Molecular Force Field for Ionic Liquids Composed of Triflate or Bistriflylimide Anions

2 AUTHORS:

Jose Nuno A Canongia Lopes
Technical University of Lisbon
179 PUBLICATIONS **8,333** CITATIONS

SEE PROFILE

Agílio A H Pádua
Université Blaise Pascal - Clermont-Ferrand II
210 PUBLICATIONS **5,979** CITATIONS

SEE PROFILE

Molecular Force Field for Ionic Liquids Composed of Triflate or Bistriflylimide Anions

José N. Canongia Lopes

Centro de Química Estrutural, Instituto Superior Tećnico, Lisboa, Portugal

Agílio A. H. Pádua*

Laboratoire de Thermodynamique des Solutions et des Polymères, Université Blaise Pascal Cllermont-Ferrand/CNRS, France

A set of force field parameters is proposed for the molecular simulation of ionic liquids containing the anions trifluoromethylsufate and bis(trifluoromethylsulfonyl)imide, also known as triflate and bistriflylimide, respectively. The new set can be combined with existing force fields for cations in order to simulate common room-temperature ionic liquids, such as those of the dialkylimidazolium family, and can be integrated with the OPLS-AA or similar force fields. Ab initio quantum chemical calculations were employed to obtain molecular geometry, torsional energy profiles, and partial charge distribution in the triflate and bistriflylimide anions. One of the torsions in bistriflylimide, corresponding to the dihedral angle S−N−S−C, has a complex energy profile which is precisely reproduced by the present parameter set. A new set of partial electrostatic charges is also proposed for the pyrrolidinium and tri- and tetra-alkylammonium cations. Again, these parameters can be combined with the OPLS-AA specification for amines in order to simulate alkylammonium salts. The force-field models were validated against crystal structures and liquid-state densities.

Introduction

Room-temperature ionic liquids (ILs) are promising reaction and separation media for the chemical industry, offering advantages in terms of efficiency and ease of recovery when compared to the usual organic solvents.[1] ILs can be synthesized in a wide variety of cation−anion combinations, enabling a fine-tuning of their properties as solvents. The reason an organic salt is liquid at room temperature is connected to some kind of asymmetry or complexity in its molecular structure which renders crystallization difficult. The novelty and variety of ILs, combined with their nontrivial molecular shapes, are some of the reasons their interactions with other chemical species are not yet well understood. In particular, the mechanisms governing solvation in ILs are at present the subject of investigations by molecular modeling.[2−4] Such studies require the formulation of force fields capable of representing the energetics and structure of condensed phases.

In the present work, new force field parameters were determined for the IL anions trifluoromethylsufate, or triflate [chemical formula $CF_3SO_3^-$ (tf^-)], and bis(trifluoromethylsulfonyl)imide, or bistriflylimide [chemical formula $(CF_3SO_2)_2N^-$ (tf_2N^-)]. The proposed models for anions can be combined with previously published interaction potentials for dialkylimidazolium cations,[5] in order to simulate a large variety of room-temperature ionic liquids, such as [bmim][tf$_2$N], for example. A small set of missing parameters was also generated so that when used in combination with the OPLS-AA force field for amines,[6] the system enables the representation of alkylammonium cations. Ions of this family are frequently used in the formulation of ILs, including some heterocyclic molecules such as *N,N*-dialkylpyrrolidinium cations.

The methodology used in the construction of the present force field is close to the one used in the development of the OPLS-AA parametrization for perfluoroalkanes,[7] and it has been applied by the authors in previous publications.[5,8] It consists of (i) quantum chemical calculations to derive the geometrical and conformational parameters (bond lengths, valence angles, torsion energy profiles) that are not yet available for the molecules under investigation in the OPLS-AA[9] or AMBER[10] force fields; (ii) the use of electrostatic surface potential methods to determine the partial atomic charge distributions in the molecules; and (iii) molecular dynamics simulations to validate the models against crystal structure and liquid density experimental data.

