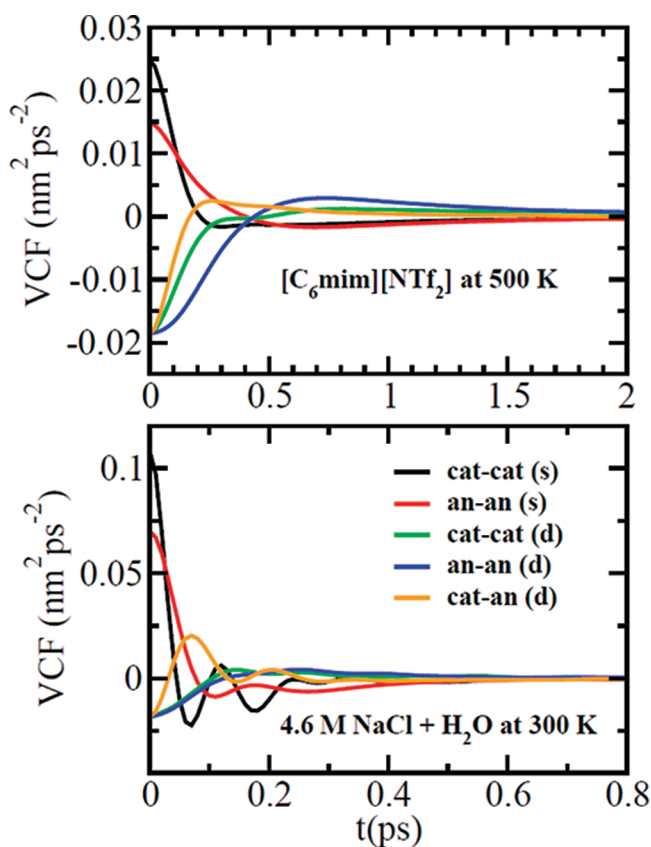
Figure 6. Comparison of self and distinct velocity correlation functions in ionic liquid and concentrated solution of NaCl in water. Notice that these plots include the $^1/_3$ factor in eqs A6–A10.

is different. In the case of ionic liquids and molten salts the decrease in conductivity is due to overall anticorrelated motion of ions of the same charge. In fact the motion of ions of opposite charge enhances the conductivity in these systems! We emphasize that

since $D_{\text{cat,an}}^{\text{d}}$ is negative in all proper internal reference frames (see Appendix D), this observation is quite general.

4.2. Self- and Distinct Velocity Time Correlation Functions. Self and distinct diffusion coefficients are derived from integrals of ensemble averaged velocity correlation functions. Figure 6 shows these correlation functions which after integration over time produce the time dependent diffusion coefficients shown in Figure 5. Clearly, in the case of the electrolyte solution, cationic—anionic motion starts anticorrelated followed by a longer period of fairly large amplitude positively correlated motion. Subsequent oscillations of this function are of small amplitude, and the integral of this function is dominated by the positive period resulting in an overall positive distinct diffusion coefficient that decreases conductivity.

In contrast we see in the top part of Figure 6 that the integral of the cation—anion velocity correlation function in the case of the ionic liquid (and molten salt, not shown) is dominated by initial anticorrelated motion that never gets significantly offset by later positively correlated contributions. This results in cation—anion correlations increasing the conductivity of the ionic liquid.

Both in the case of the electrolyte solution and ionic liquid, the overall anion—anion and cation—cation distinct correlation coefficients contribute to a decrease in conductivity. This can be explained because initial negative values of the velocity correlation function never get compensated by later positive values resulting in integrals that are overall negative.

It is also apparent from Figure 6 that motion in the ionic liquid is initially overdamped, but long tails in the VCFs decay very slowly to zero.

5. CONCLUSIONS

In this article we have shown that conductivities derived from impedance measurements and self-diffusion coefficients derived from NMR can be used to establish the value of distinct diffusion coefficients in the barycentric reference frame for ionic liquids. This study has allowed us to appreciate that the origin of the decrease in impedance conductivity with respect to NMR derived conductivity in the case of ionic liquids is very different from that in the case of ionic solutions. In the case of electrolyte solutions, correlated motion of opposite charge ions contributes to the decrease in conductivity, whereas anticorrelated motion of ions of opposite charge increases the conductivity in the case of ionic liquids and molten salts. We therefore conclude that cation—anion motional coupling decreases conductivity in the case of electrolyte solutions whereas it increases conductivity in the case of pure salts and RTILs. On the other hand, our simulations on RTILs, high temperature molten salt, and electrolyte solution indicate that cation—cation and anion—anion motion is anticorrelated and hence decreases conductivity. From a theoretical perspective we rigorously establish that in the case of pure salts and RTILs the Nernst—Einstein approximation can only apply because of a large number cancellations, but never because of small correlations between charged particles. One should be cautious when invoking this approximation in the case of RTILs and salts.

