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# Molecular Force Field for Ionic Liquids IV: Trialkylimidazolium and Alkoxy carbonyl-Imidazolium Cations; Alkylsulfonate and Alkylsulfate Anions

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This is the fourth article of a series that describes the parametrization of a force field for the molecular simulation of common ionic liquids within the framework of statistical mechanics. The force field was developed in the spirit of the OPLS-AA model and is thus oriented toward the calculation of equilibrium thermodynamic and structural properties in the condensed (liquid) phase. The ions modeled in the present paper are cations of the 1,2,3-trialkylimidazolium and alkoxy carbonyl imidazolium families and alkylsulfate and alkylsulfonate anions. As in previous publications, the force field is built in a stepwise manner that allows, for example, the construction of models for an entire family of cations or anions, with alkyl side chains of different length. Because of the transferability of the present force field, the ions studied here can be combined with those reported in our three previous publications to create a large variety of ionic liquids that can be studied by molecular simulation. The extension of the force field was validated by comparison of simulation results with the corresponding crystal structure and liquid density experimental data.

## Introduction

Alkylimidazolium cations are among the most widely used ionic components of room-temperature ionic liquids. In previous publications<sup>1,2</sup> we have proposed a molecular force field for some families of these cations. In this report, two additional subfamilies of imidazolium-based cations were added to the force field model: trialkylimidazolium and alkoxy carbonyl imidazolium cations. The first subfamily, which differs from the more usual 1,3-dialkylimidazoliums by the methylation of the C<sub>2</sub> carbon of the imidazolium ring (C<sub>RM</sub> in the nomenclature adopted in this work, see Chart 1 below), has been used in situations where the acidic hydrogen atom attached to C<sub>2</sub> was undesirable, or the effect of its presence was being studied. The second subfamily, which contains an ester group in the alkyl side chain, has been proposed as a more biodegradable version of imidazolium cations (at least at the level of the long alkyl side-chain).<sup>3</sup> In both cases, the major part of the molecular edifice had been parametrized, but specific terms had to be included to take into account the methyl group in C<sub>2</sub> or the ester group in the side chain. We performed calculations of electrostatic charge distributions and of torsion energy profiles that will complete the parametrization of the two subfamilies in the context of the above-mentioned force field.

Concerning the anions analyzed in this study, it has been recently anticipated that ionic liquids containing alkylsulfonate or alkylsulfate anions are better options from an environmental perspective than ionic liquids containing anions with fluorine atoms, such as the (now ubiquitous) hexafluorophosphate or bis(trifluoromethanesulfonyl)amide ions.<sup>4</sup>

In spite of the widespread use of alkylsulfate and alkylsulfonate anions as anionic surfactants, the literature describing force field models for such ions has some limitations. Although the geometrical and electrostatic parameters for sulfate and sulfonate groups were introduced by different authors as early as the past decade of the previous century,<sup>5–8</sup> we could not find detailed conformational studies describing the attachment of the alkyl tails to the polar heads. Also, the existing models (including more recent studies<sup>9–12</sup> that are refinements of the works cited above and that in some cases include sulfate-based ionic liquids) describe the alkyl chains within the framework of united-atom models.

Therefore in this work we improved the description of the sulfate and sulfonate anions by: (i) calculation of electrostatic charge distributions using a higher theoretical level and a larger basis set than had been previously done; (ii) calculation of specific torsion energy profiles to provide an accurate description of the conformational energies; (iii) integration in the model of an all-atom description of the alkyl group. The main objective of the three points just presented is to develop a parametrization of the sulfate and sulfonate anions that is completely compatible with the OPLS-AA-based force field developed for other cations and anions present in commonly used ionic liquids.<sup>1,2,13</sup> The quantum chemistry and molecular simulation methods used in the force field development have been presented and justified in the publications just cited. All ions under discussion in this work as well as the adopted nomenclature are illustrated in Chart 1.