Construction of the Force Field

The present model is intended to be compatible with the OPLS-AA framework;[9] therefore, it adopts the same kind of functional form of this widely used molecular force field. The energy of a pair of molecules is given by

$$U_{12} = \sum_b \frac{k_{r,b}}{2}(r_b - r_{0,b})^2$$
$$+ \sum_a \frac{k_{\theta,a}}{2}(\theta_a - \theta_{0,a})^2$$
$$+ \sum_d \sum_{m=1}^{n} \frac{V_{m,d}}{2}[1 + (-1)^{m+1} \cos(m\varphi_d)]$$
$$+ \sum_i \sum_j \left\{ 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}} \right\} \quad (1)$$

where the sums are over bonds, angles, dihedrals, and non-

* To whom correspondence should be addressed. E-mail: agilio.padua@univ-bpclermont.fr.

bonded interaction sites, respectively. The sole difference between eq 1 and the functional form of OPLS-AA is that the values of harmonic force constants for bond stretching and angle bending in the latter correspond to $k/2$ in eq 1. Parameters already available in OPLS-AA or AMBER for intramolecular terms (bond lengths, valence angles, torsional profiles) or in OPLS-AA for intermolecular terms (Lennard-Jones potentials, electrostatic charges) will be used whenever possible. The anions studied here are rich in heteroatoms (those different from C or H) in arrangements not commonly present in traditional organic liquids, amino acids, or nucleotides. As a consequence, terms had not yet been defined in the OPLS-AA/AMBER literature, whose main focus is the simulation of biomolecules.

Special attention is devoted here to torsion energy profiles, which play an important role in defining the molecular configurations, and to the distributions of partial atomic charges, that affect the interactions. Values of bond lengths and valence angles are also proposed according to our quantum chemical calculations. The force constants concerning bond stretching and angle bending are for a large part taken from the literature, since the accuracies of these terms are not so stringent when calculating thermodynamic and structural properties of condensed phases.

Quantum calculations reported here fall into three categories: (i) Molecular geometries were optimized at the HF/6-31G(d) level, as is current practice in force-field development. Most geometry optimizations consisted of relaxed potential energy scans, in which an internal coordinate (typically a dihedral angle under study) is held fixed at a series of established values while the remaining internal coordinates are allowed to relax toward a potential energy minimum. (ii) Single-point energies were then calculated for the optimized geometries at the MP2/cc-pVTZ(-f) level, thus including electron correlation and using a suitable, extended basis set. This basis set is created by removing the f functions from the cc-pVTZ basis set.[11] These combinations of basis sets and theory levels for geometry optimizations and single point energies have been shown to yield accurate conformational energetics on a large variety of molecules (the Halgren test).[12] (iii) Distributions of partial atomic charges were fitted to electrostatic surface potentials according to the CHelpG procedure,[13] using electron densities generated at the MP2/cc-pVTZ(-f) level.

The Gaussian package[14] was used for the ab initio calculations. Molecular dynamics simulations were executed with the DL_POLY program.[15]

Molecular Geometries. The equilibrium values of bond lengths and valence angles proposed for the present force field were deduced from the ab initio geometry optimizations. The force constants for bond stretching were available in the OPLS-AA and AMBER force fields and were taken from these sources. Normal-mode analyses were performed on the triflate and bistriflylimide in an attempt to obtain angle bending force constants, but difficulties arose because the normal mode matrices were not diagonal enough. In view of this, the angle force constants proposed here are the result of an empirical correlation suggested by Halgren[16] to overcome this kind of problem. The set of stretching and bending parameters is listed in Table 1.

Atomic Charges. The Coulomb interactions were represented by partial charges placed on the atomic sites, in accord with OPLS-AA philosophy.[9] Electrostatic surface potential fits yield charges which vary with the configurations of the molecule; therefore, the values proposed here are a compromise between several criteria. First, the charges should match closely those

