An Improved Four-Site Ionic Liquid Model
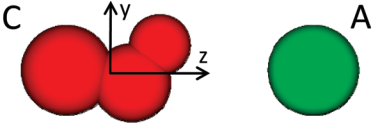
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Computer simulations provide insight into the molecular-level details responsible for the unique properties of ionic liquids. Due to the sluggish dynamics and nanostructured nature of many ionic liquids, coarse-grained models are an important complement to fully atomistic simulations because they enable simulation of much larger system sizes and much longer times, which are often of interest. This paper reports a four-site, coarse-grained model for studying ionic liquids and their solutions. It is intended to be a generic model representative of common ionic liquids currently in use, but it is parametrized to fit the properties of 1-butyl-3-methylimidazolium hexafluorophosphate, [Im_{41}][PF_6]. The present model is a variant of one introduced in *J. Phys. Chem. B* **114**, 8410 (2010). Reduction of ion charges to $\pm 0.78e$ and fine-tuning Lennard-Jones parameters from the original model leads to a remarkable improvement in the realism of the model and surprisingly good agreement between simulation and experiment for a variety of static and dynamic properties of [Im_{41}][PF_6]. This idealized model should prove valuable for studies of solute-based dynamics and other phenomena occurring on nanosecond and longer time scales, which are not feasible with all-atom simulations.

We recently reported[1] on an idealized model of a room temperature ionic liquid roughly approximating the prototypical liquid 1-butyl-3-methylimidazolium hexafluorophosphate, [Im_{41}][PF_6]. Like other coarse-grained representations,[2−5] the motivation for use of such a model was to reduce computation times relative to all-atom models, in our case to facilitate studies of solute-based dynamics on nanosecond time scales. The model described in ref 1 consisted of the three-site cation ("C") and single-site anion ("A") shown in Figure 1. Compared with an all-atom representation of [Im_{41}][PF_6], which involves 175 interactions between a single ion pair, the fact that only 3 C−A interactions are present in this coarse-grained representation leads to a huge computational savings. Of course, this saving comes at the expense of some realism of the model.

In ref 1, we described the static and dynamical properties of the neat liquid in some detail and compared them with experimental data on [Im_{41}][PF_6]. We found that the main shortcoming of the model was that its dynamics are much slower than those of experimental ionic liquids at a given temperature (a feature sometimes encountered even in all-atom representations[6]). To reach agreement between quantities such as diffusion coefficients and experimental data, we found it necessary to simulate the model at temperatures ~100 K higher than the experimental system, after which the temperature dependence of these quantities resembled those of the real liquid. In ref 1 we did not attempt to optimize the model so as to achieve better agreement with experiment. Instead, we proposed that comparisons with real ionic liquids be made by applying this temperature adjustment and focused on using the model to examine the heterogeneous nature of ionic liquid dynamics and highlight the similarities among ionic liquids, supercooled liquids, and molten alkali halides. Herein, we describe simple adjustments to the original four-site model that lead to surprisingly good agreement with the properties of [Im_{41}][PF_6] measured in experiment. The level of realism achieved here

Figure 1. Schematic of the cation (C) and anion (A) of ILM2 and the model parameters. Site−site interaction energies are of the form, $u_{ij}(r_{ij}) = 4\varepsilon_{ij}\{(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^{6}\} + q_i q_j/4\pi\varepsilon_0 r_{ij}$ where r_{ij} is the distance between sites, ε_0 is the permittivity of free space, and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, $\varepsilon_{ij} = (\varepsilon_i\varepsilon_j)^{1/2}$.

Site	x /Å	y /Å	z /Å	m /m_u	σ_i /Å	ε_i /kJ mol^{-1}	q_i /e
C_1	0	-0.527	1.365	67.07	4.38	2.56	.4374
C_2	0	1.641	2.987	15.04	3.41	0.36	.1578
C_3	0	0.187	-2.389	57.12	5.04	1.83	.1848
A	0	0	0	144.96	5.06	4.71	-.7800

should render this modified model the preferred representation for many purposes in which all-atom simulations are not feasible.

