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Molecular dynamics simulation of imidazolium-based ionic liquids. I. Dynamics and diffusion coefficient

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Molecular dynamics simulations are used to study the dynamics and transport properties of 12 room-temperature ionic liquids of the 1-alkyl-3-methylimidazolium [amim]$^+$ (alkyl=methyl, ethyl, propyl, and butyl) family with PF_6^-, NO_3^-, and Cl^- counterions. The explicit atom transferable force field of Canongia Lopes *et al.* [J. Phys. Chem. B **108**, 2038 (2004)] is used in the simulations. In this first part, the dynamics of the ionic liquids are characterized by studying the mean-square displacement (MSD) and the velocity autocorrelation function (VACF) for the centers of mass of the ions at 400 K. Trajectory averaging was employed to evaluate the diffusion coefficients at two temperatures from the linear slope of MSD(t) functions in the range of 150–300 ps and from the integration of the VACF(t) functions at 400 K. Detailed comparisons are made between the diffusion results from the MSD and VACF methods. The diffusion coefficients from the integration of the VACFs are closer to experimental values than the diffusion coefficients calculated from the slope of MSDs. Both methods can show good agreement with experiment in predicting relative trends in the diffusion coefficients and determining the role of the cation and anion structures on the dynamical behavior of this family of ionic liquids. The MSD and self-diffusion of relatively heavier imidazolium cations are larger than those of the lighter anions from the Einstein results, except for the case of [bmim][Cl]. The cationic transference number generally decreases with temperature, in good agreement with experiments. For the same anion, the cationic transference numbers decrease with increasing length of the alkyl chain, and for the same cation, the trends in the cationic transference numbers are $[NO_3]^- < [Cl]^- < [PF_6]^-$. The trends in the diffusion coefficient in the series of cations with identical anions are $[emim]^+ > [pmim]^+ > [bmim]^+$ and those for anions with identical cations are $[NO_3]^- > [PF_6]^- > [Cl]^-$. The [dmim]$^+$ has a relatively low diffusion coefficient due to its symmetric structure and good packing in the liquid phase. The major factor for determining the magnitude of the self-diffusion is the geometric shape of the anion of the ionic liquid. Other important factors are the ion size and the charge delocalization in the anion. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3035978]

I. INTRODUCTION

Room-temperature ionic liquids (RTILs) are molten salts usually composed of relatively large organic cations and organic or inorganic anions which are liquid below 100 °C.[1–3] In the past decade there has been rapidly growing interest in ionic liquids because of their unique properties. Many RTILs are nonvolatile, nonflammable, and nonexplosive, possess high chemical and thermal stability, and have a large electrochemical potential window, high ionic conductivity, large liquid temperature range, and remarkable dissolution properties. Ionic liquids are often recyclable solvents for a range of organic, inorganic, organometallic, and polymeric material applications. They are immiscible with a number of organic solvents and can be used as alternatives to water in multiphase systems. Their low vapor pressure and high thermal stability make them potential substitutes for volatile organic solvents both in industry and academia. Although the ionic liquids themselves may have toxic properties and must be dealt with caution, the substitution of ionic liquids for traditional solvents could potentially have environmental benefits and save industry clean-up costs and lead to dramatic reductions in air pollution resulting from air-borne solvents. Nowadays, many ionic liquids are relatively easy to purchase and simple to prepare.

An important advantage of ionic liquids is the tunable physical and chemical properties of this family. Some of their physical and chemical properties[1–4] (e.g., density, viscosity, conductivity, melting point, solvation hydrophobicity, and hydrogen-bonding capability) can be tailored by the selection of suitable cations, anions, and substituent groups on the ions. In recent years, many articles and monographs have been published on ionic liquids with various emphases on the history of discovery,[5] properties,[3] experimental characterizations,[1,6,7] reactions,[1,6] and their interesting applications.[8–12]

The experimental study of ionic liquids is difficult due to large effects of common impurities such as water and chlo-

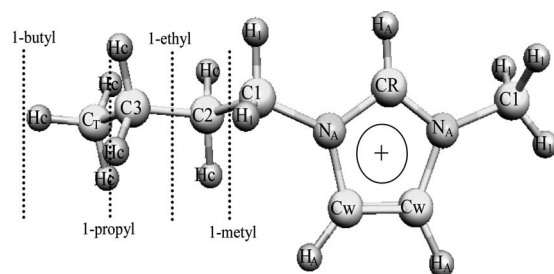a)Electronic mail: saman.alavi@nrc-cnrc.gc.ca.

FIG. 1. The atomic labels of the 1-alkyl-3-methylimidazolium cation according to the AMBER/OPLS scheme.

ride ions on the properties of these materials. Modeling and computational science could greatly aid in predicting properties and performance of ionic liquids. The computational studies of complex ionic liquids have initially focused on the molecular dynamics (MD) simulation of substituted imidazolium salts. Imidazolium-based ionic liquids, an important class of RTILs, are usually air and water stable and are used in a wide variety of applications. In this study, we modeled the ionic liquid family with 1-alkyl-3-methylimidazolium [amim]$^+$ cation, (alkyl=methyl, ethyl, propyl, and butyl, see Fig. 1), with counterions, PF$_6^-$, NO$_3^-$, and Cl$^-$. A total of 12 ionic liquids are simulated. One of the goals of this study is to systematically compare the dynamics and transport properties, such as the velocity autocorrelation function (VACF), mean-square displacement (MSD), diffusion coefficient, electrical conductivity, and viscosity of the imidazolium-based ionic liquids. These properties of the ionic liquids play a critical role in many applications of these compounds in electrochemical devices,[13] lubricants for heat transfer,[14,15] industrial solvents, stationary phases for high performance liquid chromotography (HPLC), or gas chromatography and matrix-assisted laser desorption/ionization (MALDI) matrices in mass spectroscopy.[16,17] Due to the vast number of different ionic liquids that can be synthesized by combining different cations and anions, demands for more detailed descriptions of the properties of these materials have increased. Despite the current level of research activity on ionic liquids, correlations between chemical structure and transport properties are still not completely understood. The second purpose of this work is to determine the effect of the cation and anion structures on the dynamic behavior and transport properties of the imidazolium-based ionic liquids. The third aim in this study is to compare the use of the slope of the MSD and the integration of the VACF methods for the numerical calculation of the diffusion coefficient.

The first publication of a specific force field and the MD simulation of the imidazolium-based ionic liquids appeared in 2001 for the [dmim][Cl] ionic liquid.[18] By 2004, a wide range of potentials and simulations for these compounds had been reported and this process has continued to the present. A number of different published force fields for RTILs have recently been comprehensively summarized.[19]

For this work, we needed a general transferable force field (instead of the specific force fields for individual ionic liquids) which was validated for the systematic study of imidazolium-based family. A general force field for a large class of dialkylimidazolium cations with PF$_6^-$, NO$_3^-$, and

Cl$^-$ anions was developed by Canongia Lopes *et al.*[20] in 2004. This transferable-ion force field was based on the optimized potential for liquid simulations-all atom/assisted model building with energy refinement (OPLS-AA/AMBER) framework. This force field was appropriate for performing the systematic set of simulations in this work. *Ab initio* calculations were performed to obtain torsion energy profiles and the distribution of atomic point charges. A detailed analysis of the validation and performance of this force field was carried out by comparing the simulated and experimental data of the ionic liquids in both the solid-state crystallographic data and liquid-state densities.[20] Simulated densities with this force field agreed with experiments with deviations between 1% and 5%. The parameters developed by Canongia Lopes *et al.*[20] have also been used as a basis for calculating melting point and liquid-state properties of [emim][PF$_6$] (Ref. 21) and the transport properties and solvation dynamics of [dmim][Cl] ionic liquid.[22]

A number of experimental studies of the dynamics and transport properties of imidazolium-based ionic liquids have been reported.[23–27] Computational studies of the dynamics and transport properties of this family of RTILs from the MD simulations have recently begun. In the following, we report MD simulations of imidazolium-based ionic liquids that were performed with the goal of computing dynamical and transport properties of this family.

In 2001, Hanke *et al.*[18] developed the first force field for imidazolium-based ionic liquids. In these simulations, the imidazolium rings were taken to be rigid and calculations with both united atom and explicit methyl group models were performed. The 192 [dmim]$^+$ or [emim]$^+$ cations with Cl$^-$ or PF$_6^-$ counterions were simulated at three temperatures (400, 450, and 500 K). The calculated MSDs and diffusion coefficients for [dmim][Cl] from the united atom and explicit methyl group models showed significant differences. Hanke *et al.*[18] stated that the dynamics in the liquid are greatly affected by the nature of the chloride-methyl group interactions and that the united atom model is not adequate to simulate the dynamic properties of ionic liquids. The diffusion coefficients reported in their work from both potential models are significantly different from more recent simulation studies in the literature (see below). Hanke *et al.*[18] calculated the MSDs from simulation data in the range of 5–100 ps, which may be too short for the onset of the diffusive regime.[28]

In 2002, Margulis *et al.*[29] computed the MSDs for [bmim][PF$_6$] at 303 K and determined the diffusion coefficients using the Einstein relation, $\lim_{t \to \infty} \text{MSD} = 6Dt$, in the linear range of 20–40 ps and estimated molar conductivities using the Nernst–Einstein relation. They initially equilibrated the system for 200 ps with an *NpT* simulation. The final configurations of the *NpT* simulations were used for starting production runs for 20 independent *NVE* simulations each of 50 ps time. The behavior of the MSDs for the centers of mass of the ions as a function of time indicated that the ionic liquid system exhibited slow and complex dynamics. The observed MSDs up to 40 ps consist of three different time scales: a fast process on a time scale of about 2–3 ps with quadratic time dependency indicating ballistic motion, then a

nonlinear intermediate-time motion, which is likely associated with basin hopping and related to "cage escape," and finally the long-time motion (after about 15 ps) due to diffusive linear behavior. Margulis et al.[29] also computed the MSD for ions from a simple generalized Langevin model and these results agreed with their simulation values. Because of the simplicity of the Langevin model, the intermediate region related to basin hopping is not described as well as the other regions. The calculated diffusion coefficients for the ions from the Einstein relation are about two orders of magnitude smaller than the diffusivity of simple molecular liquids such as water at the same temperature. This observation is in agreement with the results of other research groups[28,30] and is consistent with the fact that ionic liquids generally have a much higher viscosity than water. Their production runs of up to 50 ps are rather short and may not be adequate for determining the dynamics in ionic liquids.