■ APPENDIX

A. Conductivity of Pure Salts in the Linear Response Regime. The Green—Kubo expression for the static or zero frequency conductivity in the linear response regime is[75]

$$\sigma_{\text{CACF}} = \lim_{\omega \to 0} \sigma(\omega) = \frac{1}{3k_{\text{B}}TV}\int_0^\infty \left\langle \vec{J}(t)\cdot\vec{J}(t=0)\right\rangle \mathrm{d}t \tag{A1}$$

where $\vec{J}(t)$ is microscopic charge current defined as

$$\vec{J}(t) = e\sum_{i=1}^{N} z_i\,\vec{v}_i(t)$$

$$= e\sum_{i_{cat}=1}^{N_{cat}} z_{cat}\,\vec{v}_{i_{cat}}(t) + e\sum_{i_{an}=1}^{N_{an}} z_{an}\,\vec{v}_{i_{an}}(t) \tag{A2}$$

Substituting the second equality of eq A2 in eq A1 we get

$$\sigma_{\text{CACF}} = \frac{e^2}{3k_{\text{B}}TV}\left[\begin{array}{l}\int_0^\infty \left\langle z_{cat}^2 \sum_{i_{cat}=1}^{N_{cat}}\sum_{j_{cat}=1}^{N_{cat}} \vec{v}_{i_{cat}}(t)\cdot\vec{v}_{j_{cat}}(t=0)\right\rangle \mathrm{d}t + \int_0^\infty \left\langle z_{an}^2 \sum_{i_{an}=1}^{N_{an}}\sum_{j_{an}=1}^{N_{an}} \vec{v}_{i_{an}}(t)\cdot\vec{v}_{j_{an}}(t=0)\right\rangle \mathrm{d}t \\ + \int_0^\infty \left\langle z_{cat}z_{an}\sum_{i_{cat}=1}^{N_{cat}}\sum_{j_{an}=1}^{N_{an}} \vec{v}_{i_{cat}}(t).\vec{v}_{j_{an}}(t=0)\right\rangle \mathrm{d}t + \int_0^\infty \left\langle z_{an}z_{cat}\sum_{i_{an}=1}^{N_{an}}\sum_{j_{cat}=1}^{N_{cat}} \vec{v}_{i_{an}}(t)\cdot\vec{v}_{j_{cat}}(t=0)\right\rangle \mathrm{d}t\end{array}\right] \tag{A3}$$

Separating the self ($i_{\text{cat}}=j_{\text{cat}}$ and $i_{\text{an}}=j_{\text{an}}$) and distinct ($i_{\text{cat}}\neq j_{\text{cat}}$ and $i_{\text{an}}\neq j_{\text{an}}$) parts in eq A3 and multiplying and dividing by the total number of ions N we get