TABLE 1: Internal Stretching and Bending Parameters Compared with X-ray Data

	bond	this work		X-ray[17−23]	
		r_0 (Å)	$k_r{}^a$ (kJ mol^{-1} Å^{-2})	r_0 (Å)	r_0 (Å)
NO_3^{-2}	N−O	1.226	5307	1.220	
PF_6^{-b}	P−F	1.606	3100	1.596	1.566
tf$^-$, tf$_2$N$^-$	C−F	1.323	3697	1.324	1.310
	C−S	1.818	1970	1.797	1.823
	S−O	1.442	5331	1.426	1.423
	N−S	1.570	3113	1.579	1.576

	angle	this work		X-ray[17−23]	
		θ_0 (deg)	$k_\theta{}^b$ (kJ mol^{-1} rad^{-2})	θ_0 (deg)	θ_0 (deg)
NO_3^{-b}	O−N−O	120.0	1011	120.0	
PF_6^{-b}	F−P−F	90.0	1165	90.0	90.0
	F−P−F	180.0	291	180.0	180.0
tf$^-$, tf$_2$N$^-$	F−C−F	107.1	781	106.9	106.2
	S−C−F	111.8	694	112.0	111.7
	C−S−O	102.6	870	103.1	103.5
tf$^-$	O−S−O	115.3	969	115.0	114.6
tf$_2$N$^-$	O−S−O	118.5	969	115.0	114.7
	O−S−N	113.6	789	112.6	112.1
	C−S−N	100.2	816	103.7	104.0
	S−N−S	125.6	671	125.0	124.7

^{a} The values given here for force constants should be divided by 2 for full compatibility with the AMBER and OPLS-AA functional forms. ^{b} These force constants, in complement of the parameters given in a previous publication,[5] enable the treatment of these anions as flexible molecules.

TABLE 2: Nonbonded Parameters^a

	atom	q (e)	σ (Å)	ϵ (kJ mol^{-1})
tf$^-$, tf$_2$N$^-$	C	+0.35	3.50	0.27614
	F	−0.16	2.95	0.22175
	S	+1.02	3.55	1.04600
tf$^-$	O	−0.63	2.96	0.87864
tf$_2$N$^-$	O	−0.53	2.96	0.87864
	N	−0.66	3.25	0.71128
R$_3$NH$^+$	H	+0.31	2.50	0.12552
R$_3$NH$^+$, R$_4$N$^+$	N3	+0.03, +0.12	3.25	0.71128
	C1^b	−0.17	3.50	0.27614
	H1^c	+0.13	2.50	0.12552
	C2^d	+0.01	3.50	0.27614
	CS^e	−0.12	3.50	0.27614
	CT^f	−0.18	3.50	0.27614
	HC^g	+0.06	2.50	0.12552

^{a}Atomic partial charges were calculated in the present work. Lennard-Jones parameters were taken from OPLS-AA. ^{b} C bonded to N3. ^{c} H bonded to C1. ^{d} C bonded to C1. ^{e} C in generic −CH$_2$−. ^{f} C in generic −CH$_3$. ^{g} H bonded to C2, CS, or CT.

obtained at optimized geometries, since these energy minima represent the most probable configurations. Second, in the interest of simplicity, the set of charges should form a scheme which is transferable between similar molecules, for example along a homologous series. Third, the charge scheme should merge easily with other molecular fragments described within OPLS-AA, so in some cases the overall electrostatic charge of a functional group can be constrained. These last two arguments imply that in some cases the accuracy with respect to the ab initio values had to be sacrificed. The set of nonbonded parameters proposed is listed in Table 2.

Charges for tri- and tetra-alkylammonium cations were calculated with the main objective of modeling salts composed by these cations (including pyrrolidinium), combined with anions such as triflate and bistriflylimide. Since all of the remaining terms necessary to represent ammonium cations are available in the OPLS-AA force field for amines,[6] the set of