## Results and Discussion

**Force Field Development.** The potential function used in this work has the general form

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$$u_{\alpha,\beta} = \sum_{ij}^{\text{bonds}} \frac{k_{r,ij}}{2} (r_{ij} - r_{0,ij})^2 + \sum_{ijk}^{\text{angles}} \frac{k_{\theta,ijk}}{2} (\theta_{ijk} - \theta_{0,ijk})^2 + \sum_{ijkl}^{\text{dihedrals}} \sum_{m=1}^4 \frac{V_{m,ijkl}}{2} [1 + (-1)^m \cos(m \varphi_{ijkl})] + \sum_i \sum_{j \neq i} \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \right\} \quad (1)$$

The right side of eq 1 represents the traditional decomposition of the potential energy into covalent bonds, valence angles, torsion dihedral angles, and atom–atom pairwise repulsive, dispersive, and electrostatic interactions. The repulsive and dispersive terms are described by the Lennard-Jones 12–6 potential and, together with the Coulombic interactions given by point charges, they act between sites in different molecules but also between sites within the same molecule separated by three or more bonds. For sites of a same molecule separated by exactly three bonds, a scaling factor of 0.5 is applied to the Lennard-Jones and Coulombic interactions. It must be stressed that the function in eq 1 does not follow exactly the OPLS-AA convention:<sup>14</sup> in our case, the bonded interactions (bonds and angles) described by harmonic potentials have their force constants divided by a factor of 2, a situation that does not happen in the OPLS-AA case.

**Bond and Angle Parametrization.** As a starting point for the present model, covalent bond and valence angle parameters were taken from recent OPLS-AA<sup>14</sup> literature when available.

For sulfate and sulfonate anions published force field works are few, and we found no recent studies using high-level, post-Hartree–Fock methods and extended basis sets. Therefore, for these anions, we calculated in the present work essentially all the terms concerning molecular geometry (equilibrium bond lengths and valence angles), and the respective force constants, for the sulfate and sulfonyl groups. Only the parameters for the alkyl side chain were taken from OPLS-AA.<sup>14</sup> The quantum chemistry method used for geometries and force constants was HF/6-31G(d), as recommended by Friesner et al.<sup>15</sup> The values obtained are collected in Table 1. Some bonds and angles that appear in sulfates and sulfonates, for example the S–O and C–S bonds and the O–S–O and O–S–C angles, had already been parametrized by us for the triflate and bis(trifluoromethanesulfonyl)amide anions.<sup>13</sup> Since the difference between

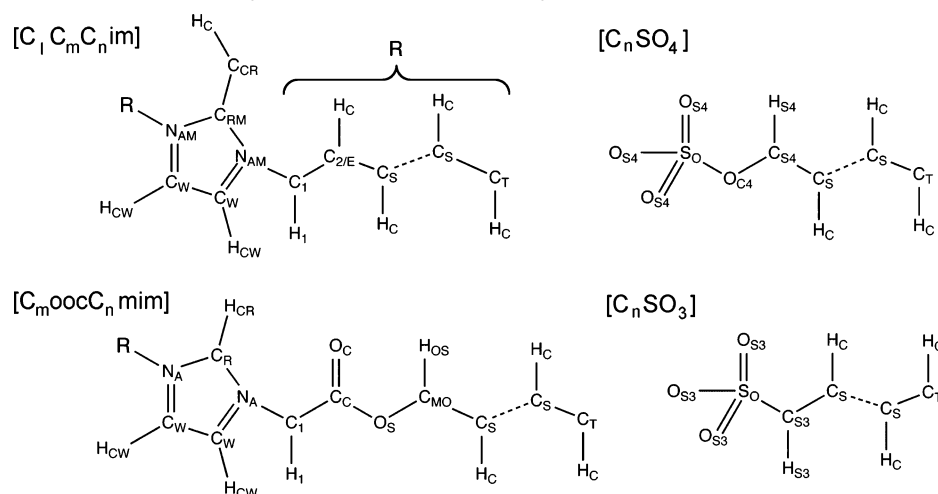
the results obtained in that work and those calculated now are very small (always less than 2 pm or 1 degree of arc), we decide to retain the parameters already postulated for the bonds and angles of triflate or bistriflamide.

It is important to stress that, while ab initio geometry optimizations directly yield the equilibrium bond lengths and angles, the corresponding stretching and bending force constants must be estimated through the calculation of the frequencies of the different internal molecular modes. In some cases, ill-conditioned matrices render these calculations ineffective when converting from normal into the required internal molecular coordinates. Whenever this occurred, the correlation proposed by Halgren<sup>21</sup> was used to assign the corresponding angle-bending force constants.