Morrow and Maginn[28] used the combination of density functional theory calculations and the Chemistry in Harvard Macromolecular Mechanics (CHARMM) 22 force field[31] parameters in MD simulations of $[bmim][PF_6]$ at 298, 323, and 343 K. Dynamic properties were investigated by calculating the MSD, the diffusion coefficient, and the rotational time constant for the cations and anions from the long simulation runs of 3–4 ns. A block averaging technique was applied for calculating the MSDs. The diffusion coefficients were extracted for the cation and the anion from the Einstein relation using data in the range of 200–1000 ps. The mechanism for diffusion of the ions is described via the computation of the cage correlation functions. The validity of the calculated diffusion coefficient from MD simulation is tested with both of the Stokes–Einstein and random walk diffusion models.

The structure and dynamics of $[emim][NO_3]$ were studied by Del Pópolo and Voth[32] in 2004 using MD simulations. They used the AMBER (Ref. 33) and the Hanke et al.[18] force fields. The dynamical behaviors of the ions were determined by the VACFs, the MSDs, and the rotational orientation and electric-current autocorrelation functions. As in supercooled liquids, the behavior of the MSD as a function of time indicates three time regimes that are similar to the other studies of ionic liquids in the literature.[28,30] In a follow-up study, Yan et al.[34] added electronic polarizability to the force field and calculated the structural and dynamical properties with the polarizable and nonpolarizable force field models. The main observation was that including polarizability in the potential increases the calculated diffusion coefficients and mobility and substantially decreases the viscosity of the ions. The polarizable model results were in better agreement with the experimental values. Yan et al.[34] concluded that the inclusion of polarization effects in the force field are necessary for the accurate computation of dynamic properties.

Liu et al.[30] developed a refined force field for molecular simulation of imidazolium-based ionic liquids and they calculated the diffusion coefficients with the Einstein relation for some imidazolium salts.

Urahata and Ribeiro[35] proposed a new set of partial atomic charges for imidazolium cations obtained by a Mulliken analysis of ab initio calculations. They used the equilibrium bond lengths, angles, dihedral angle parameters, and

the corresponding force constants of Ref. 28 and the Lennard-Jones (LJ) parameters of Ref. 36. They also reported the united atom force field and studied the equilibrium structure of imidazolium-based ionic liquids. In a follow-up study, Urahata and Ribeiro studied microscopic dynamics in ten ionic liquids containing 1-alkyl-3-methylimidazolium cations with different alkyl substituents (1-methyl, 1-ethyl, 1-butyl, and 1-octyl), and F^-, Cl^-, Br^-, and PF_6^- anions from MD simulations at 400 K.[37] Calculations were performed with the united atom force field reported in their previous study.[35] The hydrogen atoms of the cation are not explicitly considered in these calculations but the ring is fully flexible and the anions are represented as a single LJ interaction site with a full -1 electrostatic charge. The dynamics behavior of the ions is determined by the MSD, diffusion coefficient, van Hove self-correlation function, reorientational time-correlation function, and vibrational density of states obtained by Fourier transforming the VACF. They observed that the MSD increases with the length of the alkyl chain from 1-metyl to 1-butyl, but then decreases for the 1-octyl derivatives. See below for a further discussion on this point. As a result, the relative magnitudes of the ionic displacements are generally consistent with the observed trends in the melting temperatures of these salts. However, they observed that the calculated MSD for $[bmim][Cl]$ is larger than that for $[bmim][PF_6]$, whereas the experimental melting point T_m of the former (340 K) is higher than that in the latter (279 K), see below for further discussion. They stated that the delocalization of charge in PF_6^- needs to be considered and representation of the anion as a single united atom is too simplistic. In spite of the smaller size and mass of the anions, the observed ionic displacements of the imidazolium cations were higher than those of the anions, as observed in some previous MD simulations. They stated that this could be mainly due to the less hindered dynamics along the direction of the C_R carbon (in the ring plane), which is located between the two nitrogen atoms in the imidazolium ring (see Fig. 1). The diffusion coefficients obtained are in the order of 10^{-11} $m^2 s^{-1}$, which is consistent with experimental values[25,26] and other computational work on RTILs with imidazolium cations.[28,29,32,38] However, as discussed above, some of the values seem problematic, particularly for $[emim][PF_6]$ and $[bmim][Cl]$. Urahata and Riberio stated that the diffusive regime develops after ~400 ps and so longer simulation runs may be required for these systems to get better equilibration. Additionally, the defects of the united atom force field and the simplicity of the PF_6^- anion shape (assumed to be a single LJ interaction site with full -1 charge) in this model may be sources of error. In their work, anisotropy is also observed in the reorientational dynamics of imidazolium cations, where the alkyl chain allows for librational motion of the imidazolium ring and the cation as a whole rotates slowly.

In 2005, Lee et al.[39] used the combination of ab initio calculations and the CHARMM 22 force field[31] parameters in MD simulation of the $[bmim][X]$ salts, with PF_6^-, CF_3COO^-, $C_3F_7COO^-$, $CF_3SO_3^-$, and $C_4F_9SO_3^-$ anions. The proposed force field was validated by calculating liquid densities, diffusion coefficients, and ionic conductivities. The

predicted densities of the systems from simulations were in good agreement with the experimental data with an average deviation of 3%. The ensemble-averaging method was used to calculate the MSDs and the self-diffusion coefficient was obtained from the Einstein relation. The calculated self-diffusion coefficient was generally about ten times smaller than in previous reports.[28,29] From the plots of the MSDs of centers of mass in this study, it could be that the systems had not fully converged.

In 2005, Bhargava and Balasubramanian[22] calculated the self-diffusion coefficient, shear viscosity, and electrical conductivity of [dmim][Cl] at 425 K using MD simulations. They also studied the solvation dynamics time-correlation function for dipolar and ionic probes using equilibrium simulations. Bhargava and Balasubramanian[22] employed the fully flexible, all-atom force field developed by Canongia Lopes *et al.*[20] and observed that in spite of the smaller mass of the chloride anions, the imidazolium cations diffuse faster than the chloride anions. They rationalized this observation by stating that the anion lies in a deeper potential well than that of the cation.

In 2006–2007, Rey-Castro *et al.*[40,41] published two articles on equilibrium MD simulations of the transport properties of 1-ethyl-3-methylimidazolium ionic liquids. In the first work,[40] they analyzed the temperature dependence of the self-diffusion, shear viscosity, and electrical conductivity of [emim][Cl] using the simple rigid model of Shim *et al.*[42] In the second work,[41] they studied the effect of two different force fields on the properties of [emim][Cl] and determined the influence of the anion type on the structural and transport properties of [emim][Cl], [emim][NO_3], and [emim][PF_6] ionic liquids. They used both the rigid model force field of Shim *et al.*[42] and the flexible model of Urahata and Ribeiro.[35] Rey-Castro *et al.*[41] observed that the VACFs are particularly sensitive to the relative sizes/masses of the anion and cation, but the self-diffusion coefficients from the integrated VACFs do not show significant differences between the Cl^-, NO_3^-, and PF_6^- salts. The different force fields for [emim][Cl] lead to diffusion rates that differ by one order of magnitude. Although the corresponding normalized VACFs agree almost exactly in all cases, the diffusion rates of the cation are higher than those of the anions, which is consistent with experimental data.[1,27,43]

In 2007, Bagno *et al.*[44] reported experimental NMR data and computer simulation results of the translational diffusion of the [bmim][BF_4] ionic liquid. They used the Canongia Lopes *et al.*[20] force field for [bmim]$^+$, while the force field for [BF_4]$^-$ was taken from Andrade *et al.*[38] Diffusion coefficients were calculated by linear fitting of the MSD(t) function in the range of 200–800 ps. The diffusion obtained from the MD simulations has the order of 10^{-12} m^2 s^{-1}, which is in acceptable agreement with the Diffusion-Ordered Spectroscopy (DOSY) NMR experimental results, which have the correct order of 10^{-11} m^2 s^{-1}. They also investigated the effect of pairwise additivity of the force field and found that nonadditive effects of the intermolecular interaction, particularly those related with the static polarizability, are quite substantial. Finally, they suggested that a polarizable force field needs to be used when dynamic properties are studied.

Picálek and Kolafa[45] performed a series of MD simulations of imidazolium-based ionic liquids using five different force fields obtained from literature.[18,20,30,35,36] They examined the temperature dependence of the self-diffusion coefficients and ionic conductivities of [bmim][BF_4], [bmim][PF_6], and [emim][PF_6]. They also reported the effect of force field type on the calculated transport properties of the [bmim][PF_6], and their results show the importance of the force field on the predicted values of these properties. They also observed slow dynamics in ionic liquids and they determined the diffusion coefficient to be in the order of 10^{-11} m^2 s^{-1}. These studies verified that the computation of dynamic properties of ionic liquids converged slowly, especially in the case of all-atom force fields where the large ions hinder each other's motion. Furthermore, they tested the finite-size effects using the all-atom force field by Canongia-Lopes *et al.*[20] for 100, 200, or 300 ion pairs of [bmim][PF_6]. The results of the diffusion coefficient were not influenced by the number of the particles under their simulation conditions.

In summary, since 2001 a number of research groups have calculated the dynamics and transport properties of imidazolium-based ionic liquids via MD simulations, but systematic investigations of the correlation between chemical structure and transport properties of ionic liquids have been rare,[37] and detailed microscopic information in this area is still not completely understood especially with explicit all-atom force fields. These simulations are rather costly and computationally demanding because of the large number of atoms in the imidazolium cations, the long alkyl chains, strong Coulombic long-range interactions, complex and slow dynamics in ionic liquids, and, consequently, long simulation times that are needed for computing the dynamical properties in each of the ionic liquid salts. We are interested in determining the role of the cation and anion structures on the transport properties of the imidazolium-based ionic liquids. Particular attention has been given to the effects of the alkyl chain length in the cations, and the influence of the shape and mass of the anions has been investigated for the present study.