Molecular Force Field for Ionic Liquids

J. Phys. Chem. B, Vol. 108, No. 43, 2004 **16895**

charges proposed here was the only element required to enable the simulation of ammonium ions having either linear or cyclic aliphatic side chains. When compared to the original OPLS (united atom version) charges for ammonium cations,[24] our ab initio calculations using the MP2/cc-pVTZ(-f) wave functions give some significant differences when compared with the HF/6-31G* results of OPLS-UA. In our case, nitrogens have small positive charges whereas in OPLS-UA they have negative or null charges. For example, Mulliken population analysis with our wave functions produced charges on N of +0.01 in $(CH_3)_4N^+$ whereas in OPLS-UA the value found was -0.16.[24] In the charge scheme proposed by the authors of OPLS-UA, the charge on N was empirically set to zero on quaternary ammonium cations. Interestingly, the authors state that "the negative charges may be somewhat surprising; however, the nitrogens are more positive than in the corresponding amines". When using the CHelpG procedure with the present wave functions, the N charges are of +0.01 in $(CH_3)_3NH^+$, +0.18 in $(CH_3)_4N^+$, and of +0.13 in both *N,N*-dimethylpyrrolidinium and *N*-methyl-N-propylpyrrolidinium. This leads us to propose a value of +0.12 in our scheme. Therefore, although N is the more electronegative atom, evidence arising from the use of a better theory level and a larger basis set, MP2/cc-pVTZ(-f), indicates that in ammonium cations this atom takes a significant part of the positive charge.

It is curious to see that the same charge scheme devised for the alkyl side chains in dialkylimidazolium cations[5] is transferable to the ammonium cations. The sole case where charges attributed following that scheme deviate significantly from the ESP charges concerns the C1 carbons of the pyrrolidinium ring. In fact, charges of -0.03 for these carbons and of +0.06 for the attached hydrogens would reproduce more closely the values given by CHelpG. The charges proposed in Table 2 are -0.17 and +0.13, respectively. Although these are quite different from the CHelpG values, the overall charge of a $-CH_2-$ group is +0.09 in both cases. In the interest of a simpler specification of the force field and also of consistency, we opted for the latter values.

Lennard-Jones parameters were taken from OPLS-AA.[9] For the fluorine atoms in triflate and bistriflylimide anions, we adopted Lennard-Jones parameters from the OPLS-AA model for perfluoroalkanes.[7] These differ from the F parameters that are considered specifically for PF_6^- also within OPLS-AA.[25]

Torsion Energy Profiles. As in previous works,[5,8] a building-up procedure was followed in order to generate a consistent set of parameters representing the potential energy associated with torsion around dihedral angles, as in previous work.[5,8] Often it is necessary to consider simpler molecules, similar to fragments of the structures under study, from which some of the torsion energy profiles are deduced.

The dihedral functions in OPLS-AA, expressed by a cosine series, do not render the full potential energy related to the torsion around a covalent bond (the same is true in other force field specifications). This is because nonbonded interactions, i.e., Lennard-Jones and Coulombic terms, also act between sites within the same molecule connected by three or more bonds. In OPLS-AA, such nonbonded intramolecular interactions are described by the same parameters used in intermolecular interactions, only scaled by a factor of 0.5. These nonbonded, steric effects account for a part, sometimes predominant, of the torsion energy profile. Therefore, the parameters of the cosine series cannot simply be fitted to the total torsion energy profile calculated ab initio, but instead to the difference between this full profile and the profile corresponding to the nonbonded part
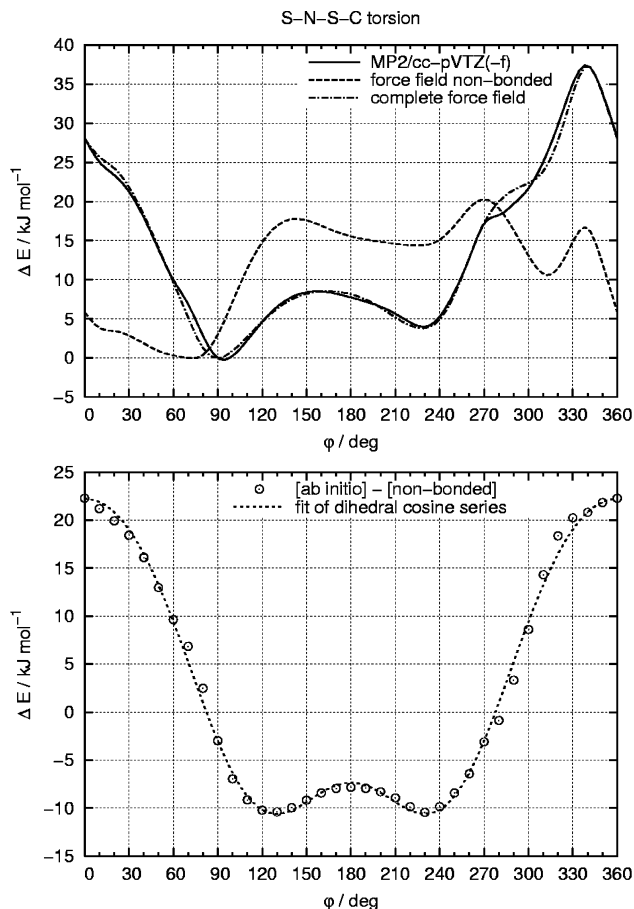