For the cations of the imidazolium family studied here, bond and angle parameters were taken either from one of our previous works on imidazolium cations<sup>1</sup> or from OPLS-AA/AMBER for the ester groups present in the side chain.<sup>22</sup>

The comparison between the equilibrium bond lengths and angles calculated ab initio (isolated ions) and the corresponding values obtained by X-ray diffraction methods (ions included in crystalline solids) yield, in most cases, differences lower than 1 pm or 2 degrees of arc. These differences reflect not only the accuracy of the experimental determinations and the approximations performed during the ab initio calculations (geometry optimization) but also the change in the environment felt by the ions on each case. Nevertheless the differences are small enough to warrant the use of ab initio calculations (and the existing OPLS geometrical parameters) to model these ions. One notable exception to this trend is the difference between the distances obtained by the two methods in the bonds involving a “bridge” oxygen atom (present both in alkoxy-carbonyl-imidazolium cations and sulfate anions, as O<sub>S</sub> and O<sub>C4</sub>, respectively): in this case, ab initio calculations tend to overestimate the length of one of the “bridge” bonds relative to the experimental X-ray data, a fact that is reversed when the other “bridge” bond is taken into account. The larger difference can probably be attributed to particularly weak bonds, where the presence or absence of intermolecular interactions causes an important effect. Nonetheless, and as the two differences tend to cancel-out when the whole “bridge” group is taken into consideration, the corresponding values obtained ab initio (part of the general OPLS parametrization) were also retained in this case.

**CHART 1.** Adopted Nomenclature for the Interaction Sites in 1,2,3-Trialkylimidazolium ( $C_l C_m C_n \text{im}$ ), 1-Alkoxy-carbonyl-3-alkyl-imidazolium ( $C_m \text{ooc} C_n \text{mim}$ ), Alkylsulfate ( $C_n \text{SO}_4$ ), and Alkylsulfonate ( $C_n \text{SO}_3$ ) Ions



**TABLE 1: Force-Field Parameters for Ionic Liquids Containing Trialkylimidazolium, 1-Alkoxy carbonyl-3-methylimidazolium, Alkylsulfate, and Alkylsulfonate Ions<sup>a</sup>**