In this work, we use MD simulations to study 12 1-alkyl-3-methylimidazolium-based ionic liquids (alkyl =methyl, ethyl, propyl, and butyl) with the PF_6^-, NO_3^-, and Cl^- counterions. Of the 12 simulated ionic liquids in this study, 1,3-dimethylimidazolium chloride, [dmim][Cl], is one of the most commonly reported imidazolium-based ionic liquids in the literature and is valuable as a reference model for the study of the more complex unsymmetrical alkyl imidazolium salts. To our knowledge, this work is the first MD study of 1-propyl-3-methylimidazolium-based ionic liquids, [pmim][*X*], and additionally, there are only a few experimental data published on the properties of [pmim][*X*] to date.

In this work, the dynamics of the ionic liquids are characterized by the velocity autocorrelation function (VACF) and the MSD for the centers of mass of the ions at 400 K. The trajectory-averaging technique[46] was employed to evaluate the diffusion coefficients at two different temperatures by the Einstein relation for each of the ions. The diffusion coefficients are also calculated from the integration of the

VACF and detailed comparisons are made between the diffusion results from the VACF and MSD methods. The cationic transference numbers are estimated from the diffusion coefficients and the present observed trends are in good agreement with the experimental results. We emphasize the uniform methodology for the determination of the transport coefficients and correlate the effects of the cation and anion structures on the dynamics and transport behavior of the imidazolium-based ionic liquids in a systematic scheme. It is possible to get better agreement between calculated transport coefficients and experimental values by employing specifically designed force fields for individual ionic liquids instead of using the general transferable force field.

This paper is organized as follow. In Sec. II the force field, simulation details, and methodology applied to calculate the dynamics and transport properties for 1-alkyl-3-methylimidazolium-based ionic liquids are presented. In Sec. III the results of the MD simulations are discussed. The paper ends with a summary and conclusions in Sec. IV.

II. COMPUTATIONAL METHODS

A. The force field

The force field used in this work for dialkylimidazolium salts is from the systematic all-atom force field developed by Canongia Lopes et al.[20] based on the OPLS and AMBER framework with some minor modifications. The bond lengths in the cations and anions are derived from the crystallographic x-ray structure[47] of solid [emim][PF$_6$]. All of the species in simulations are fully flexible except for the PF$_6^-$ anion which is considered in the rigid form. The NO$_3^-$ potential parameters are given in Ref. 48.

The potential energy of the systems was modeled using the following standard functional form:

$$V_{tot} = \sum_{bonds} k_b(r - r_{eq})^2 + \sum_{angles} k_\theta(\theta - \theta_{eq})^2$$
$$+ \sum_{dihedrals} \sum_{i=1}^{3} \frac{V_i}{2}[1 + (-1)^{i-1}\cos(i\Phi)]$$
$$+ \sum_{i=1}^{N-1} \sum_{j>1}^{N} \left\{ 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right\}.$$

(1)

The first three terms represent the intramolecular bond, angle, and torsional interactions. Harmonic functions with force constants k_b and k_θ describe the intramolecular bond stretching and angle bending motions, respectively, and a cosine series describes the torsional motions. The sums are taken over all bonds, angles, and dihedrals in each of the 12 ionic liquid salts. The values of the force constants and other parameters of Eq. (1) are given in Ref. 20, with the atomic labels shown in Fig. 1. Intermolecular interactions are described by the last term of Eq. (1), including the pairwise additive atom-atom 12-6 LJ potential for the van der Waals interactions and the Coulombic term for the electrostatic interactions between point charges centered on the atoms. The ε_{ij} are the energy minima for the LJ interactions for atoms i and j on different ions and the σ_{ij} are the equilibrium inter-

atomic separations at zero potential. The parameters for like-atom interactions, ε_{ii} and σ_{ii}, are taken from the force field of Canongia Lopes et al.[20] and cross term parameters for $i \neq j$ interactions are obtained from the conventional combination rules, $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$. The charges on atoms i and j are q_i and q_j and ε_0 is the dielectric permittivity constant for vacuum. The partial charges on the cation atoms were determined by fitting the MP2/cc-pVTZ(-f) electrostatic potential of the optimized structure using the charges from electrostatic potential using a grid (CHELPG) method as described in Ref. 20.

B. Molecular dynamics calculations

Molecular dynamics simulations of twelve 1-alkyl-3-methylimidazolium-based ionic liquids, (alkyl=methyl, ethyl, propyl, and butyl, with counterions, PF$_6^-$, NO$_3^-$, and Cl$^-$), were done on systems consisting of 150–294 ion pairs. Initial configurations were generated by placing replicas of a randomly interacting cation-anion pair into the simulation box and equilibrating the system. The simulations were performed with the Nosé–Hoover thermostat/barostat algorithm[49,50] and the modification of Melchionna et al.[51] as implement in the DL_POLY program[52] version 2.15. The relaxation times used for the thermostat and barostat are 0.1 and 2.0 ps, respectively. Periodic boundary conditions were employed, and the equations of motion were integrated using the Verlet leapfrog scheme.[46] The initial extensive MD simulations were performed in the NpT ensemble for $p = 1$ atm and $T = 400$ K until the total energy of the system converged. All intermolecular interactions between the atoms in the simulation box and the nearest image sites were calculated within a cutoff distance of $R_{cutoff} = 13.5$ Å for all simulated systems. The electrostatic long-range interactions were calculated using the Ewald summation method,[46,53] with a precision of 1×10^{-6}. The time step of the simulations was 1 fs. Each system was equilibrated with a set of 14 runs, each with a total of 10^6 time steps with 400 000 equilibration steps. The end configuration of each stage was the beginning configuration of the next 10^6 step simulation. Afterwards, the MSDs were averaged over a set of six NVE simulations each with a total 200 000 time step equilibration followed by 550 000 time steps for data collecting. The starting point of each NVE simulation was the equilibrated configuration of the NpT simulation. By the end of the equilibration, the total energies and volumes were monitored until the corresponding time series were stationary. Finally, the VACF results were obtained by averaging results from the ten short runs each of 55 ps length in the NVE ensemble after finishing long runs for determining MSDs. Ionic liquids have slow and complex dynamics and the computed dynamic properties of ionic liquids converge slowly, especially in the case of all-atom force fields.

C. Dynamic and transport properties

The dynamics behavior and the microscopic motion of the ions are studied by calculating the reduced VACF, $C_v(t)$,

and the MSD, $\Delta|\mathbf{r}(t)|^2$, for the centers of mass of the ions with MD simulations. The VACF is calculated in dimensionless form,

$$C_v(t) = \frac{\langle \mathbf{v}^c(t) \cdot \mathbf{v}^c(0) \rangle}{\langle \mathbf{v}^c(0) \cdot \mathbf{v}^c(0) \rangle}, \tag{2}$$

where $\mathbf{v}^c(t)$ is the velocity of the center of mass of the ion and the angular brackets $\langle \ \rangle$ represent an ensemble average over all time origins. The VACF is a single-particle correlation function and its statistical precision is improved by averaging over all particles in the system.

In the time-correlation function theory, the transport properties can be calculated from integrals of flux timecorrelation functions via the Green-Kubo formulas. Alternatively, the slope of generalized MSDs (Einstein relations) can be used. These two methods are rigorously equivalent but are subject to different numerical errors in finite time MD simulations of finite-size systems. We will therefore determine the diffusion coefficient using both methods.

For a pure liquid in thermodynamic equilibrium, thermal agitation causes the translational motion of the particles. This motion is called self-diffusion.[1] From the molecular point of view, the self-diffusion coefficient gives a microscopic detailed description of the single-particle motion. The self-diffusion coefficient of ion i is given by the Green-Kubo integral formula[54,55]

$$D_i = \frac{1}{3} \int_0^\infty \langle \mathbf{v}_i^c(t) \cdot \mathbf{v}_i^c(0) \rangle dt. \tag{3}$$

In an ionic liquid, separate diffusion coefficients can be determined for the cation and anion.

The MSD is defined by

$$\text{MSD} = \frac{1}{N} \left\langle \sum_{i=1}^{N} |\mathbf{r}_i^c(t) - \mathbf{r}_i^c(0)|^2 \right\rangle = \Delta|\mathbf{r}(t)|^2, \tag{4}$$

where $\mathbf{r}_i^c(t)$ is the location of the center of mass of ion i at time t. The self-diffusion coefficient can also be obtained from the long-time limit of the MSD using the well-known Einstein relation

$$D_i = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle |\mathbf{r}_i^c(t) - \mathbf{r}_i^c(0)|^2 \rangle. \tag{5}$$

Ionic liquids can be used as electrolytes in electrochemical processes and devices. In most practical electrolyte applications, in addition to high total conductivity, which will be discussed in our future work, the relative contributions of the charged species to the transfer of the total charge is also important.[13] For simple 1:1 electrolytes, MX consisting of monovalent ions M^+ and X^-, such as the ionic liquids of interest in this study, transference numbers may be estimated from the diffusion coefficients of the cation and anion,

$$t_+ = \frac{D_+}{(D_+ + D_-)} \quad \text{and} \quad t_- = \frac{D_-}{(D_+ + D_-)}, \tag{6}$$

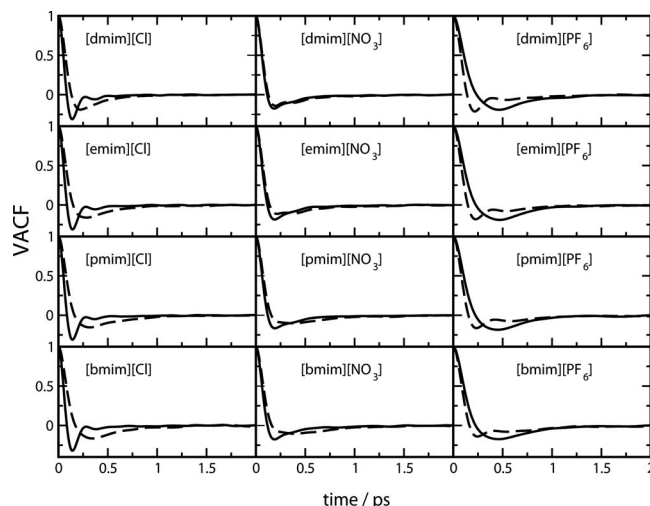where $t_+ + t_- = 1$ and $0 \le t_i \le 1$.