$$\sigma_{\text{CACF}} = \frac{e^2 N}{3k_{\text{B}}TV}\left[\begin{array}{l}\int_0^\infty \left\langle \frac{N_{cat}}{N}z_{cat}^2\frac{1}{N_{cat}}\sum_{i_{cat}=1}^{N_{cat}} \vec{v}_{i_{cat}}(t)\cdot\vec{v}_{i_{cat}}(t=0)\right\rangle \mathrm{d}t + \int_0^\infty \left\langle \frac{N_{cat}^2}{N^2}z_{cat}^2\frac{N}{N_{cat}^2}\sum_{i_{cat}=1}^{N_{cat}}\sum_{j_{cat}\neq i_{cat}}^{N_{cat}} \vec{v}_{i_{cat}}(t)\cdot\vec{v}_{j_{cat}}(t=0)\right\rangle \mathrm{d}t + \\ \int_0^\infty \left\langle \frac{N_{an}}{N}z_{an}^2\frac{1}{N_{an}}\sum_{i_{an}=1}^{N_{an}} \vec{v}_{i_{an}}(t)\cdot\vec{v}_{i_{an}}(t=0)\right\rangle \mathrm{d}t + \int_0^\infty \left\langle \frac{N_{an}^2}{N^2}z_{an}^2\frac{N}{N_{an}^2}\sum_{i_{an}=1}^{N_{an}}\sum_{j_{an}\neq i_{an}}^{N_{an}} \vec{v}_{i_{an}}(t)\cdot\vec{v}_{j_{an}}(t=0)\right\rangle \mathrm{d}t + \\ \int_0^\infty \left\langle \frac{N_{cat}N_{an}}{N^2}z_{cat}z_{an}\frac{N}{N_{cat}N_{an}}\sum_{i_{cat}=1}^{N_{cat}}\sum_{j_{an}=1}^{N_{an}} \vec{v}_{i_{cat}}(t)\cdot\vec{v}_{j_{an}}(t=0)\right\rangle \mathrm{d}t + \\ \int_0^\infty \left\langle \frac{N_{an}N_{cat}}{N^2}z_{an}z_{cat}\frac{N}{N_{an}N_{cat}}\sum_{i_{an}=1}^{N_{an}}\sum_{j_{cat}=1}^{N_{cat}} \vec{v}_{i_{an}}(t)\cdot\vec{v}_{j_{cat}}(t=0)\right\rangle \mathrm{d}t\end{array}\right] \tag{A4}$$

Invoking microscopic reversibility and noticing that velocities are odd functions under time reversal symmetry we obtain eq A5 which is the same as eq 3 in the main text.

$$\sigma_{\text{CACF}} = \frac{\rho e^2}{k_B T}[x_{\text{cat}}z_{\text{cat}}^2 D_{\text{cat}}^s + x_{\text{an}}z_{\text{an}}^2 D_{\text{an}}^s + x_{\text{cat}}^2 z_{\text{cat}}^2 D_{\text{cat}}^d$$

$$+ x_{\text{an}}^2 z_{\text{an}}^2 D_{\text{an}}^d + 2x_{\text{cat}}x_{\text{an}}z_{\text{cat}}z_{\text{an}}D_{\text{cat, an}}^d] \qquad (A5)$$

The self (D_{cat}^s, D_{an}^s) and distinct (D_{cat}^d, D_{an}^d, and $D_{\text{cat,an}}^d$) diffusion coefficients are defined as

$$D_{\text{cat}}^s = \frac{1}{3}\int_0^\infty \left\langle \vec{v}_{\text{cat}}^s(t)\cdot\vec{v}_{\text{cat}}^s(t=0)\right\rangle dt$$

$$= \frac{1}{3}\int_0^\infty \left\langle \frac{1}{N_{\text{cat}}}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{i_{\text{cat}}}(t=0)\right\rangle dt \qquad (A6)$$

$$D_{\text{an}}^s = \frac{1}{3}\int_0^\infty \left\langle \vec{v}_{\text{an}}^s(t)\cdot\vec{v}_{\text{an}}^s(t=0)\right\rangle dt$$

$$= \frac{1}{3}\int_0^\infty \left\langle \frac{1}{N_{\text{an}}}\sum_{i_{\text{an}}=1}^{N_{\text{an}}}\vec{v}_{i_{\text{an}}}(t)\cdot\vec{v}_{i_{\text{an}}}(t=0)\right\rangle dt \qquad (A7)$$

$$D_{\text{cat}}^d = \frac{1}{3}\int_0^\infty \{N\langle \vec{v}_{\text{cat}}^d(t)\cdot\vec{v}_{\text{cat}}^d(t=0)\rangle\} dt$$

$$= \frac{1}{3}\int_0^\infty \left\{N\left\langle \frac{1}{N_{\text{cat}}(N_{\text{cat}}-1)}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\sum_{j_{\text{cat}}\neq i_{\text{cat}}}^{N_{\text{cat}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{j_{\text{cat}}}(t=0)\right\rangle\right\} dt$$

$$\approx \frac{1}{3}\int_0^\infty \left\{N\left\langle \frac{1}{N_{\text{cat}}^2}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\sum_{j_{\text{cat}}\neq i_{\text{cat}}}^{N_{\text{cat}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{j_{\text{cat}}}(t=0)\right\rangle\right\} dt \qquad (A8)$$

$$D_{\text{an}}^d = \frac{1}{3}\int_0^\infty \{N\langle \vec{v}_{\text{an}}^d(t)\cdot\vec{v}_{\text{an}}^d(t=0)\rangle\} dt$$