To optimize the model, we left the geometry of the cation unchanged and examined the effect of the charges and Lennard-Jones parameters on the equilibrium and dynamical properties of the neat liquid. For target quantities, we focused on matching the temperature dependence of the molar volume (V_m) and the diffusion coefficients (D_C, D_A) with experimental data on [Im_{41}][PF_6]. As had been observed in several previous studies,[7−9] we found that the net charges on the cation and anion have a dramatic effect on the fluidity of ionic liquid models. To obtain agreement with experimental diffusion coefficients, we found that a reduction of about 20% in the ion charges was necessary. Fine tuning this charge scaling factor simultaneously with an overall scaling of the size (σ) parameters of the Lennard-Jones interactions was sufficient to achieve the agreement with $V_m(T)$ and the $D_i(T)$ shown in Figure 2. The final model parameters obtained in this way are listed in Figure 1. In the following discussion, we will refer to this revised model as ILM2 and the original model as ILM1. The simulation and analysis methods
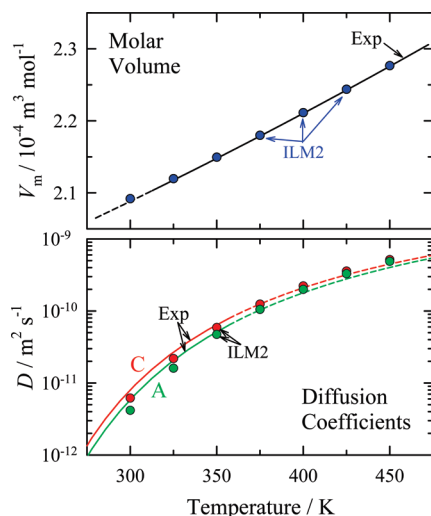
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Figure 2. Temperature dependence of the molar volume and cation (C) and anion (A) diffusion coefficients of ILM2 (points) and experiment (curves). ILM2 parameters were optimized to achieve best agreement with the experimental properties of [Im$_{41}$][PF$_6$]. The solid curves are parametrizations of the experimental data of Machida et al.[10] (V_m) and Tokuda et al.[17] (D_i), and the dashed extensions are extrapolations of these data. Uncertainties in the simulated quantities are smaller than the sizes of the symbols.
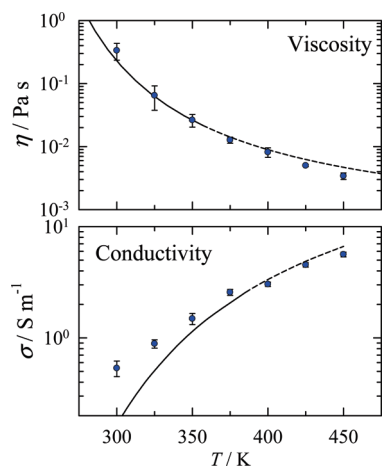

Figure 3. Temperature dependence of the viscosity and conductivity of ILM2 (points) compared with experiment (curves). Experimental data are represented by the parametrizations of Tokuda et al.[17] and Zech et al.[18] (solid curves) and their extrapolations (dashed curves).

used in this work are identical to those from ref 1 and will not be repeated here.

In addition to molar volumes and diffusion coefficients, other properties not specifically included in the parametrization are also reproduced with reasonable accuracy by ILM2. Figure 3 illustrates the temperature dependence of the viscosity and conductivity. Viscosities of ILM2 are within 40% of values measured for [Im$_{41}$][PF$_6$] over the entire temperature range studied. Conductivities do not compare as favorably, and are more than 2-fold larger than experimental values at the lowest temperatures. Other static properties that can be compared with experiment are the thermal expansion coefficient α_P, the isothermal compressibility κ_T, and enthalpy of vaporization $\Delta_{vap}H$. By virtue of the model having been tuned to reproduce molar volumes, the coefficient of thermal expansion, 6.0×10^{-4} K^{-1}, is nearly identical to the experimental value, 5.8×10^{-4} K^{-1}. The isothermal compressibilities of the model (Figure S1a of the Supporting Information) are, on average, 30% high

compared with values measured for [Im$_{41}$][PF$_6$]. But, at the maximum pressures typically used in experiment (200 MPa[10]), this difference implies only a 2−3% error in molar volumes. In addition, the values of κ_T and α_P fall within the range characteristic of room temperature ionic liquids (Figure S1b of the Supporting Information). The enthalpy of vaporization at 298 K is 146 ± 2 kJ/mol (Table S1 of the Supporting Information), close to the best estimates for [Im$_{41}$][PF$_6$], 162 ± 10 kJ/mol.[11,12] This brief survey shows that ILM2 provides a good, albeit not perfect, representation of [Im$_{41}$][PF$_6$]. More importantly, we believe that it should be a reliable model for simulating typical ionic liquid behavior near room temperature.