FIG. 2. The calculated VACFs of 12 ionic liquids. In all panels, the anion VACF is shown by full line and the cation by dashed line.

III. RESULTS AND DISCUSSION

A. Velocity autocorrelation functions and mean-square displacements

The VACFs for 12 ionic liquids from trajectory averaging of ten short *NVE* simulations at 400 K are shown in Fig. 2. The influence of the length of the alkyl chain in the cations and the effect of the shape and mass of the anions on the computed VACFs are shown in Figs. 2–4. In all systems the time scales of the VACFs are similar and the first zero in the VACFs indicates a mean collision time of approximately 0.1–0.25 ps. For example, in the [dmim][Cl] the first zeros in the VACFs of [Cl]$^-$ and [dmim]$^+$ appear near 0.1 and 0.13 ps, respectively. This time is a measure of the mean collision time for each ion. Negative VACFs after the first collision correspond to a cage effect that extends up to $\sim$0.5 ps for [Cl]$^-$ and $\sim$0.7 ps for [dmim]$^+$, after which the VACF for
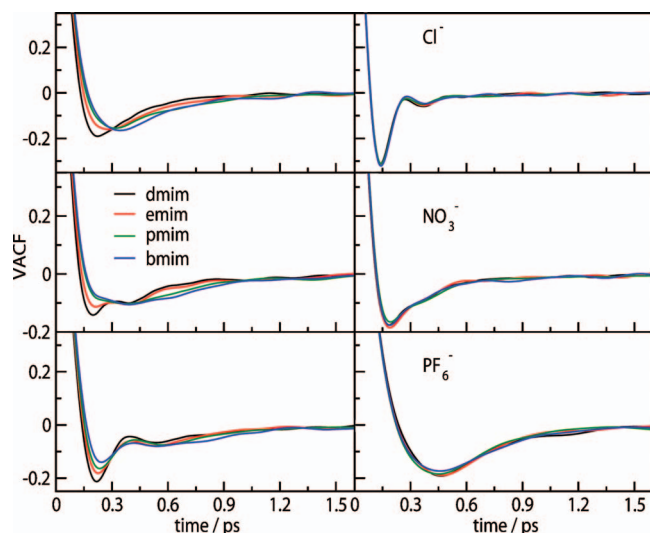

FIG. 3. (Color) The difference between the calculated VACFs of imidazolium cations with the same counterions (left curves), and the difference between the VACFs of the same anions with different imidazolium cations (right curves).
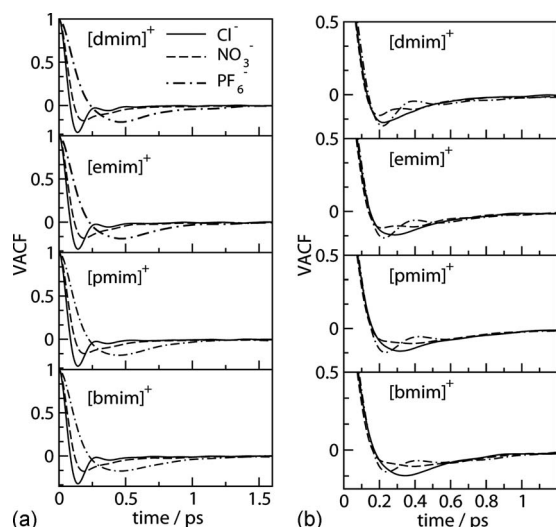
FIG. 4. (a) The calculated VACFs of three different anions with the same imidazolium counterions (left) and (b) the VACFs of the same cations with different counterions (right).

[Cl]$^-$ oscillates about zero. These zeros in the VACF are a measure of the velocity randomization times.

In the VACF plots shown in Fig. 2, between the mean collision times and the velocity randomization times, the lighter of the two ions in each ionic liquid shows clear oscillations. The molar mass of the cations and the anions of the ionic liquids of this study are given in Table I. The effect of the relative mass of the anion and cation on the oscillations of the VACF in the RTILs was discussed by Rey-Castro *et al.*[41] for the [emim]$^+$ cation with [Cl]$^-$, [NO$_3$]$^-$, and [PF$_6$]$^-$ counterions. The results in Fig. 2 show good agreement with their trends. In all cases studied, the [Cl]$^-$ and [NO$_3$]$^-$ anions are lighter than the [amim]$^+$ cations and show oscillations in the anion VACFs. The [amim]$^+$ cations are all lighter than the [PF$_6$]$^-$ anions and the cation VACF oscillates in these salts.

In the [amim][Cl] and [amim][NO$_3$] series, the anions are lighter and the first collision time (*x* intercept) occurs at shorter times for the anion than that of the cation. For the [amim][PF$_6$] series, the cations have the shorter first collision times. In the different cases, the VACFs of the lighter ions decay to zero at shorter over all times. The greater number of collisions involving the lighter ions randomizes their velocities sooner. The velocities of the lighter ions are generally randomized within ~0.5 ps while the velocities of the heavier ions are randomized within ~1 ps.

TABLE I. The molar mass and the van der Waals radii of the ions.

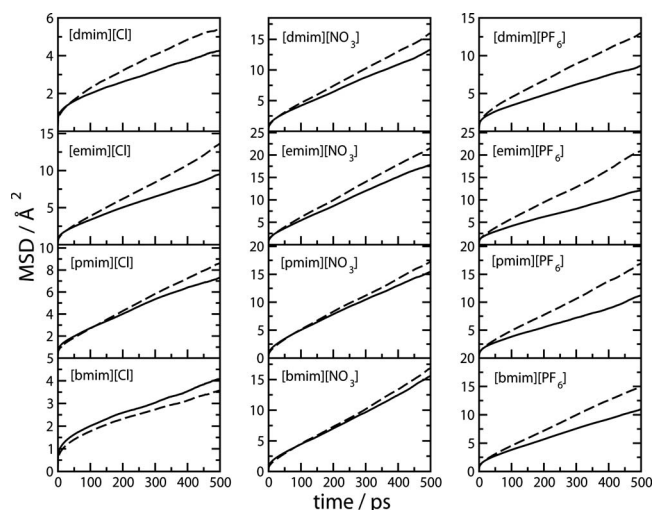| Ion	M_w (g/mol)	r_s (nm)[a]
[Cl]$^-$	35.4530	0.18
[NO$_3$]$^-$	62.0067	<0.254
[PF$_6$]$^-$	144.9620	0.254
[dmim]$^+$	97.1395	0.287
[emim]$^+$	111.1663	0.303
[pmim]$^+$	125.1931	0.319
[bmim]$^+$	139.2199	0.335

[a]References 27 and 65.

FIG. 5. The calculated MSDs of 12 ionic liquids in the range of 0–500 ps. In all curves, the anion has been shown with the full line and the cation by the dashed line. For all systems, in agreement with experiment the MSD of the cation becomes higher than the MSD of the anion.

The VACFs for the cations and anions in the different ionic liquids are compared in Fig. 3. We can see that the VACFs of the anions are independent of the alkyl chain length in the [amim]$^+$ family of ionic liquids. However, the detailed behaviors of the cations are different for each anion. The order for the mean collision times and the velocity randomization times for the cations is [dmim]$^+$<[emim]$^+$ <[pmim]$^+$<[bmim]$^+$. The velocity of the lightest cation, [dmim]$^+$, is randomized at the shortest time and the velocity of the heaviest cation, [bmim]$^+$, is randomized at the longest time.

The VACFs for the possible anions for each [amim]$^+$ are shown in Fig. 4(a). For each cation, the mean collision times and velocity randomization times are ordered as [Cl]$^-$ <[NO$_3$]$^-$<[PF$_6$]$^-$. The VACFs for identical cations in different [amim][X] salts are shown in Fig. 4(b). The mean collision times and velocity randomization times of each [amim]$^+$ remain roughly constant for the different anions. However, the relative masses of the cation and anion determine the detailed oscillation behavior of the cation dynamics between the mean collision time and velocity randomization time.

The time variations of the MSDs from *NVE* simulations of 12 ionic liquids for the centers of mass of cations and anions up to a time of 500 ps are shown in Fig. 5. For the [amim][Cl] and [amim][NO$_3$] ionic liquids, with increasing alkyl chain length, the MSD curves (and diffusion coefficients, see below) of the cations and anions become closer in magnitude. This is also observed in the experimental diffusions of the cations and anions in the [amim][(CF$_3$SO$_2$)$_2$N] family of ionic liquids reported by Tokuda *et al.*[27]

The short-time behaviors of the MSDs are shown in Fig. 6. At short times the anions for all ionic liquids have the faster motion and larger MSDs than the cations, and with the exception of [bmim][Cl], a crossing point invariably appears and the cation MSD (and diffusivity) becomes higher than that of the anion. Long trajectories (≥500 ps), proper equilibration, and trajectory averaging are required in order to ob-
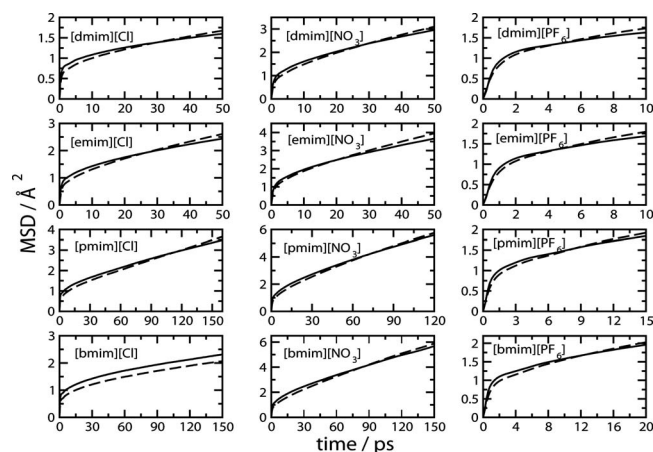
FIG. 6. The crossing points of the MSDs of anions and cations for 12 ionic liquids at 400 K. In all curves, the anions are shown by full lines and the cations by dashed lines.
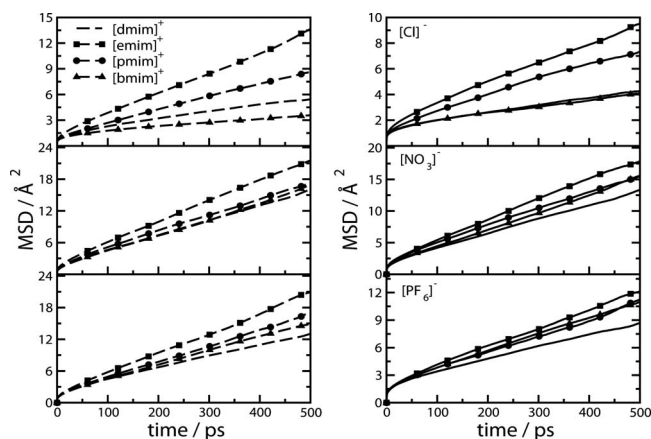

FIG. 7. The calculated MSDs of imidazolium cations (dashed lines) with the same counterions (left), and the MSDs of the same anions (full lines) with different imidazolium cations (right) at 400 K.

serve the proper trends in the MSD curves for the different ionic liquids. For the cases of [pmim][Cl], [pmim][NO$_3$], [bmim][Cl], and [bmim][NO$_3$], in particular, the MSDs and diffusion coefficients of the cation and anion are close to one another and trends can only be discerned after averaging over many trajectories.