Figure 1. Torsion energy profile associated with the dihedral angle S−N−S−C in bistriflylimide.

of the force field. The latter can be generated by MD simulation with the cosine series zeroed for the dihedral angle in question.[5,8] For the reason given here, the dihedral parameters depend on the values of the electrostatic charges.

The first dihedral angle investigated was the torsion energy profile F−C−S−O, already present in the triflate (tf⁻) anion, $CF_3-SO_3^-$. The barrier to internal rotation in this anion was calculated ab initio, and the value of the V_3 parameter of the dihedral cosine series was adjusted to it (the nonbonded part was taken into account as described above). When combined with the remaining terms of the force field, this dihedral is sufficient for the simulation of the triflate anion.

Having defined the F−C−S−O dihedral, the F−C−S−N function could be parametrized next, by scanning the torsion around the C−S bond in the bistriflylimide anion (tf₂N⁻). Due to the 3-fold symmetry still present because of the CF_3 group, only 60° needed to be scanned.

Two additional functions were necessary to describe the conformations of tf₂N⁻: S−N−S−O and S−N−S−C. Their contributions cannot be isolated from a conformational analysis of this anion alone; therefore, the anion $CF_3-SO_2-N-SO_3^{2-}$ was considered for the purpose of fitting the parameters of the S−N−S−O dihedral. Once again, the 3-fold symmetry found here simplifies the issue to an internal rotation barrier around 60°. Finally, the S−N−S−C torsion could be considered. This particular term has a complicated form that can be seen in Figure 1.

It is remarkable how a cosine series with only three terms can represent this profile accurately. In fact, it is the nonbonded interactions that account for most of the asymmetry of the profile, leaving to the cosine series the role of adjusting a

16896 *J. Phys. Chem. B, Vol. 108, No. 43, 2004*

Canongia Lopes and Pádua

TABLE 3: Dihedral Angle Cosine Series Parameters (V_i in kJ mol^{-1})

dihedral	V_1	V_2	V_3
F−C−S−O	0.000	0.000	1.451
S−N−S−O	0.000	0.000	−0.015
F−C−S−N	0.000	0.000	1.322
S−N−S−C	32.773	−10.420	−3.195

difference which, although significant in magnitude, is much more symmetrical in terms of angular dependence. The set of dihedral angle parameters developed in this work is summarized in Table 3.

Validation of the Force Field

Since most of the currently available experimental results concerning the thermophysical characterization of ILs are related to their volumetric properties, we decided to test the performance of the proposed force field in the estimation of molar densities of ILs containing either the triflate or bistriflylimide anions, in both the crystalline and liquid phases.

Crystal Structures. Four IL crystalline structures containing the two anions under discussion were selected from the Cambridge Crystallographic Database (CCDB). These include the 1,3-di-*tert*-butyl-imidazolium triflate IL[26] and the bistriflylimide salts of tetraethylammonium, trimethylammonium, and *N,N*-dimethylpyrrolidinium.[27] While the choice of the triflate salt was motivated by the fact that the molecular force field for imidazolium-based cations was developed recently by the authors,[5] the choice of the ILs based on bistriflylimide was dictated by the fact that most ILs of this family that exhibit a high-temperature melting point contain ammonium-based cations.

The objective of the simulations is to test the performance of the force field in predicting both the crystal density and its structural properties (dimensions and director angles of the crystal's unit cell). The stringency of the test was confirmed with simulation runs where ad hoc parameters were introduced and large distortions were observed in the unit cell of the

crystalline lattice. Conversely, a simulation that was accidentally started from a wrong initial configuration (the symmetry of the crystal was set to space group $P2_1/c$ instead of $P2_1/n$) managed to evolve to the right configuration, overcoming a distortion where an entire plane of ions had been shifted (plane-gliding translation).