$$= \frac{1}{3}\int_0^\infty \left\{N\left\langle \frac{1}{N_{\text{an}}(N_{\text{an}}-1)}\sum_{i_{\text{an}}=1}^{N_{\text{an}}}\sum_{j_{\text{an}}\neq i_{\text{an}}}^{N_{\text{an}}}\vec{v}_{i_{\text{an}}}(t)\cdot\vec{v}_{j_{\text{an}}}(t=0)\right\rangle\right\} dt$$

$$\approx \frac{1}{3}\int_0^\infty \left\{N\left\langle \frac{1}{N_{\text{an}}^2}\sum_{i_{\text{an}}=1}^{N_{\text{an}}}\sum_{j_{\text{an}}\neq i_{\text{an}}}^{N_{\text{an}}}\vec{v}_{i_{\text{an}}}(t)\cdot\vec{v}_{j_{\text{an}}}(t=0)\right\rangle\right\} dt \qquad (A9)$$

$$D_{\text{cat, an}}^d = \frac{1}{3}\int_0^\infty \{N\langle \vec{v}_{\text{cat}}^d(t)\cdot\vec{v}_{\text{an}}^d(t=0)\rangle\} dt$$

$$= \frac{1}{3}\int_0^\infty \left\{N\left\langle \frac{1}{N_{\text{cat}}N_{\text{an}}}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\sum_{j_{\text{an}}=1}^{N_{\text{an}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{j_{\text{an}}}(t=0)\right\rangle\right\} dt \qquad (A10)$$

where $\langle...\rangle$ means an equilibrium ensemble average and $\{...\}$ is the thermodynamic limit operation. The second equalities in eqs A6, A7, and A10 and the third equalities in eqs A8 and A9 correspond to the formulas used to calculate these transport coefficients from the data collected in the molecular dynamics simulations.

After further rearranging the terms in eq A5, a more convenient representation of electrical conductivity is obtained[75]

$$\sigma_{\text{CACF}} = \frac{\rho e^2}{k_B T}[x_{\text{cat}}z_{\text{cat}}^2 D_{\text{cat}}^s + x_{\text{an}}z_{\text{an}}^2 D_{\text{an}}^s] \times [1-\Delta] \qquad (A11)$$

where

$$\Delta = -\frac{[x_{\text{cat}}^2 z_{\text{cat}}^2 D_{\text{cat}}^d + x_{\text{an}}^2 z_{\text{an}}^2 D_{\text{an}}^d + 2x_{\text{cat}}x_{\text{an}}z_{\text{cat}}z_{\text{an}}D_{\text{cat, an}}^d]}{[x_{\text{cat}}z_{\text{cat}}^2 D_{\text{cat}}^s + x_{\text{an}}z_{\text{an}}^2 D_{\text{an}}^s]} \qquad (A12)$$

The conductivity estimate that can be obtained from NMR self-diffusion experiments, known as the Nernst−Einstein (NE) equation for the conductivity, is obtained from eq A11 by making $\Delta = 0$; i.e.

$$\sigma_{\text{NE}} = \frac{\rho e^2}{k_B T}[x_{\text{cat}}z_{\text{cat}}^2 D_{\text{cat}}^s + x_{\text{an}}z_{\text{an}}^2 D_{\text{an}}^s] \qquad (A13)$$

B. Momentum Conservation Law for Ionic Liquids and Molten Salts.

In the molecular dynamics ensemble the condition $\vec{w}_M = 0$ is enforced at every time in the simulation run. This corresponds to linear momentum conservation for the simulated system in the particular case that the total momentum is zero. This implies that in the molecular dynamics ensemble the velocities of the ions are linearly related at all times. In particular we have that

$$m_{\text{cat}}\sum_{j_{\text{cat}}=1}^{N_{\text{cat}}}\vec{v}_{j_{\text{cat}}}(t=0) = -m_{\text{an}}\sum_{j_{\text{an}}=1}^{N_{\text{an}}}\vec{v}_{j_{\text{an}}}(t=0) \qquad (B1)$$

Taking the dot product with $\vec{v}_{i_{\text{cat}}}(t)$ on both sides of eq B1 and summing over all i_{cat} we obtain

$$\frac{m_{\text{cat}}}{3N_{\text{cat}}^2}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\sum_{j_{\text{cat}}=1}^{N_{\text{cat}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{j_{\text{cat}}}(t=0)$$

$$= -\frac{m_{\text{an}}}{3N_{\text{cat}}N_{\text{an}}}\frac{N_{\text{an}}}{N_{\text{cat}}}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\sum_{j_{\text{an}}=1}^{N_{\text{an}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{j_{\text{an}}}(t=0) \qquad (B2)$$