Given the improved realism of the present model, it is of interest to re-examine the insights derived from simulations of ILM1 to determine which of the conclusions reached in ref 1 might be modified. By performing all of the same analyses discussed in ref 1, we find that, after applying the 100 K temperature correction needed to align ILM1 with experiment, the basic conclusions regarding structural and dynamical characteristics of ILM1 apply with very little change to ILM2. For completeness, we have included figures and tables analogous to those discussed at length in ref 1 in the Supporting Information. Here, we mention only the key features. Reduction of the ion charges in ILM2 obviously decreases the relative importance of electrostatic interactions compared to Lennard-Jones interactions (Table S1). Nevertheless, electrostatic interactions still provide 82% of the cohesive energy of the liquid (compared with 89% in ILM1). The striking similarities noted between ILM1 near room temperature and NaCl near its melting point are still valid for ILM2. For example, the ratio of electrostatic to thermal energies in the two systems, $q^2\rho^{1/3}/(4\pi\varepsilon_0 k_B T) = 48$ for ILM2 at 298 K versus ∼50 for NaCl near 1100 K. The (properly scaled) center-of-mass and charge distribution functions of ILM2 are close to those of NaCl(T_f), just as they were in ILM1 (Figure S2 of the Supporting Information).

After making a 100 K temperature shift, the dynamics observed in the two models are also quite similar. Figure 4 compares translational and rotational mean-squared displacements (MSDs) of ILM2 at 350 K with those of ILM1 at 450 K. The near equality of these functions as well as orientational correlation functions (Figure S3) and van Hove distributions (Figure S4) supports our original contention that ILM1 should provide a reasonable model for real ionic liquids simply by making a 100 K temperature compensation. Observations of heterogeneous dynamics resembling those of supercooled liquids, descriptions of the nondiffusive rotational dynamics, and the importance of 180° reorientations apply equally well to ILM2 as to ILM1. Although the large departures from hydrodynamic predictions of the orientational MSDs are somewhat reduced in ILM2 (Figures S5, S6; Table S2 of the Supporting Information) the qualitative features and explanations of this unusual behavior provided in ref 1 are equally valid for ILM2. Finally, comparisons of ILM2 to its corresponding "neutral mixture" (NM) in which charges are eliminated (Tables S2, S3 of the Supporting Information), lead to the same interpretation of the slow, heterogeneous dynamics of ionic liquids as being due to the lattice-like structure created by electrostatic interactions. Thus, we conclude that the qualitative insights derived from simulations of ILM1 are not significantly altered using this improved model.

Finally, we ask how realistic it is to simulate an ionic liquid using ion charges reduced to ±0.78e, as is done here. This approach is not without precedent, and, in fact, this charge

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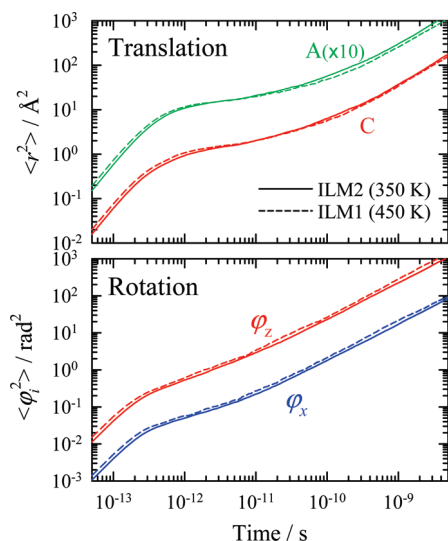*J. Phys. Chem. B, Vol. 114, No. 39, 2010* **12631**

Figure 4. Translational and rotational mean squared displacements of ILM2 at 350 K and ILM1 at 450 K illustrating the similarity in the dynamics of the two models under a 100 K temperature shift. In the top panel, the anion (A) MSDs have been multiplied by a factor of 10 for clarity. φ_x and φ_z denote rotations about the x and z inertial axes of the cation as defined in Figure 1. The MSDs of φ_y are nearly indistinguishable from those of φ_x and are omitted for clarity.

reduction is quite similar to what has been employed in all-atom simulations by other workers.[7,13,8] For example, in simulations of [Im$_{41}$][PF$_6$], Bhargava and Balasubramanian[7] found that use of charges of $\pm0.8e$ improved agreement both with structural data derived from ab initio simulations and with experimental ion diffusion coefficients. In a similar study, Youngs and Hardacre[8] also compared structural data obtained from ab initio simulations of 1−3-dimethylimidazolium chloride ([Im$_{11}$][Cl]) with results of classical simulations in which ion charges ranged between ±0.5 and $1e$. The simulated diffusion coefficients varied several hundred-fold over this range of charges; best agreement with ab initio structures and estimates of experimental diffusion coefficients was achieved for charges between ±0.7 and $0.8e$.