The simulation boxes and initial configurations were set by taking into account the dimensions and occupancy of the unit cells of each crystalline structure given by the CCDB data. Because the dimensions of the unit cells of most of the crystals are too small to accommodate a sufficiently large cutoff distance, several cells were stacked together to form a sufficiently large and well proportioned simulation box, with cutoff distances of 10 Å. Long range corrections were applied beyond the cutoff distance, and the Ewald method was implemented to take into account the long-range character of the electrostatic interactions. The initial position, orientation, and conformation of each molecule within the simulation box was the one defined by the lattice coordinates at the CCDB. Since the overall size of the simulation box is defined by the dimensions of the unit cell of each crystal, simulations with different box sizes and cutoff distances (up to 16 Å) were run to check that the dimensions of the simulation box/cutoff were sufficiently large to make negligible any finite-size effects. The simulations were performed using a Nosé−Hoover thermostat coupled with an anisotropic Hoover barostat that allowed the simulation box to change volume and shape under constant (N, p, T) conditions. The temperatures were fixed to match those used during the crystallographic experiments, and the pressure was set to a null value. All runs were allowed to equilibrate for a period of 100 ps, followed by production times of 200 ps. These simulation times were found appropriate since the runs are started from a known initial configuration (the experimental equilibrium structure), and it was observed that the relaxation is complete before the end of the equilibration period.

The simulation details for each crystal are given in Table 4. As in a previous publication concerning the imidazolium cations,[5] the densities of all crystals are predicted with an

TABLE 4: Comparison of Simulated Crystal Structures with Experimental Data from the Cambridge Database[a]

	dtbmim^{+b} tf$^-$	mmpy^{+c} tf$_2$N$^-$	N3333^{+d} tf$_2$N$^-$	N1110^{+e} tf$_2$N$^-$	emim$^+$ NO$_3^-$	emim$^+$ PF$_6^-$
CCDCref	NAQJOE[28]	XOMDIM[23]	XOMDOS[23]	XOMDAE[23]	KUCPED[17]	HAYBUE[19]
space group	61 *Pbca*	14 $P2_1/c$	14 $P2_1/n$	14 $P2_1/c$	14 $P2_1/n$	14 $P2_1/c$
sim pairs	64	48	36	48	96	192
	$2 \times 2 \times 2$	$3 \times 2 \times 2$	$3 \times 1 \times 3$	$3 \times 2 \times 2$	$6 \times 2 \times 2$	$4 \times 4 \times 3$
cutoff (Å)	10	10	10	10	10	10
T (K)	298	298	298	298	298	298
molecules/cell	8	4	4	4	4	4
a_{exp} (Å)	14.41	8.50	9.74	7.61	4.54	8.76
a_{sim} (Å)	14.50	8.56	9.63	7.90	4.51	8.78
b_{exp} (Å)	12.03	13.83	22.86	14.22	14.81	9.34
b_{sim} (Å)	12.10	13.70	23.30	13.55	14.20	9.45
c_{exp} (Å)	18.70	12.81	10.03	12.51	13.45	13.70
c_{sim} (Å)	18.85	12.85	9.83	12.55	13.50	13.53
α_{exp} (deg)	90.0	90.0	90.0	90.0	90.0	90.0
α_{sim} (deg)	90.0	89.9	90.1	90.2	90.0	90.1
β_{exp} (deg)	90.0	98.8	97.6	106.6	95.7	103.1
β_{sim} (deg)	90.0	96.3	96.0	107.2	94.5	102.9
γ_{exp} (deg)	90.0	90.0	90.0	90.0	90.0	90.0
γ_{sim} (deg)	90.0	90.0	89.9	90.0	90.0	90.0
V_{exp} (Å^3)	3241	1489	2213	1297	899	1092
V_{sim} (Å^3)	3312	1508	2200	1288	858	1096
ρ_{exp} (mol/L)	4.098	4.461	3.001	5.121	7.383	6.082
ρ_{sim} (mol/L)	4.010	4.404	3.019	5.156	7.740	6.059
$\Delta\rho$ (%)	−2.1	−1.3	0.6	0.7	4.8	−0.4

[a] The codes in the line labeled CCDCref are references for the Cambridge Crystallographic Data Centre. [b] 1,3-Di-*tert*-butylimidazolium. [c] *N,N*-Dimethylpyrrolidinium. [d] *N,N,N,N*-Tetrakis(*n*-propyl)ammonium. [e] *N,N,N*-Trimethylammonium.