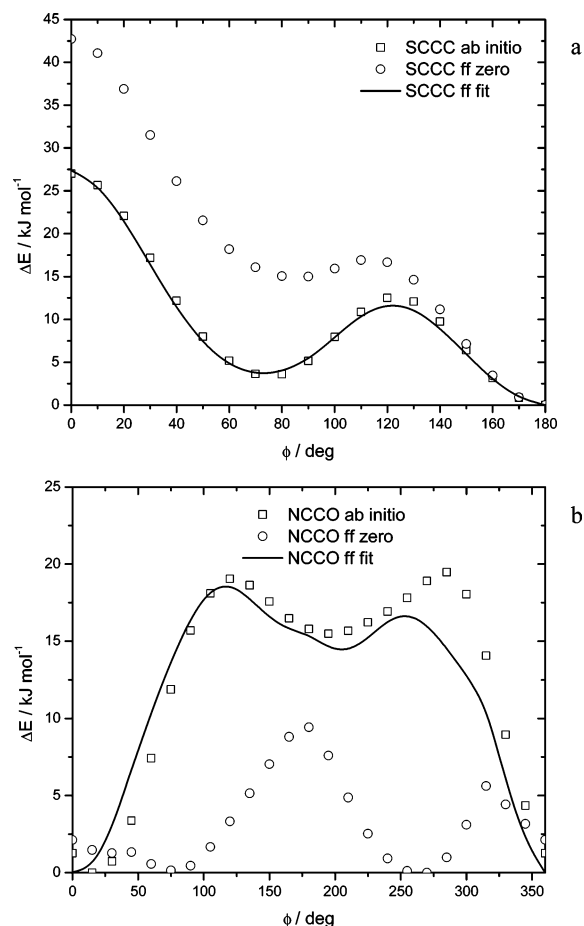
Trialkylimidazolium							
atoms	$q$ (e)	$\epsilon$ (kJ mol <sup>-1</sup> )	$\sigma$ (Å)	dihedrals	$V_1$ (kJ mol <sup>-1</sup> )	$V_2$ (kJ mol <sup>-1</sup> )	$V_3$ (kJ mol <sup>-1</sup> )
C <sub>RM</sub>	0.19	<b>0.293</b>	<b>3.55</b>	C <sub>RM</sub> -N <sub>AM</sub> -C <sub>1</sub> -C <sub>2/E</sub>	1.0009	0	0
N <sub>AM</sub>	0.04	<b>0.711</b>	<b>3.25</b>	N <sub>AM</sub> -C <sub>1</sub> -C <sub>2/E</sub> -C <sub>S/T</sub>	-2.1522	-0.3149	4.9504
C <sub>CR</sub>	-0.26	<b>0.276</b>	<b>3.50</b>				
1-Alkoxy carbonyl-3-methylimidazolium							
atoms	$q$ (e)	$\epsilon$ (kJ mol <sup>-1</sup> )	$\sigma$ (Å)	angles	$\theta_0$ (deg)	$k_\theta$ (kJ mol <sup>-1</sup> rad <sup>-2</sup> )	$\theta_0$ (deg) XR <sup>b</sup>
C <sub>C</sub>	0.76	<b>0.439</b>	<b>3.75</b>	C <sub>1</sub> -C <sub>C</sub> -O <sub>C</sub>	<b>125.0</b>	<b>669.0</b>	122.5
O <sub>C</sub>	-0.43	<b>0.879</b>	<b>2.96</b>	H <sub>1</sub> -C <sub>1</sub> -C <sub>C</sub>	<b>109.5</b>	<b>313.8</b>	106.6
O <sub>S</sub>	-0.50	<b>0.712</b>	<b>3.00</b>	O <sub>S</sub> -C <sub>C</sub> -O <sub>C</sub>	<b>125.0</b>	<b>694.5</b>	125.0
C <sub>MO</sub>	0.30	<b>0.276</b>	<b>3.50</b>	O <sub>S</sub> -C <sub>C</sub> -C <sub>1</sub>	<b>110.0</b>	<b>677.8</b>	112.5
H <sub>OS</sub>	0.00	<b>0.06</b>	<b>2.42</b>	C <sub>MO</sub> -O <sub>S</sub> -C <sub>C</sub>	<b>115.0</b>	<b>694.5</b>	116.9
				H <sub>OS</sub> -C <sub>MO</sub> -O <sub>S</sub>	<b>109.5</b>	<b>418.4</b>	110.1
				C <sub>S</sub> -C <sub>MO</sub> -O <sub>S</sub>	<b>109.5</b>	<b>418.4</b>	108.0
				N <sub>A</sub> -C <sub>1</sub> -C <sub>C</sub>	<b>112.7</b>	<b>500.0</b>	112.7
bonds	$r_0$ (Å)	$k_r$ (kJ mol <sup>-1</sup> Å <sup>-2</sup> )	$r_0$ (Å) XR	dihedrals	$V_1$ (kJ mol <sup>-1</sup> )	$V_2$ (kJ mol <sup>-1</sup> )	$V_3$ (kJ mol <sup>-1</sup> )
C <sub>C</sub> -O <sub>C</sub>	<b>1.200</b>	<b>4770.0</b>	1.195	C <sub>W</sub> -N <sub>A</sub> -C <sub>1</sub> -C <sub>C</sub>	4.1274	0	0
C <sub>1</sub> -C <sub>C</sub>	<b>1.522</b>	<b>2653.0</b>	1.513	N <sub>A</sub> -C <sub>1</sub> -C <sub>C</sub> -O <sub>C</sub>	-9.1642	14.1359	1.0771
C <sub>C</sub> -O <sub>S</sub>	<b>1.344</b>	<b>1791.0</b>	1.338				
Alkylsulfate							
atoms	$q$ (e)	$\epsilon$ (kJ mol <sup>-1</sup> )	$\sigma$ (Å)	angles	$\theta_0$ (deg)	$k_\theta$ (kJ mol <sup>-1</sup> rad <sup>-2</sup> )	$\theta_0$ (deg) XR <sup>c</sup>
S <sub>O</sub>	1.180	<b>1.046</b>	<b>3.55</b>	O <sub>S4</sub> -S <sub>O</sub> -O <sub>S4</sub>	114.0	<b>969.0</b>	113.5