The crossing points of the anion and cation MSDs in the ionic liquids are seen in Fig. 6. The crossing points of the MSD curves occur at shorter times for the [amim][PF$_6$] family and at the longer times for the [amim][Cl] family. The average MSD plot for the [bmim][Cl] does not show the crossing point for times up to 500 ps. The crossing times are sensitive to the proper equilibration and trajectory averaging in the *NVE* simulations for each ionic liquid. For the [bmim][NO$_3$] ionic liquid, in particular, the crossing points are difficult to determine with great accuracy since the MSDs are almost parallel for the cation and anion. This similarity of the MSDs and diffusion coefficients of the cation and the anion indicates the strong association of the counterions in [bmim][NO$_3$].

The observed MSDs in Fig. 5 show three different time scale behaviors. To distinguish the different time scales, the exponent β can be computed over a range of time scales using

$$\beta(t) = \frac{d \log(\Delta r^2(t))}{d \log(t)}. \qquad (7)$$

At short times the motions of the ions are almost ballistic so that $\beta = 2$. At long times the systems should exhibit normal linear diffusive behavior after the molecules have undergone many collisions, and $\beta = 1$. In the intermediate-time range, the motion shows subdiffusive dynamics similar to a supercooled liquid,[56] which is related to cage escape, and $\beta < 1$.

The influence of the alkyl chain length in the cations on the computed MSDs is shown in Fig. 7. With the exception of the very low ionic diffusivity of [bmim][Cl], for all three anions, the [dmim]$^+$ cation has a relatively low MSD. This can be due to the symmetry of the [dmim]$^+$ cation and the small size of the [Cl]$^-$ and [NO$_3$]$^-$ anions which allows better packing of ions in the liquid and leads to a higher melting

point.[37] With an increase in the length of the alkyl side chain, the MSD of the cation decreases according to the trend MSD[emim]$^+ >$ MSD[pmim]$^+ >$ MSD[bmim]$^+$. This trend is opposite that observed by Urahata and Ribeiro.[37] A similar trend holds for the anions in each [amim]$^+$ series. For example, MSD(Cl$^-$)$_{[emim]} >$ MSD(Cl$^-$)$_{[pmim]} >$ MSD(Cl$^-$)$_{[bmim]}$. This is in excellent agreement with the experimental trends observed by Tokuda *et al.*[27] who also gave a very good discussion of the effect of alkyl side chain length on the diffusion coefficient and the electrical conductivity of [amim]$^+$ based ionic liquids.

As expected, with increasing alkyl chain length, the densities of the ionic liquid decrease. For example, with increasing the alkyl chain length, we observe in the [amim][NO$_3$] series that the densities (g/cm^3) are 1.27, 1.22, 1.17, and 1.14. The lengthening of the alkyl chain causes a dispersion of the charge centers and weakening of the electrostatic attractions between the cations and anions but enhances the total strength of the van der Waals interactions. The balance between the two opposing effects of side chain length determines the ionic character and diffusion coefficients in different members in each series of ionic liquids. Increasing the alkyl chain length in ILs also enhances the viscosity owing to frictional forces among ions, aggregates, and clusters.[27]

The MSDs of the same [amim]$^+$ cations with the different anions [X]$^-$ are shown in Fig. 8(a). In the [bmim][X] family, the MSD of the [bmim]$^+$ in [bmim][PF$_6$] is larger than the MSD of [bmim]$^+$ in [bmim][Cl] (contrary to the observations of Urahata and Ribeiro[37]) and this observation is in agreement with the trends in the melting points of these ionic liquids, 279 K for [bmim][PF$_6$] and 340 K for [bmim][Cl]. The MSDs for the [amim][X] ionic liquids are plotted for different anions X$^-$ with the same [amim]$^+$ group in Fig. 8(b). In the most cases, especially for the [emim]$^+$ family, the trends in the MSDs and diffusion coefficients are in agreement with the observed melting points for these materials, T_m([emim][Cl]) = 360 K $> T_m$([emim][PF$_6$]) = 333 K $> T_m$([emim][NO$_3$]) = 312 K. In all the series, the MSDs of the different anions are well resolved. Rey-Castro *et al.*[41] observed that for the united atom potential and rigid cation structure, the self-diffusion coefficients of the [emim]$^+$ cat-
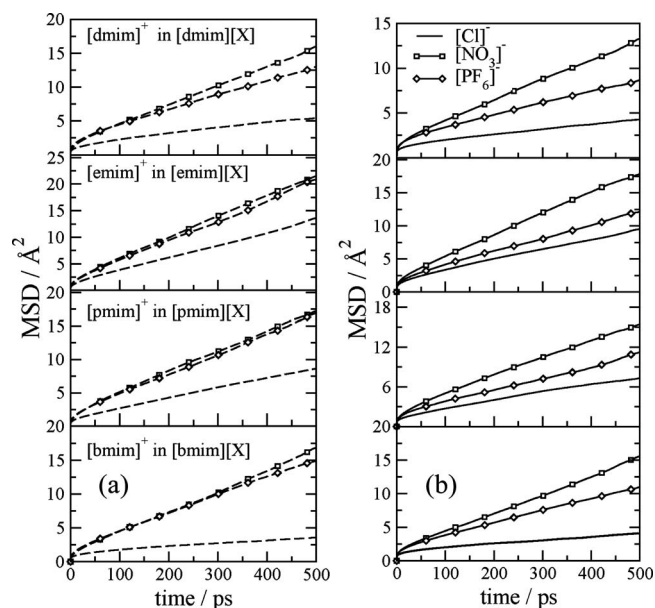
FIG. 8. (a) The difference between the MSDs of the same cations with different anion counterions (left) and (b) the calculated MSDs of three different anions with the same imidazolium counterions (right).

ions do not show significant differences for the $[Cl]^-$, $[PF_6]^-$, and $[NO_3]^-$ anions. Our work shows significant differences between the MSDs and self-diffusions calculated for these three families of ionic liquids.

The $[Cl]^-$ anion is the lightest and smallest of the three anions studied in this work. It may appear that the heaviest anion $[PF_6]^-$ can also be considered as a spherical structure but the larger size of $[PF_6]^-$ requires charge delocalization to reproduce proper dynamics in simulations.[37] The $[NO_3]^-$ has a planar structure and intermediate size and mass. The $[PF_6]^-$ anion is the largest of the three anions and has low surface electrical charge density, while $[Cl]^-$ has a relatively high surface electrical charge density and good packing efficiency in the liquid due to its small size. From the results shown in Fig. 8(b), for the three anions studied, it seems that the major factor determining the magnitude of the self-diffusion is the geometric shape of the anion.

B. Diffusion coefficients and cationic transference numbers

We calculated diffusion coefficients for each of the ions initially from the linear fitting of the slope of MSD(t) functions [Eq. (5)] using data in the range of 150–300 ps. The calculated diffusion coefficients of the 12 simulated ionic liquid salts at two temperatures in this study are summarized in Tables II and III. As expected, the calculated diffusion coefficients increase with temperature.[26] In Table III, the β values calculated using Eq. (7) are reported for the anions and cations at 400 K. The diffusion coefficients at 400 K were also determined for each of the ions using the Green-Kubo relation, Eq. (3), by evaluating the integral with an upper time limit between 10 and 25 ps and averaging the resulting values. These results are also given in Table III. Our results predict the diffusion coefficients of the ions in ionic liquids to be of the order of 10^{-11} m^2 s^{-1}, which is

consistent with other computational and experimental studies of imidazolium salts that are summarized in Table IV. Besides the diffusion coefficients calculated in this work for ionic liquids, only the diffusion coefficient data of Rey-Castro et al.[41,42] were calculated from the Green-Kubo relation. Rey-Castro et al.[42] had a brief comparison to the diffusion coefficients from the MSD and VACF for $[emim][Cl]$. To our knowledge, a comprehensive calculation and comparison of the diffusion coefficients from both the Einstein relation and Green-Kubo integral within a consistent framework by a single research group has not been reported.

Generally, pulsed field gradient spin-echo NMR experiments show that over a wide temperature range, cations of the $[amim][X]$ family have larger self-diffusion coefficients than that of anions, even if the cationic radius is larger than that of the anion.[27] This has been mainly attributed to the planar structure of the imidazolium cations and the greater friction for the translational motions of the anions compared

TABLE II. Simulated cation and anion diffusion coefficients D_i (in 10^{-11} m^2 s^{-1}) and cationic transference numbers of ionic liquids at different temperatures from MSD plots. The melting points for ionic liquids from literature are also reported.