Molecular Force Field for Ionic Liquids

J. Phys. Chem. B, Vol. 108, No. 43, 2004 **16897**

TABLE 5: Comparison of Simulated Liquid Densities with Experimental Data

	bmim tf$_2$N	emim tf$_2$N	mmim tf$_2$N	pmpy[a] tf$_2$N	emim tf
			300 K		
ρ_{exp} (kg/L)	1.44[29,30]	1.52[29,30]	1.57[30]	1.45[31]	1.38[32]
ρ_{sim} (kg/L)	1.48	1.57	1.63	1.46	1.43
$\Delta\rho$ (%)	3.1	3.3	3.9	0.8	3.5
			343 K		
ρ_{exp} (kg/L)	1.40[30]	1.48[30]	1.52[30]	-	-
ρ_{sim} (kg/L)	1.45	1.54	1.59	-	-
$\Delta\rho$ (%)	3.6	4.1	4.6	-	-

[a] *N*-Methyl-*N*-propylpyrrolidinium.

accuracy around 2%. In the case of the salts of alkylammonium with bistriflylimide, the results are slightly better (cf. also the liquid-phase simulation results below).

It is important to notice that (i) the deviations are of the same order of magnitude as those obtained by other authors when comparing the performance of their IL models against experimental density data; (ii) the level of agreement is very good considering that the calculations are purely predictive, as all parameters used were either taken as such from the OPLS-AA/AMBER force field or calculated ab initio, none was adjusted to match experimental data; and (iii) in some cases experimental IL density results from different sources also exhibit deviations in the 2−4% range.

Liquid-State Properties. Systems consisting of 200 ion pairs were simulated by molecular dynamics in periodic cubic boxes. Cutoff was taken at 12 Å for short-range Lennard-Jones interactions, with appropriate tail corrections, and the long-range coulomb forces were handled by Ewald sums. Nosé−Hoover thermostat and barostat were activated to maintain temperature and pressure, with time constants of 0.1 and 0.5 ps, respectively. Calculated densities are compiled in Table 5 and compared with experiment.

The simulated density results are systematically larger than the experimental ones, except for *N*-methyl-*N*-propylpyrrolidinium for which good agreement is obtained. This general situation is in contrast with the results obtained for dialkylimidazolium chlorates and hexafluorophosphates simulated previously[5] (using the same models for the cations), where simulated densities were typically 3% below the experimental data. For dialkylimidazolium nitrates, calculated densities were higher than experimental ones by less than 2%.

The agreement of simulated densities with experiment could be improved by fine-tuning the parameters for several families of anions. This would imply major changes in many parameters, therefore abandoning the OPLS-AA framework, with the consequent loss of transferability. On the other hand, a modification of the parameters of the imidazolium cations would be unlikely to solve the problem, since deviations are of opposite sign depending on the family of the anion. We feel that an accuracy of ±3% in liquid densities is reasonable and justified by the generality of the present model.

Conclusion

A molecular force field was developed in a systematic way for a number of anions, namely triflate and bistriflylimide, that compose commonly used room-temperature ionic liquids. The proposed model is compatible with OPLS-AA and with a previously published model for imidazolium cations.[5] No specific parametrizations existed so far for the anions treated here, in particular for partial electrostatic charges and torsion energy profiles.

The force field was tested through predictions of crystal structures and liquid densities using the molecular dynamics method. A number of crystal structures are correctly reproduced by the model, in terms of geometry (unit cell distances and angles) and density. Liquid densities of triflate and bistriflylimide ionic liquids are slightly overpredicted in the majority of cases (by about 3%). These density deviations have the opposite sign of those obtained using the same imidazolium cations[5] but different anions. Therefore, it appears that the model for the cations is compatible with different types of anion, of varied molecular shape and chemical composition. The predictions would unlikely be as accurate overall if the models were fine-tuned to just one family of ionic liquids in particular.