Multiplying both sides by N and rearranging we obtain

$$m_{\text{cat}}\frac{N}{3N_{\text{cat}}^2}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\sum_{j_{\text{cat}}=1}^{N_{\text{cat}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{j_{\text{cat}}}(t=0)$$

$$= -m_{\text{an}}\frac{N_{\text{an}}}{N_{\text{cat}}}\frac{N}{3N_{\text{cat}}N_{\text{an}}}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\sum_{j_{\text{an}}=1}^{N_{\text{an}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{j_{\text{an}}}(t=0) \qquad (B3)$$

Taking the equilibrium average over the molecular dynamics ensemble, and formally applying the thermodynamic operation, we derive

$$m_{\text{cat}}\left[\frac{N}{3N_{\text{cat}}}\left\langle\frac{1}{N_{\text{cat}}}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{i_{\text{cat}}}(t=0)\right\rangle\right.$$

$$\left.+\frac{1}{3}\left\{N\left\langle\frac{1}{N_{\text{cat}}^2}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\sum_{j_{\text{cat}}\neq i_{\text{cat}}}^{N_{\text{cat}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{j_{\text{cat}}}(t=0)\right\rangle\right\}\right]$$

$$= -m_{\text{an}}\frac{N_{\text{an}}}{3N_{\text{cat}}}\left\{N\left\langle\frac{1}{N_{\text{cat}}N_{\text{an}}}\sum_{i_{\text{cat}}=1}^{N_{\text{cat}}}\sum_{j_{\text{an}}=1}^{N_{\text{an}}}\vec{v}_{i_{\text{cat}}}(t)\cdot\vec{v}_{j_{\text{an}}}(t=0)\right\rangle\right\} \qquad (B4)$$

or

$$m_{cat}\left[\frac{1}{3x_{cat}}\langle\,\vec{v}^{\,s}_{cat}(t)\cdot\vec{v}^{\,s}_{cat}(t=0)\rangle+\frac{1}{3}\{N\langle\,\vec{v}^{\,d}_{cat}(t)\cdot\vec{v}^{\,d}_{cat}(t=0)\rangle\}\right]$$
$$=-m_{an}\frac{x_{an}}{3x_{cat}}\{N\langle\,\vec{v}^{\,d}_{cat}(t)\cdot\vec{v}^{\,d}_{an}(t=0)\rangle\} \tag{B5}$$

which is equivalent to

$$m_{cat}\left[\frac{1}{3}\langle\,\vec{v}^{\,s}_{cat}(t)\cdot\vec{v}^{\,s}_{cat}(t=0)\rangle+\frac{x_{cat}}{3}\{N\langle\,\vec{v}^{\,d}_{cat}(t)\cdot\vec{v}^{\,d}_{cat}(t=0)\rangle\}\right]$$
$$=-m_{an}\frac{x_{an}}{3}\{N\langle\,\vec{v}^{\,d}_{cat}(t)\cdot\vec{v}^{\,d}_{an}(t=0)\rangle\} \tag{B6}$$

Similarly, multiplying both sides of eq B1 by $\vec{v}_{i_{an}}(t)$, summing over all i_{an}, and noticing that velocity is an odd function of time, from time reversal symmetry (i.e., $\langle\vec{v}^{\,d}_{cat}(t)\cdot\vec{v}^{\,d}_{an}(t=0)\rangle=\langle\vec{v}^{\,d}_{an}(t)\cdot\vec{v}^{\,d}_{cat}(t=0)\rangle$) we obtain eq B7:

$$m_{an}\left[\frac{1}{3}\langle\,\vec{v}^{\,s}_{an}(t)\cdot\vec{v}^{\,s}_{an}(t=0)\rangle+\frac{x_{an}}{3}\{N\langle\,\vec{v}^{\,d}_{an}(t)\cdot\vec{v}^{\,d}_{an}(t=0)\rangle\}\right]$$
$$=-m_{cat}\frac{x_{cat}}{3}\{N\langle\,\vec{v}^{\,d}_{cat}(t)\cdot\vec{v}^{\,d}_{an}(t=0)\rangle\} \tag{B7}$$