IL ($[amim][X]$)	T (K)	D_+	D_-	t_+	T_{mp} (K)
$[dmim][Cl]$	423	2.70	1.85	0.593	398[a]
$[dmim][NO_3]$	383	3.94	2.95	0.572	357[a]
$[dmim][PF_6]$	376	3.83	2.04	0.652	362[b]
$[emim][Cl]$	377	2.43	1.53	0.614	360[a]
$[emim][NO_3]$	379	5.03	3.86	0.566	312[a]
$[emim][PF_6]$	370	3.66	2.05	0.641	333[a]
$[pmim][Cl]$	384	1.55	1.38	0.529	333[a]
$[pmim][NO_3]$	377	4.12	3.43	0.546	⋯
$[pmim][PF_6]$	373	3.36	1.85	0.645	313[a]
$[bmim][Cl]$	380	0.68	0.64	0.515	340[a]
$[bmim][NO_3]$	379	2.59	2.29	0.531	⋯
$[bmim][PF_6]$	374	2.70	2.01	0.573	279[a]

[a]From Refs. 4 and 66.
[b]From Dzyuba and Bartsch, Ref. 67.

TABLE III. The diffusion coefficient (in 10^{-11} m^2 s^{-1}) for the cations and anions from the slope of MSD plots (with β values in parentheses) and integration of the VACFs (with the standard deviations in parentheses) and the cationic transference number t_+ for 12 ionic liquids at $T=400$ K.

IL ($[amim][X]$)	MSD			VACF		
	D_+ (β)	D_- (β)	t_+	D_+	D_-	t_+
$[dmim][Cl]$	1.46 (0.56)	0.96 (0.45)	0.60	2.9$_{(0.7)}$	2.7$_{(0.7)}$	0.52
$[dmim][NO_3]$	4.72 (0.78)	3.91 (0.75)	0.55	7.2$_{(0.6)}$	6.0$_{(0.8)}$	0.54
$[dmim][PF_6]$	3.69 (0.67)	2.31 (0.60)	0.62	6.6$_{(1.1)}$	4.4$_{(1.1)}$	0.60
$[emim][Cl]$	3.78 (0.74)	2.59 (0.62)	0.59	5.7$_{(1.1)}$	5.6$_{(1.3)}$	0.50
$[emim][NO_3]$	6.74 (0.82)	5.61 (0.78)	0.55	9.3$_{(1.2)}$	8.4$_{(1.3)}$	0.53
$[emim][PF_6]$	5.74 (0.75)	3.04 (0.61)	0.65	7.8$_{(1.4)}$	4.8$_{(1.6)}$	0.62
$[pmim][Cl]$	2.61 (0.74)	2.20 (0.68)	0.54	4.9$_{(0.8)}$	5.5$_{(0.9)}$	0.47
$[pmim][NO_3]$	4.97 (0.74)	4.47 (0.70)	0.53	8.2$_{(0.7)}$	8.3$_{(0.9)}$	0.50
$[pmim][PF_6]$	4.71 (0.74)	2.79 (0.63)	0.63	5.0$_{(1.0)}$	4.3$_{(1.0)}$	0.54
$[bmim][Cl]$	0.72 (0.39)	0.75 (0.37)	0.49	2.5$_{(1.0)}$	3.2$_{(1.2)}$	0.44
$[bmim][NO_3]$	4.70 (0.78)	4.47 (0.78)	0.51	5.4$_{(1.1)}$	4.9$_{(1.2)}$	0.53
$[bmim][PF_6]$	4.56 (0.77)	3.15 (0.68)	0.59	5.8$_{(1.0)}$	4.8$_{(1.0)}$	0.55

TABLE IV. Cation and anion diffusion coefficients D_i (in 10^{-11} m^2 s^{-1}) for various ionic liquids from the present simulations at 400 K and the recent literature. In all references, the simulated diffusion coefficients are calculated from the Einstein relation except for Refs. 40 and 41 which used integration of the VACF(t).

	D_+			D_-		
RTIL	Our work	Simulations	Expt.	Our work	Simulations	Expt.
[dmim][Cl]	1.46	1.09,[a] 11,[b] 43[c]		0.96	0.88,[a] 8,[b] 38[c]	
[dmim][PF$_6$]	3.69	2.6,[a] 4.7,[d] 12[b]		2.31	1.3,[a] 3.2,[d] 6[b]	
[emim][Cl]	3.78	17.0,[a] 34,[e] 3.6[f]		2.59	9.4,[a] 19.9,[e] 1.4[f]	
		3.1,[g] 9.6,[h] 5.1,[i]			1.65,[g] 5.8,[h] 4.8,[i]	
[emim][NO$_3$]	6.74	14.9[j]		5.61	15.5[j]	
[emim][PF$_6$]	5.74	2.3,[i] 5.6,[k] 0.13[a]		3.04	1.05,[i] 3.54,[k] 0.13[a]	
[bmim][Cl]	0.72	22.3,[a] 1.4[l]		0.75	11.4,[a] 3.1[l]	
[bmim][NO$_3$]	4.70	5.3,[m] 23.8[n]		4.47	4.5,[m] 27.5[n]	
[bmim][PF$_6$]	4.56	5.6,[a] 14.1,[o] 24.4,[p] 3.5[q]	20.91[r]	3.15	2.8,[a] 6.2,[o] 20.5,[p] 2.9[q]	17.86[r]

[a]Reference 37.
[b]Reference 18, united atom force field.
[c]Reference 18, explicit atom force field.
[d]Reference 30.
[e]Reference 41, force field of Urahata and Ribeiro, Ref. 35.
[f]Reference 40, 404 K, force field of Shim *et al.*, Ref. 42.
[g]Reference 41, force field of Shim *et al.*, Ref. 42.
[h]Reference 32.
[i]Reference 34, using a nonpolarizable force field.
[j]Reference 34, using a polarizable force field.

[k]Reference 45, force field of Hanke *et al.*, Ref. 18.
[l]Reference 58.
[m]Reference 59, 363 K.
[n]Reference 59, 423 K.
[o]Reference 68.
[p]Reference 64, refined force field of Bhargava and Balasubramanian, Ref. 64.
[q]Reference 64, force field of Canongia Lopes *et al.*, Ref. 20.
[r]Reference 27(a), experimental values from the VFT equation.

to the planar imidazolium cations. This makes the imidazolium cations good electron carriers in view of their molecular sizes.[57]

Except for the [bmim][Cl] case at 400 K, all calculated diffusion coefficients (from the slope of the MSD plots) for the cations are higher than those for the anions and the cationic transference numbers are larger than 0.5, the same as observed in previous studies.[25–29,32,38] The $t_+ > 0.5$ reflects the crossing over of the MSD plots that was shown in Fig. 6. The calculated cationic transference numbers in imidazolium-based ionic liquids determined from the MSDs are $0.49 \leq t_+ \leq 0.65$. For the same anion, t_+ decreases with the increasing length of the alkyl chain (see Tables II and III). Also, in good agreement with experiments, the calculated cationic transference number often decreases with temperature in imidazolium-based ionic liquids.[27] This observation implies that in the Vogel–Tamman–Fulcher (VFT) equation for the temperature dependence of the diffusion coefficient,

$$D = D_0 \exp[-B(T - T_0)], \qquad (8)$$

the activation energy to diffusion, B, for the anions is greater than that of the cations.[27] In the four experimental cases studied in Ref. 27, the activation energies for anion diffusions are higher than those of the cations.

The relative magnitude of the diffusion coefficients in these cases are very sensitive to the potential used and the temperature of the simulation. Urahata and Ribeiro[58] simulated [bmim][Cl] with a united atom force field at 400 K and observed a reversal of the magnitudes of the cation and anion diffusion coefficients with $D[\text{bmim}]^+ = 1.4 \times 10^{-11}$ m^2 s^{-1} and $D[\text{Cl}^-] = 3.1 \times 10^{-11}$ m^2 s^{-1}. They used a time step of 3.0 fs with 1 ns equilibration runs and 1 ns long production runs in an *NVE* ensemble. We observe a similar behavior and that

[bmim][Cl] is the only ionic liquid which has $t_+ < 0.5$ at 400 K. Cadena and Maginn[59] reported MD simulations for [bmim][NO$_3$] and several triazolium-based ionic liquids. For [bmim][NO$_3$], they determined $D[\text{bmim}]^+ = 5.3 \times 10^{-11}$ m^2 s^{-1} and $D[\text{NO}_3^-] = 4.5 \times 10^{-11}$ m^2 s^{-1} at 363 K, but the magnitude of the diffusions was reversed at 423 K with $D[\text{bmim}]^+ = 23.8 \times 10^{-11}$ m^2 s^{-1} and $D[\text{NO}_3^-] = 27.5 \times 10^{-11}$ m^2 s^{-1}. This ionic liquid has similar magnitudes for the cation and anion diffusion coefficients and may also have $t_+ < 0.5$ at certain temperatures.

The calculated cationic transference numbers from the diffusion results of the Green-Kubo formalism in Table III show values in the range of 0.44–0.62. As mentioned, the cationic transference numbers are higher than 0.5 because of the planar structure of the cationic backbone.[27] This explanation gains credence when we see that the ionic transference numbers are significantly closer to or lower than 0.5 for the ionic liquids of the planar NO$_3^-$ anion. Generally, when the diffusions of cation and anion are very close in magnitude, strong association occurs in the liquid phase. This point has been shown in the [dmim][Cl], [emim][Cl], [pmim][Cl], [emim][NO$_3$], [pmim][NO$_3$], and [bmim][NO$_3$] cases (see the VACF results in Table III).

The trends in the diffusion coefficients in both Tables II and III in the series are $D[\text{emim}]^+ > D[\text{pmim}]^+ > D[\text{bmim}]^+$ for the cations. The [emim]$^+$ cation is smaller and is expected to diffuse more quickly through the liquid than the large [bmim]$^+$ cation with its long alkyl chain which should restrict its mobility and reduce free space among the ions. The [dmim]$^+$ shows a relatively low diffusion due to its symmetric structure and good liquid-state packing. The observed decrease in the diffusion with increasing alkyl chain length is in good agreement with previous experimental observations on the imidazolium-based ionic liquids.[26,27] The absolute

values of the diffusion coefficients from the MSDs in Tables II and III are numerically lower than the experimental values. Generally, the magnitudes of the diffusion coefficients from the Green-Kubo relation given in Table III are in better agreement with experimental values but have larger error bars.