O <sub>S4</sub>	-0.650	<b>0.837</b>	<b>3.15</b>	O <sub>C4</sub> -S <sub>O</sub> -O <sub>S4</sub>	103.5	1239.6	105.1
O <sub>C4</sub>	-0.450	<b>0.586</b>	<b>2.90</b>	C <sub>S4</sub> -O <sub>C4</sub> -S <sub>O</sub>	116.6	300.5	115.3
C <sub>S4</sub>	0.220	<b>0.276</b>	<b>3.50</b>	H <sub>S4</sub> -C <sub>S4</sub> -O <sub>C4</sub>	109.7	488.7	108.6
C <sub>S</sub>	-0.120	<b>0.276</b>	<b>3.50</b>	C <sub>S</sub> -C <sub>S4</sub> -O <sub>C4</sub>	107.8	765.6	106.3
H <sub>S4</sub>	0.000	<b>0.126</b>	<b>2.50</b>				
bonds	$r_0$ (Å)	$k_r$ (kJ mol <sup>-1</sup> Å <sup>-2</sup> )	$r_0$ (Å) XR	dihedrals	$V_1$ (kJ mol <sup>-1</sup> )	$V_2$ (kJ mol <sup>-1</sup> )	$V_3$ (kJ mol <sup>-1</sup> )
C <sub>S4</sub> -O <sub>C4</sub>	1.402	745.83	1.437	O <sub>S4</sub> -S <sub>O</sub> -O <sub>C4</sub> -C <sub>S4</sub>	0	0	2.4815
O <sub>S4</sub> -S <sub>O</sub>	1.455	<b>5331.0</b>	1.446	S <sub>O</sub> -O <sub>C4</sub> -C <sub>S4</sub> -H <sub>S4</sub>	0	0	1.6858
O <sub>C4</sub> -S <sub>O</sub>	1.633	1789.6	1.599	S <sub>O</sub> -O <sub>C4</sub> -C <sub>S4</sub> -C <sub>S</sub>	-6.0142	-3.1133	1.4941
				O <sub>C4</sub> -C <sub>S4</sub> -C <sub>S</sub> -H <sub>C</sub>	0	0	2.0698
				O <sub>C4</sub> -C <sub>S4</sub> -C <sub>S</sub> -C <sub>S</sub>	4.3893	-1.8273	2.9705
Alkylsulfonate							
atoms	$q$ (e)	$\epsilon$ (kJ mol <sup>-1</sup> )	$\sigma$ (Å)	angles	$\theta_0$ (deg)	$K_\theta$ (kJ mol <sup>-1</sup> rad <sup>-2</sup> )	$\theta_0$ (deg) XR <sup>d</sup>
S <sub>O</sub>	1.180	<b>1.046</b>	<b>3.55</b>	O <sub>S3</sub> -S <sub>O</sub> -O <sub>S3</sub>	114.0	<b>969.0</b>	112.3
O <sub>S3</sub>	-0.680	<b>0.837</b>	<b>3.15</b>	C <sub>S3</sub> -S <sub>O</sub> -O <sub>S3</sub>	104.5	<b>870.0</b>	106.5
C <sub>S3</sub>	-0.140	<b>0.276</b>	<b>3.50</b>	H <sub>S3</sub> -C <sub>S3</sub> -S <sub>O</sub>	107.3	390.3	108.7
C <sub>S</sub>	-0.120	<b>0.276</b>	<b>3.50</b>	C <sub>S</sub> -C <sub>S3</sub> -S <sub>O</sub>	113.3	583.0	112.9
H <sub>S3</sub>	0.000	<b>0.126</b>	<b>2.50</b>				
bonds	$r_0$ (Å)	$k_r$ (kJ mol <sup>-1</sup> Å <sup>-2</sup> )	$r_0$ (Å) XR	dihedrals	$V_1$ (kJ mol <sup>-1</sup> )	$V_2$ (kJ mol <sup>-1</sup> )	$V_3$ (kJ mol <sup>-1</sup> )
C <sub>S3</sub> -S <sub>O</sub>	1.792	<b>1970.0</b>	1.757	O <sub>S3</sub> -S <sub>O</sub> -C <sub>S3</sub> -H <sub>S3</sub>	0	0	1.625
O <sub>S3</sub> -S <sub>O</sub>	1.455	<b>5331.0</b>	1.453	O <sub>S3</sub> -S <sub>O</sub> -C <sub>S3</sub> -C <sub>S</sub>	0	0	1.3938
				S <sub>O</sub> -C <sub>S3</sub> -C <sub>S</sub> -H <sub>S</sub>	0	0	1.3797
				S <sub>O</sub> -C <sub>S3</sub> -C <sub>S</sub> -C <sub>S</sub>	-16.1	-2.0046	0.7674