Integration of eqs B6 and B7 with respect to time results in eqs B8, which are eqs 8 in the main text.

$$m_{cat}[D^s_{cat}+x_{cat}D^d_{cat}]=-m_{an}x_{an}D^d_{cat,\,an} \tag{B8a}$$

$$m_{an}[D^s_{an}+x_{an}D^d_{an}]=-m_{cat}x_{cat}D^d_{cat,\,an} \tag{B8b}$$

C. Deriving the Distinct Diffusion Coefficients in the Case of RTILs and Molten Salts from NMR Diffusivities and Impedance Conductivities. We start by defining Δ' as

$$\Delta'=\frac{\Lambda_{imp}-\Lambda_{NMR}}{\rho e^2/ck_BT} \tag{C1}$$

From eq A5 we have

$$x^2_{cat}z^2_{cat}D^d_{cat}+x^2_{an}z^2_{an}D^d_{an}+2x_{cat}x_{an}z_{cat}z_{an}D^d_{cat,\,an}=\Delta' \tag{C2}$$

Inserting the values of D^d_{cat} and D^d_{an} from eqs B8a and B8b, into C2, we obtain

$$D^d_{cat,\,an}=-\frac{m_{cat}m_{an}[\Delta'+x_{cat}z^2_{cat}D^s_{cat}+x_{an}z^2_{an}D^s_{an}]}{x_{cat}x_{an}[z_{cat}m_{an}-z_{an}m_{cat}]^2}$$
$$=-\frac{m_{cat}m_{an}\Lambda_{imp}}{(\rho e^2/ck_BT)x_{cat}x_{an}[z_{cat}m_{an}-z_{an}m_{cat}]^2} \tag{C3a}$$

The second equality in the above equation has been obtained via the use of eqs A5, A13, C1, and C2.

Similarly, from eqs A5, A13, B8, C1, and C2, we obtain D^d_{cat} and D^d_{an}

$$D^d_{cat}=-\left[\frac{D^s_{cat}}{x_{cat}}-\frac{m^2_{an}[\Delta'+x_{cat}z^2_{cat}D^s_{cat}+x_{an}z^2_{an}D^s_{an}]}{x^2_{cat}[z_{cat}m_{an}-z_{an}m_{cat}]^2}\right]$$
$$=-\left[\frac{D^s_{cat}}{x_{cat}}-\frac{m^2_{an}\Lambda_{imp}}{(\rho e^2/ck_BT)x^2_{cat}[z_{cat}m_{an}-z_{an}m_{cat}]^2}\right] \tag{C3b}$$

$$D^d_{an}=-\left[\frac{D^s_{an}}{x_{an}}-\frac{m^2_{cat}[\Delta'+x_{cat}z^2_{cat}D^s_{cat}+x_{an}z^2_{an}D^s_{an}]}{x^2_{an}[z_{cat}m_{an}-z_{an}m_{cat}]^2}\right]$$
$$=-\left[\frac{D^s_{an}}{x_{an}}-\frac{m^2_{cat}\Lambda_{imp}}{(\rho e^2/ck_BT)x^2_{an}[z_{cat}m_{an}-z_{an}m_{cat}]^2}\right] \tag{C3c}$$

Equations C3 are eqs 12 in the main text.

D. $D^d_{cat,an}$ Is Negative in Any Proper Reference Frame. In this section we first prove that the conductivity is independent of the choice of any proper internal reference frame and then show that $D^d_{cat,an}$ is negative for arbitrary internal reference frames.

Similar to eq 2 in the main text we can write the expression for the charge current as

$$\vec{J}(t)=e\sum_{i=1}^N z_i\vec{v}_i(t)=e\left[z_{cat}N_{cat}\left(\frac{1}{N_{cat}}\sum_{i_{cat}=1}^{N_{cat}}\vec{v}_{i_{cat}}(t)\right)\right.$$
$$\left.+z_{an}N_{an}\left(\frac{1}{N_{an}}\sum_{i_{an}=1}^{N_{an}}\vec{v}_{i_{an}}(t)\right)\right] \tag{D1}$$

Note that here velocity $\vec{v}_i(t)$ is defined relative to laboratory reference frame (or the origin of the simulation cell).