The general observed trend in the simulated diffusion coefficients for the anions in Tables II and III are $D[NO_3]^- > D[PF_6]^- > D[Cl]^-$. A number of factors can influence the diffusion coefficients of the anions and cations in ionic liquids. Some of these factors are the relative cationic and anionic sizes, geometric shape, and mass, strength of local van der Waals interactions between the cations and anions, strength of Coulombic interactions between the cation and anion which depends on the localization of charge on ions, and surface electrical charge density on the ions. The calculated diffusion coefficients from the MSDs and the VACFs of three of the anions in this work show the geometric shape of the ions as the major factor for determining the ionic motion and diffusion. The NO_3^- anion has a planar shape similar to the imidazolium ring and exhibits the highest ionic diffusion within the anions.

It can be observed in Table II that the larger size of both the $[PF_6]^-$ and $[NO_3]^-$ anions compared to the $[Cl]^-$ anion resulted in a decrease in the melting point and increase in both the cationic and anionic diffusion coefficients of the salts containing the former anions.

In the series of $[amim][X]$ ionic liquids with $X = Cl^-, BF_4^-, \ldots$ and alkyl=C1–C4, with increasing alkyl chain length, the melting points of the salt decrease.[60] This is due to an increase in the ionic radii (see Table I), and consequently an increase in the strength of van der Waals interactions, but a decrease in the strength of Coulombic interactions.[37] The symmetry of the cation is another important factor in determining the melting points. The symmetric $[dmim]^+$ cation permits more efficient packing in the crystalline phase which leads to a larger melting point, namely, $T_{mp}[dmim][X] \gg T_{mp}[emim][X]$. This same factor also explains the low diffusion of the $[dmim]^+$ salts and leads to the observed trends in the melting points of the salts for different anions, $T_{mp}([amim][Cl]) > T_{mp}([amim][PF_6]) > T_{mp}([amim] \times [BF_4])$.[60]

Due to differences in computational details, such as the type of force field, equilibration times, overall simulation time, number of production runs, and method for calculating diffusion coefficients (using the MSD or VACF), the direct comparison of our computed diffusion coefficients with other simulations is difficult.

The integration of the VACF (Green-Kubo relation) generally gives higher values for the diffusion coefficient than the calculation of the slope of the MSD plot in the linear regime (Einstein relation), especially at low temperatures (less than 450 K), see Ref. 40, Fig. 4. For example, for $[emim][Cl]$ at 400 K using the united atom force field of Urahata,[37] the MSD plots (between 0 and 600 ps) give $D_+ = 17.0 \times 10^{-11}$ m^2 s^{-1} and $D_- = 9.4 \times 10^{-11}$ m^2 s^{-1},[37] whereas the same potential using the VACF (between 0 and 2 ps) gives $D_+ = 34 \times 10^{-11}$ m^2 s^{-1} and $D_- = 19.9 \times 10^{-11}$ m^2 s^{-1}.[41]

Our results for the diffusion coefficients of the Green-Kubo relation (Table III) are also larger than those for the diffusion coefficients from the Einstein formula. For example, our MSD results at 400 K for $[bmim][NO_3]$ give $D_+ = 4.7 \times 10^{-11}$ m^2 s^{-1} and $D_- = 4.5 \times 10^{-11}$ m^2 s^{-1}, whereas the VACF results give $D_+ = 5.4 \times 10^{-11}$ m^2 s^{-1} and $D_- = 4.9 \times 10^{-11}$ m^2 s^{-1}, in agreement with the values of diffusion coefficients from the MSD plots reported by Cadena and Maginn[59] at different temperatures. Our MSD results for $[emim][Cl]$ give $D_+ = 3.8 \times 10^{-11}$ m^2 s^{-1} and $D_- = 2.6 \times 10^{-11}$ m^2 s^{-1}, whereas the VACF results are $D_+ = 5.7 \times 10^{-11}$ m^2 s^{-1} and $D_- = 5.6 \times 10^{-11}$ m^2 s^{-1}.

Simulations of systems with higher melting points (e.g., $[dmim][Cl]$ with $T_{mp} = 398$ K) or highly viscous IL (e.g., $[bmim][Cl]$) are difficult at 400 K because of the very slow dynamics of these ionic liquids and β from Eq. (7) becomes small for these simulations. As shown in Table III, for the other systems, β generally is ≈ 0.75. The fact that the ionic liquids may still be in the subdiffusive regime and the $\beta < 1$ within the time range used for determining the slope of the MSD may be some of the reasons why the diffusion coefficients determined from the MSDs are smaller than those calculated from integration of the VACFs. Furthermore, we observe that in the same ionic liquid, β(cation) $> \beta$(anion). This observation is likely correlated with the greater mobility of the planar $[amim]^+$ cations in these systems.

The effect of force field on the diffusion coefficients has been illustrated in Refs. 45 and 61. Prado and Freitas[61] calculated the ionic self-diffusion coefficients of $[bmim][BF_4]$ at 300 K with different force fields. They stated that the diffusion process depends on several factors such as volume, mass, cohesion energy, and coordination numbers. They observed a strong dependence of the values of self-diffusion coefficients on the set of partial charges employed in the force field and stated that special care is needed when determining point charges at the time of force field construction of ionic liquids.[61] The CHELPG charges (with different van der Waals parameter sets) were stated to give best agreements with the experimental results of Tokuda et al.[27]

Recent reports have correctly emphasized the effect of the force field on differences in the calculated diffusion coefficients and other transport properties of ionic liquids. Our experience in this work shows that the simulation conditions and quality of the equilibration can be just as important as the force field in determining the calculated values of transport coefficients. Factors of importance to the quality of the result include the potential truncation at the cutoff radius, finite-size effects due to the use of small simulation cells, numerical imprecision in the integration of the equation of motion, and, perhaps most important of all these factors, insufficient equilibration of the system before the production phase of a simulation.[62] These factors can introduce systematic errors in the simulation which give rise to major differences in calculated transport coefficients. With careful choice of simulation parameters, some of these systematic errors can be eliminated. It is not known a priori how the simulation parameters must be chosen, and a systematic investigation of their influence on the results for macroscopic properties become very important to the accuracy of the final

results.[63] An illustration of the effect of the simulation time can be seen with reference to the MSD curves shown in Fig. 5. The particle motion in these systems only becomes diffusive within the time frame of several hundred picoseconds. Furthermore, averaging over a number of independent trajectories is required to get accurate representations of the relative diffusions of the cations and anions.

Kelkar and Maginn[62] showed that the use of nonequilibrium simulations enables diffusive behavior to be observed on simulation time scales while the equilibrium simulations for greater than 2 ns are still in the subdiffusive regime for the [emim][NTf$_2$]. They used the nonequilibrium MD method to compute the viscosity and suggest that equilibrium simulations much longer than 1 ns are required to obtain proper transport properties. It seems that the equilibrium MD is not the most efficient method for estimating the transport properties especially at low temperatures when the target system has the slow dynamics and high viscosity, as is the case in ionic liquids. Ultimately, the choice of simulation method for calculating ionic liquid transport properties is a trade-off between computational costs, the complexity of the IL, the specific property to be computed, the temperature of simulation, and the accuracy required.[19]

From a comparison of computed values with different force fields, we see that the quality of the force field (not exclusively the inclusion of polarizability in the force field) can be as important as the selected simulation methodology (equilibrium or nonequilibrium) for getting better agreement between calculated diffusion coefficients and experimental values. While ionic liquids often do have large polarizable ions and may need polarizable force fields to represent their behavior, we believe that it is important to ensure that other simulation parameters are correctly adjusted before making definite judgment on the nature of the force field. The work of Bhargava and Balasubramanian[64] shows that equilibrium simulations can give diffusion coefficients close to experimental values for an ionic liquid if a custom designed force field (without polarizability) is employed. Such calculations also have to be performed on a range of ionic liquids to determine the validity in different cases.

IV. SUMMARY AND CONCLUSIONS

We have systematically studied the dynamics and diffusion coefficients of the [amim][X] series of ionic liquids with alkyl=methyl to butyl and X=Cl$^-$, NO$_3^-$, PF$_6^-$ with MD simulations. Identical MD conditions have been used in all cases with care given to proper equilibration and convergence of the dynamic properties. The goal of the work is to systematically evaluate the effect of relative anion and cation masses, alkyl chain length, and ion shape on the computed VACFs, MSDs, and diffusion coefficients. We have also pursued a comprehensive comparison of the calculated diffusion coefficients from both the slope of the MSDs and the integration of the VACFs.

Long trajectories ($\geq$500 ps), proper equilibration, and trajectory averaging are required in order to observe the proper trends in the MSD curves. The slopes of the MSD plots and the integral of the VACFs predict that the diffusion

coefficient of the ions in ionic liquids is of the order of 10^{-11} m^2 s^{-1}, which is consistent with the other computational and experimental studies of imidazolium salts. However, our simulations predict diffusion coefficients which are lower than experiment. Our results indicate that in order to get larger diffusion coefficients from MSD plots, longer simulations in the range of ~5–10 ns may be required to access the truly diffusive regime of β=1. The diffusion coefficients calculated from the Green-Kubo relation are very sensitive to the selected upper time limits of VACF integrals.

Our diffusion results for most of the ionic liquid systems studied in this work from both methods (Einstein relation and Green-Kubo integral) indicate that the diffusion coefficients of the cations are larger than those of the anions. It seems that the diffusion results from the Green-Kubo relation are closer to the experimental values than the results from the Einstein relation. The results of both methods can show good trends in agreement with experiment, although it is possible to obtain closer agreement between calculated transport coefficient values in comparison with the experiment by using custom designed force fields for an individual ionic liquid instead of using a general transferable force field.[64] In good agreement with experiments on the imidazolium-based ionic liquids, the calculated cationic transference number often decreases with temperature.

In future work, calculated values of the electrical conductivity of these ionic liquids determined from the Nernst–Einstein relation and the Green-Kubo formulas will be presented. We will additionally study the viscosity and comparative structures of these ionic liquids.