Independent justification for the use of reduced charges comes from observations of charge transfer in ab initio calculations of isolated ion pairs or larger aggregates,[14,15] and bulk liquids,[16,15] which typically indicate ion charges between 0.6 and 0.9e. In some of the most recent work, Schmidt et al. simulated [Im$_{11}$][Cl] using Car−Parrinello molecular dynamics (30 ion pairs for 25 ps) and found the charge on the Cl$^-$ anion to be $0.63 \pm 0.08e$. Thus, charge transfer is a reality in ionic liquids, and it is therefore reasonable to adopt noninteger values of charge to approximate the average interactions among ions in

condensed phases. The charges derived from our empirical parametrization probably account for the related effects of charge transfer as well as electronic polarization in some effective manner. The artifice of using reduced ion charges seems to produce a model that realistically captures many of the generic properties of neat liquids. Our initial results on simulations of solvatochromic probes in ILM2 suggest that it will also prove to be a satisfactory model for examining solvation in ionic liquids.

Supporting Information Available: Three tables and six figures detailing comparisons of ILM2 with experimental data and with previous simulations of ILM1. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Roy, D.; Patel, N.; Conte, S.; Maroncelli, M. *J. Phys. Chem. B* **2010**, *114*, 8410.

(2) Wang, Y.; Feng, S.; Voth, G. A. *J. Chem. Theory Comput.* **2009**, *5*, 1091.

(3) Bhargava, B. L.; Devane, R.; Klein, M. L.; Balasubramanian, S. *Soft Matter* **2007**, *3*, 1395.

(4) Spohr, H. V.; Patey, G. N. *J. Chem. Phys.* **2009**, *130*, 104506/1.

(5) Jeong, D.; Choi, M. Y.; Kim, H. J.; Jung, Y. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2001.

(6) Tsuzuki, S.; Shinoda, W.; Saito, H.; Mikami, M.; Tokuda, H.; Watanabe, M. *J. Phys. Chem. B* **2009**, *113*, 10641.

(7) Bhargava, B. L.; Balasubramanian, S. *J. Chem. Phys.* **2007**, *127*, 114510/1.

(8) Youngs, T. G. A.; Hardacre, C. *ChemPhysChem* **2008**, *9*, 1548.

(9) Lynden-Bell, R. M.; Youngs, T. G. A. *J. Phys.: Condens. Matter* **2009**, *21*, 424120.

(10) Machida, H.; Sato, Y.; Smith, R. L., Jr. *Fluid Phase Equilib.* **2008**, *264*, 147.

(11) Verevkin, S. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 5071.

(12) Deyko, A.; Lovelock, K. R. J.; Corfield, J.-A.; Taylor, A. W.; Gooden, P. N.; Villar-Garcia, I. J.; Licence, P.; Jones, R. G.; Krasovskiy, V. G.; Chernikova, E. A.; Kustov, L. M. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8544.

(13) Zhao, W.; Eslami, H.; Cavalcanti, W. L.; Mueller-Plathe, F. *Z. Phys. Chem. (Muenchen, Germany)* **2007**, *221*, 1647.

(14) Morrow, T. I.; Maginn, E. J. *J. Phys. Chem. B* **2002**, *106*, 12807.

(15) Schmidt, J.; Krekeler, C.; Dommert, F.; Zhao, Y.; Berger, R.; Delle, S. L.; Holm, C. *J. Phys. Chem. B* **2010**, *114*, 6150.

(16) Buhl, M.; Chaumont, A.; Schurhammer, R.; Wipff, G. *J. Phys. Chem. B* **2005**, *109*, 18591.

(17) Tokuda, H.; Kikuko, H.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593.

(18) Zech, O.; Stoppa, A.; Buchner, R.; Kunz, W. *J. Chem. Eng. Data* **2010**, *55*, 1774.

JP108179N