<sup>a</sup> Values in bold refer to parameter values taken from OPLS-AA/AMBER;<sup>14</sup> values in italic were transferred from our previously published model for triflate and bis(trifluoromethanesulfonyl)amide anions.<sup>13</sup> Also included for comparison purposes are experimental values obtained by X-ray diffraction (XR) of equilibrium bond lengths and angles of crystals containing the ions under discussion. <sup>b</sup> Reference 16. <sup>c</sup> Reference 17 <sup>d</sup> References 18–20.

**Dihedral Angle Parametrization.** The terms in the force field that describe dihedral angles are important for fluid-state molecular simulations, since they determine the conformational energetics of the ions. Thus, particular attention was placed in the calculation of these contributions.

The development of a set of parameters capable of describing the conformational space of articulated molecules or ions includes: the ab initio calculation for a given dihedral angle of the corresponding torsion energy profile; the calculation by molecular dynamics of the same torsion energy profile considering only nonbonded interactions in an isolated molecule or ion;

and finally the fitting of the dihedral angle parameters ( $V_1$  to  $V_4$  in eq 1) to the difference between the two torsion energy profiles. This fitting procedure is performed for each dihedral term in a stepwise manner that guarantees a consistent set of parameters for any molecular structure in which a given dihedral term may occur. For example, in alkylsulfonates the dihedral O–S–C–H is obtained from the torsion energy barrier in methylsulfonate, then the dihedral O–S–C–C is calculated from the torsion energy profile of ethylsulfate around the S–C bond, but here the two O–S–C–H terms are already considered with the parameters that had been obtained for methylsulfonate,



**Figure 1.** Torsion profiles for two selected dihedral angles: (a)  $S_0-C_3-C_5-C_5$  dihedral in the alkylsulfonate anion; (b)  $N_A-C_1-C_2-O_C$  dihedral in an alkoxycarbonyl imidazolium cation. ( $\square$ ): total torsional energy obtained ab initio; ( $\circ$ ): nonbonded torsional energy obtained by MD simulation; solid line: total torsional energy obtained by MD simulation with the fitted dihedral parameters.

and so on. This procedure was previously described in more detail and successfully tested.<sup>1,2,13,37</sup> The different stages of the procedure can also be appreciated in Figure 1a,b.

For sulfates and sulfonates we calculated the entire set of dihedral angle parameters concerning these functional groups, including the terms required to specify the conformations of these groups with respect to the alkyl chain. These are the  $O_{S3}-S_0-C_{S3}-C_S$ ,  $O_{S3}-S_0-C_{S3}-H_{S3}$ ,  $S_0-C_{S3}-C_S-C_S$ , and  $S_0-C_{S3}-C_S-H_C$  dihedrals for sulfonates, and the  $O_{S4}-S_0-O_{C4}-C_{S4}$ ,  $S_0-O_{C4}-C_{S4}-C_S$ ,  $S_0-O_{C4}-C_{S4}-H_{S4}$ ,  $O_{C4}-C_{S4}-C_S-C_S$ , and  $O_{C4}-C_{S4}-C_S-H_C$  for sulfates, given in Table 1. The different dihedral types are added to the force field step-by-step by making first the assignments for the methyl sulfate or methyl sulfonate anions and only then increasing the alkyl side chain and the number of additional dihedral types. As an illustration, the fit of the  $S_0-C_{S3}-C_S-C_S$  dihedral in sulfonates is shown in Figure 1a. Its behavior is straightforward, and the quality of the fit between the force field and the ab initio values is excellent (differences of at most  $0.9 \text{ kJ mol}^{-1}$ ) when a series of three cosine terms is used. Analog situations are found for the dihedrals  $O_{C4}-C_{S4}-C_S-C_S$  and  $S_0-O_{C4}-C_{S4}-C_S$  in sulfates. The remaining dihedrals in these anions all have a  $60^\circ$  symmetry, and only the V3 term is non-null. The fitting process in these cases is simple and accurate.