[1] *Ionic Liquids in Synthesis*, edited by P. Wasserscheid and T. Welton (Wiley-VCH, Weinheim, 2002).
[2] *Ionic Liquids III A: Fundamentals, Progress, Challenges, and Opportunities; Properties and Structure*, edited by R. D. Rogers and K. R. Seddon (ACS, Washington, 2005); *Ionic Liquids III B: Fundamentals, Progress, Challenges, and Opportunities; Transformations and Processes*, edited by R. D. Rogers and K. R. Seddon (ACS, Washington, 2005).
[3] P. Wasserscheid and W. Keim, Angew. Chem., Int. Ed. **39**, 3772 (2000).
[4] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, and R. D. Rogers, Green Chem. **3**, 156 (2001).
[5] J. S. Wilkes, Green Chem. **4**, 73 (2002).
[6] T. Welton, Chem. Rev. (Washington, D.C.) **99**, 2071 (1999).
[7] K. N. Marsh, A. Deev, A. C.-T. Wu, E. Tran, and A. Klamt, Korean J. Chem. Eng. **19**, 357 (2002).
[8] J. F. Brennecke and E. J. Maginn, AIChE J. **47**, 2384 (2001).
[9] M. P. Stracke, G. Ebeling, R. Cataluña, and J. Dupont, Energy Fuels **21**, 1695 (2007).
[10] L. Moens, D. M. Blake, D. L. Rudnicki, and M. J. Hale, J. Sol. Energy Eng. **125**, 112 (2003).
[11] V. A. Cocalia, K. E. Gutowski, and R. D. Rogers, Coord. Chem. Rev. **250**, 755 (2006).

[12] Q. Gan, D. Rooney, M. L. Xue, G. Thompson, and Y. Zou, J. Membr. Sci. **280**, 948 (2006).

[13] M. Galiński, A. Lewandowski, and I. Stępniak, Electrochim. Acta **51**, 5567 (2006).

[14] M. E. V. Valkenburg, R. L. Vaughn, M. Williams, and J. S. Wilkes, Thermochim. Acta **425**, 181 (2005).

[15] Z. Mu, W. Liu, S. Zhang, and F. Zhou, Chem. Lett. **2004**, 524.

[16] Y. Sun, B. Cabovska, C. E. Evans, T. H. Ridgway, and A. M. Stalcup, Anal. Bioanal. Chem. **382**, 728 (2005).

[17] Y. L. Li and M. L. Gross, J. Am. Soc. Mass Spectrom. **15**, 1833 (2004).

[18] C. G. Hanke, S. L. Price, and R. M. Lynden-Bell, Mol. Phys. **99**, 801 (2001).

[19] P. A. Hunt, Mol. Simul. **32**, 1 (2006).

[20] J. N. Canongia Lopes, J. Deschamps, and A. A. H. Pádua, J. Phys. Chem. B **108**, 2038 (2004); J. N. Canongia Lopes, J. Deschamps, and A. A. H. Pádua, *ibid.* **108**, 11250E (2004).

[21] S. Alavi and D. L. Thompson, J. Chem. Phys. **122**, 154704 (2005).

[22] B. L. Bhargava and S. Balasubramanian, J. Chem. Phys. **123**, 144505 (2005); B. L. Bhargava and S. Balasubramanian, *ibid.* **125**, 219901E (2006).

[23] C. K. Larive, M. Lin, B. J. Piersma, and W. R. Carper, J. Phys. Chem. **99**, 12409 (1995).

[24] W. R. Carper, G. J. Mains, B. J. Piersma, S. L. M. Mansfield, and C. K. Larive, J. Phys. Chem. **100**, 4724 (1996).

[25] A. Noda, K. Hayamizu, and M. Watanabe, J. Phys. Chem. B **105**, 4603 (2001).

[26] H. A. Every, A. G. Bishop, D. R. MacFarlane, G. Orädd, and M. Forsyth, Phys. Chem. Chem. Phys. **6**, 1758 (2004).

[27] (a) H. Tokuda, K. Hayamizu, M. A. B. H. Susan, and M. Watanabe, J. Phys. Chem. B **108**, 16593 (2004); (b) H. Tokuda, K. Hayamizu, K. Ishii, M. A. B. H. Susan, and M. Watanabe, *ibid.* **109**, 6103 (2005); (c) H. Tokuda, K. Ishii, M. A. B. H. Susan, K. Hayamizu, and M. Watanabe, *ibid.* **110**, 2833 (2006); (d) H. Tokuda, S. Tsuzuki, M. A. B. H. Susan, K. Hayamizu, and M. Watanabe, *ibid.* **110**, 19593 (2006).

[28] T. I. Morrow and E. J. Maginn, J. Phys. Chem. B **106**, 12807 (2002).

[29] C. J. Margulis, H. A. Stern, and B. J. Berne, J. Phys. Chem. B **106**, 12017 (2002).

[30] Z. Liu, S. Huang, and W. Wang, J. Phys. Chem. B **108**, 12978 (2004).

[31] A. D. MacKerell, Jr., D. Bashford, M. Bellott, R. L. Dunbrack, Jr., J. D. Evanseck, M. J. Field, S. Fischer, J. Gao, H. Guo, S. Ha, D. Joseph-McCarthy, L. Kuchnir, K. Kuczera, F. T. K. Lau, C. Mattos, S. Michnick, T. Ngo, D. T. Nguyen, B. Prodhom, W. E. Reiher III, B. Roux, M. Schlenkrich, J. C. Smith, R. Stote, J. Straub, M. Watanabe, J. Wiórkiewicz-Kuczera, D. Yin, and M. Karplus, J. Phys. Chem. B **102**, 3586 (1998).

[32] M. G. Del Pópolo and G. A. Voth, J. Phys. Chem. B **108**, 1744 (2004).

[33] W. D. Cornell, P. Cieplak, C. L. Bayly, I. R. Gould, K. M. Merz, Jr., D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell, and P. A. Kollman, J. Am. Chem. Soc. **117**, 5179 (1995).

[34] T. Yan, C. J. Burnham, M. G. Del Pópolo, and G. A. Voth, J. Phys. Chem. B **108**, 11877 (2004).

[35] S. M. Urahata and M. C. C. Ribeiro, J. Chem. Phys. **120**, 1855 (2004).

[36] J. K. Shah, J. F. Brennecke, and E. J. Maginn, Green Chem. **4**, 112 (2002).

[37] S. M. Urahata and M. C. C. Ribeiro, J. Chem. Phys. **122**, 024511 (2005).

[38] J. de Andrade, E. S. Böes, and H. Stassen, J. Phys. Chem. B **106**, 3546 (2002).

[39] S. U. Lee, J. Jung, and Y.-K. Han, Chem. Phys. Lett. **406**, 332 (2005).

[40] C. Rey-Castro and L. F. Vega, J. Phys. Chem. B **110**, 14426 (2006).

[41] C. Rey-Castro, A. L. Tormo, and L. F. Vega, Fluid Phase Equilib. **256**, 62 (2007).

[42] Y. Shim, M. Y. Choi, and H. J. Kim, J. Chem. Phys. **122**, 044510 (2005).

[43] C. Chiappe and D. Pieraccini, J. Phys. Org. Chem. **18**, 275 (2005).

[44] A. Bagno, F. D'Amico, and G. Saielli, J. Mol. Liq. **131–132**, 17 (2007).

[45] J. Picálek and J. Kolafa, J. Mol. Liq. **134**, 29 (2007).

[46] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford Science, Oxford, 1987).

[47] J. Fuller, R. T. Carlin, H. C. de Long, and D. Haworth, J. Chem. Soc. Chem. Commun. **1994**, 299.

[48] (a) J. N. Canongia Lopes and A. A. H. Pádua, J. Phys. Chem. B **108**, 16893 (2004); (b) D. C. Sorescu and D. L. Thompson, J. Phys. Chem. A **105**, 720 (2001) (the bond and the angle parameters for NO_3^- are from (a) and the dihedral parameters for NO_3^- are from (b).

[49] S. Nosé, J. Chem. Phys. **81**, 511 (1984).

[50] W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).

[51] S. Melchionna, G. Ciccotti, and B. L. Holian, Mol. Phys. **78**, 533 (1993).

[52] W. Smith and T. R. Forester, the DL_POLY molecular simulation package, v. 2.15, Daresbury Laboratory, UK, 2005 (www.cse.scitech.ac.uk/ccg/software/DL_POLY/).

[53] K. D. Gibson and H. A. Scheraga, J. Phys. Chem. **99**, 3752 (1995).

[54] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1986).

[55] J. M. Haile, *Molecular Dynamics Simulation: Elementary Methods* (Wiley, New York, 1992).

[56] J. Qian, R. Hentschke, and A. Heuer, J. Chem. Phys. **110**, 4514 (1999).

[57] T. Umecky, M. Kanakubo, and Y. Ikushima, J. Mol. Liq. **119**, 77 (2005).

[58] S. M. Urahata and M. C. C. Ribeiro, J. Chem. Phys. **124**, 074513 (2006).

[59] C. Cadena and E. J. Maginn, J. Phys. Chem. B **110**, 18026 (2006).

[60] S. Zhang, N. Sun, X. He, X. Lu, and X. Zhang, J. Phys. Chem. Ref. Data **35**, 1475 (2006).

[61] E. R. Prado and L. C. G. Freitas, J. Mol. Struct.: THEOCHEM **847**, 93 (2007).

[62] M. S. Kelkar and E. J. Maginn, J. Phys. Chem. B **111**, 4867 (2007).

[63] K. Meier, A. Laesecke, and S. Kabelac, J. Chem. Phys. **121**, 3671 (2004).

[64] B. L. Bhargava and S. Balasubramanian, J. Chem. Phys. **127**, 114510 (2007).

[65] M. Ue, A. Murakami, and S. Nakamura, J. Electrochem. Soc. **149**, A1385 (2002); M. Ue, *ibid.* **141**, 3336 (1994).

[66] I. López-Martin, E. Burello, P. N. Davey, K. R. Seddon, and G. Rothenberg, ChemPhysChem **8**, 690 (2007).

[67] S. V. Dzyuba and R. A. Bartsch, Chem. Commun. (Cambridge) **2001**, 1466.

[68] L. T. Costa and M. C. C. Ribeiro, J. Chem. Phys. **127**, 164901 (2007).