From the electroneutrality condition

$$z_{cat}N_{cat}+z_{an}N_{an}=z_{cat}x_{cat}+z_{an}x_{an}=0 \tag{D2}$$

we have

$$\vec{J}(t)=e[z_{cat}N_{cat}\vec{v}_{cat}(t)+z_{an}N_{an}\vec{v}_{an}(t)]$$
$$=ez_{cat}N_{cat}[\vec{v}_{cat}(t)-\vec{v}_{an}(t)]$$
$$=ez_{cat}N_{cat}\vec{v}^e(t) \tag{D3}$$

where we have defined

$$\vec{v}_{cat}(t)=\left(\frac{1}{N_{cat}}\sum_{i_{cat}=1}^{N_{cat}}\vec{v}_{i_{cat}}(t)\right) \tag{D4}$$

$$\vec{v}_{an}(t)=\left(\frac{1}{N_{an}}\sum_{i_{an}=1}^{N_{an}}\vec{v}_{i_{an}}(t)\right) \tag{D5}$$

$$\vec{v}^e(t)=[\vec{v}_{cat}(t)-\vec{v}_{an}(t)] \tag{D6}$$

From eqs 1 and D3 we obtain

$$\sigma_{CACF}=\frac{\rho e^2 z^2_{cat}x^2_{cat}}{3k_BT}\int_0^\infty\{N\langle\,\vec{v}^e(t)\cdot\vec{v}^e(t=0)\rangle\}\,dt \tag{D7}$$

Notice that the conductivity is independent of the choice of the reference frame as it can be expressed in terms of the relative velocity $\vec{v}^e(t)$ where the reference velocity cancels by subtraction.

The expression for cation–anion distinct diffusion coefficient in any proper reference frame R can be written as[51]

$$D^{dR}_{cat,\,an}=\frac{1}{3}\int_0^\infty\{N\langle[\,\vec{v}_{cat}(t)-\vec{w}_R(t)]$$
$$\cdot[\,\vec{v}_{an}(t=0)-\vec{w}_R(t=0)]\rangle\}\,dt \tag{D8}$$

where the microscopic reference velocity $\vec{w}_R(t)$ is defined as

$$\vec{w}_R(t)=a^R_{cat}\vec{v}_{cat}(t)+a^R_{an}\vec{v}_{an}(t) \tag{D9a}$$

$$a^R_{cat} + a^R_{an} = 1; \qquad a^R_{cat}, \ a^R_{an} \geq 0 \qquad (D9b)$$

a^R_{cat} and a^R_{an} are the corresponding weights that specify the microscopic reference velocity.[77−79]

From eqs D6 and D9 one can obtain

$$\vec{v}_{cat}(t) - \vec{w}_R(t) = a^R_{an} \vec{v}^e(t) \qquad (D10a)$$

$$\vec{v}_{an}(t) - \vec{w}_R(t) = -a^R_{cat} \vec{v}^e(t) \qquad (D10b)$$

Inserting eqs D10 into D8 we obtain

$$D^{dR}_{cat,\,an} = -\frac{a^R_{cat} a^R_{an}}{3} \int_0^\infty \{ N \langle \vec{v}^e(t) \cdot \vec{v}^e(t=0) \rangle \} \, dt \qquad (D11)$$

From eqs D7 and D11 we get

$$D^{dR}_{cat,\,an} = -\frac{a^R_{cat} a^R_{an} k_B T}{\rho e^2 z^2_{cat} x^2_{cat}} \sigma_{CACF} \qquad (D12)$$

Using the electroneutrality condition (eq D2) one can derive eq D13.

$$D^{dR}_{cat,\,an} = -\frac{a^R_{cat} a^R_{an} k_B T}{\rho e^2 x_{cat} x_{an} |z_{cat} z_{an}|} \sigma_{CACF} \qquad (D13)$$

This implies that, unless the conductivity is zero, $D^{dR}_{cat,an} < 0$ in any internal reference frame.

In an arbitrary internal reference frame, eq 11 becomes $x^2_{cat} z^2_{cat} D^{dR}_{cat} + x^2_{an} z^2_{an} D^{dR}_{an} + 2x_{cat} x_{an} z_{cat} z_{an} D^{dR}_{cat,an} = \Delta'$ (see eq 26 of ref 53). Since $z_{cat} z_{an} < 0$, in the case of single binary molten salts and ILs the contribution of $D^{dR}_{cat,an}$ to Δ' will always be positive, and therefore, it will always increase the conductivity.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: claudio-margulis@uiowa.edu.

■ ACKNOWLEDGMENT

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