For trialkylimidazoliums, only two dihedral angles had to be calculated, in addition to those already available in the present force field model. These are the two dihedrals that include the

methyl group attached to the  $C_{RM}$  carbon in the imidazolium ring (cf. Chart 1), and how its presence affects the rotation of the alkyl side chains attached to the neighboring  $N_{AM}$  nitrogen atoms. For the alkoxycarbonyl-substituted imidazoliums, the parameters concerning the different dihedrals of the ester group were taken from the specific OPLS-AA publications on ester compounds,<sup>22</sup> but two new dihedral angles appear when the carbonyl group of the ester is only one methylene group apart from the imidazolium ring: the  $C_R-N_A-C_1-C_C$  and the  $N_A-C_1-C_C-O_C$  (cf. Chart 1). These hadn't yet been studied and were calculated here. The torsion energy profile around the dihedral  $N_A-C_1-C_C-O_C$  is rather complex because of the contribution of the nonbonded intramolecular interactions, but a cosine series with three terms could represent the torsion energies with an average deviation of  $1.8 \text{ kJ mol}^{-1}$  from the ab initio values (that unexpectedly reaches a maximum deviation of  $5 \text{ kJ mol}^{-1}$  for dihedral angles around  $280^\circ$ ). This fit is illustrated in Figure 1b. The complexity of the energy profile reflects the possibility of the ion to adopt different conformations while the  $N_A-C_1-C_C-O_C$  dihedral angle is being rotated; the use of a pair function such as a cosine series can only capture with partial accuracy the shape of that profile. Nevertheless, and since the major deviations occur near one of the maxima, we decided to use the obtained cosine series parameters.

**Point Charge Parametrization.** The coulomb parameters describing the electrostatic forces acting on each ion are determined using ab initio calculation at the MP2 theoretical level and using rather large basis sets (cc-pVTZ(-f)). This yields a robust description of the electronic density function surrounding the ion for a given conformation. The point charges placed at the center of mass of each atom of the ion are then calculated from the electronic density function using an electrostatic surface potential methodology (CHelpG). The conformation obtained by geometry optimization of the isolated ion is generally taken as the reference, but, in ions with multiple stable conformers, several ab initio calculations were performed, and an averaging process was implemented to define the charges in each atom. Since one of the objectives of the present force field is the possibility of parameter transfer within families of ionic liquids, the point charges attributed to the various molecular residues were subjected to different degrees of approximation<sup>1,2,13</sup> to find general trends that could then be applied along an entire series of analogous ionic liquids. The proposed set of parameters is included in Table 1.

In the case of the cations, only the atoms directly attached to the new residues ( $C_R$  and  $N_{AM}$  in the case of the trialkylimidazolium cation;  $C_{MO}$  and  $H_{MO}$  in the case of the alkoxycarbonyl imidazolium cation) had their charges reparametrized. Surprisingly, the  $C_1$  atom in the latter cation (also directly connected to the ester group) could retain the charge obtained in previous parametrizations. Obviously, all the atoms contained in the new residues ( $C_{RM}$  in the case of the trialkylimidazolium cation;  $O_S$ ,  $C_C$ , and  $O_C$  in the case of alkoxycarbonyl imidazolium cation) were assigned new parameters. Interestingly, the introduction of the ester group in the alkyl side chain of the imidazolium ring (leaving a methylene group between the ring and the carbonyl groups) does not cause significant changes in the electrostatics of the ring itself. Moreover the charge distribution in the substituted alkyl side chain is very similar (although slightly shifted to more positive charges) to that of normal esters. In the case of the trialkylimidazolium cation, the substitution of the hydrogen atom at  $C_R$  by a methyl group causes a large redistribution of the charge in the ring, with a significant amount



of the positive charge of the cation being channeled into the alkyl group substituted at  $C_R$ .