The scheme devised previously[5] to attribute partial atomic charges to *n*-alkylmethylimidazolium cations proved to be particularly robust, since its application in the present work to imidazolium cations with branched alkyl side chains and to quaternary ammonium, including pyrrolidinium, cations was possible without modification.

References and Notes

(1) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley VCH: New York, 2002.

(2) Hanke, C. G.; Atamas, N. A.; Lynden-Bell, R. M. *Green Chem.* **2002**, *4*, 107.

(3) Hanke, C. G.; Lynden-Bell, R. M. *J. Phys. Chem. B* **2003**, *107*, 10873.

(4) Deschamps, J.; Pádua, A. *Ionic Liquid III: Fundamentals, Progress, Challenges and Opportunities*; 2004 ACS Symposium Series 857; American Chemical Society: Washington, DC, in press.

(5) Canongia Lopes, J. N.; Deschamps, J.; Pádua, A. A. H. *J. Phys. Chem. B* **2004**, *108*, 2038.

(6) Rizzo, R. C.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1999**, *121*, 4827.

(7) Watkins, E. K.; Jorgensen, W. L. *J. Phys. Chem. A* **2001**, *105*, 4118.

(8) Pádua, A. A. H. *J. Phys. Chem. A* **2002**, *106*, 10116.

(9) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225.

(10) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M.; Fergusin, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179.

(11) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(12) Friesner, R. A.; Murphy, R. B.; Beachy, M. D.; Ringnalda, M. N.; Pollard, W. T.; Dunietz, B. D.; Cao, Y. *J. Phys. Chem. A* **1999**, *103*, 1913.

(13) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) Smith, W.; Forester, T. R. *The DL_POLY package of molecular simulation routines, version 2.12*; The Council for the Central Laboratory of Research Councils, Daresbury Laboratory: Warrington, U.K., 1999.

(16) Halgren, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 4710.

(17) Wilkes, J. S.; Zaworotko, M. J. *Chem. Commun.* **1991**, 965.

(18) Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. *J. Mater. Chem.* **1998**, *8*, 2627.

(19) Fuller, J.; Carlin, R. T.; De Long, H. C.; Haworth, D. *Chem. Commun.* **1994**, 299.

(20) Stenzel, O.; Raubenheimer, H. G.; Esterhuysen, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1132.

(21) Banks, R. E.; Besheesh, M. K.; Pritchard, R. G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2003**, *59*, m141.

(22) Golding, J. J.; MacFarlane, D. R.; Spiccia, L.; Forsyth, M.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1998**, 1593.

(23) Forsyth, C. M.; MacFarlane, D. R.; Golding, J. J.; Huang, J.; Sun, J.; Forsyth, M. *Chem. Mater.* **2002**, *14*, 2103.

(24) Jorgense, W. L.; Gao, J. *J. Phys. Chem.* **1986**, *90*, 2174.

(25) Kamiski, G. A.; Jorgensen, W. L. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2365−2375.

(26) Rijnberg, E.; Richter, B.; Thiele, K.-H.; Boersma, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 56.

(27) Forsyth, C. M.; MacFarlane, D. R.; Golding, J. J.; Huang, J.; Sun, J.; Forsyth, M. *Chem. Mater.* **2002**, *14*, 2103.

(28) Rijnberg, E.; Richter, B.; Thiele, K.-H.; Boersma, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 56.

(29) Hyun, B. R.; Dzyuba, S. V.; Bartsch, R. A.; Quitevis, E. L. *J. Phys. Chem. A* **2002**, *106*, 7579.

(30) Krummen, M.; Wasserscheid, P.; Gmehling, J. *J. Chem. Eng. Data* **2002**, *47*, 1411.

(31) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys. Chem. B* **1999**, *103*, 4164.

(32) Cooper, E. I.; O'Sullivan, J. M. In *Proceedings of the 8th International Symp.osium on Ionic Liquids*; The Electrochemical Society Proceedings Series; Pennington, NJ, 1992; p 386.