In the case of sulfates and sulfonates, the charge distributions in the alkyl side chains are not very different from those postulated in the united-atom models proposed more than one decade ago if the overall charge in the methyl and methylene groups are compared with the united-atom values.<sup>7</sup> The most notable difference is the introduction of a unique value for the positive charge in the sulfur atom in both families of anions. The assignment of the point charges using larger basis sets in the *ab initio* calculations and the CHelpG methodology also yields lower charge separation between adjoining atoms, a fact already observed in previous force field parametrizations,<sup>1,2,13</sup> and that has a positive impact when considering condensed-phase simulations of polarizable, charge-delocalized ions using a nonpolarizable force field such as the present one.

**Lennard-Jones Parameters.** The OPLS-AA force field includes repulsion–dispersion terms represented by the Lennard-Jones (12–6) potential function. The Lennard-Jones parameters for each type of atom present in the cations were taken from the OPLS-AA model of heterocyclic aromatic rings compounds.<sup>14</sup> The anion parameters were also taken from the OPLS-AA force field, namely, the values used for sulfate and sulfonate residues in other organic molecules.<sup>8</sup>

The repulsive and dispersive interactions between atoms of different types (“cross” interactions”) are calculated using geometrical-mean combining rules for both parameters

**Validation.** As in the three previous articles concerning the present force field<sup>1,2,13</sup> and since most of the currently available experimental results concerning equilibrium thermodynamic properties of ionic liquids are still related to their volumetric properties, we decided to continue to test the performance of the proposed force field by estimating the molar densities of ionic liquids containing at least one of the cations or anions under discussion, in both the crystalline and liquid phases. All simulation results discussed below describe ionic liquids systems that were, to our knowledge, not previously modeled in the context of molecular dynamics. As mentioned in the Introduction, sulfate-based ionic liquids were simulated with an united-atom model, but only for the 1-butyl-3-methylimidazolium octylsulfate,<sup>11</sup> an ionic liquid not analyzed in this work.

It must be stressed at this point that, since the publication of the last article in this series,<sup>13</sup> there have been different studies that showed the possibility of vaporizing ionic liquids at moderately high temperatures and reduced pressure.<sup>23</sup> As a consequence of those studies, some equilibrium thermodynamic properties such as the vapor pressure and the vaporization enthalpy have been determined experimentally for selected families of ionic liquids.<sup>24–26</sup> These are important data that can help refine the present force field. In fact, in recent months, a number of different publications aiming to improve the predictive power of the force field, either by tackling the question of polarizability and charge transfer<sup>27</sup> or by adjustment of the OPLS nonbonded interaction parameters,<sup>28</sup> were published. However, and since there is still some debate over the most accurate measurements concerning the enthalpies of vaporization, which exist only for a single ionic-liquid family (1-alkyl-3-methylimidazolium bistriflamide ionic liquids), the authors of the present work feel that the original strategy of establishing a force field that is transferable within a family of ionic liquids and is integrated within the OPLS-AA framework still makes sense at the present. Moreover, the basic rationale continues to be to (re)parametrize those parts of the force field that can be quantified through *ab initio* or MD calculations (geometrical

parameters, torsion profiles, electron density, and point-charge distribution) and leave the empirical nonbonded parameters (Lennard-Jones coefficients) unchanged from their OPLS-AA values. As the above-mentioned refinement by Ludwig et al.<sup>28</sup> has shown, there is ample room for improvement at the level of fitting new Lennard-Jones parameters to new experimental results, but if on one hand one gains a much better agreement between the simulated and experimental data for the particular cases where the adjustment was performed, one can also argue about the possible lack of transferability to other untested cation/anion combinations or even the lack of physical meaning of some of the choices regarding the new Lennard-Jones parameters. We therefore chose to maintain the more general character of our force field, expecting and welcoming new refinements made by the rest of the scientific community for particular families of ionic liquids as new experimental data becomes available. We also feel that the present, general force field is suitable for predicting with a good degree of confidence most of the available static thermodynamic properties (and even some transport properties)<sup>29</sup> and access important information related to the complex structure of ionic liquids.<sup>30,31</sup>

**Crystal Structures and Densities.** Seven ionic liquid crystalline structures containing alkoxycarbonyl imidazolium, alkyl-sulfate, or alkylsulfonate ions were selected from the Cambridge Structural Database (CSD).<sup>32</sup> Unfortunately, no crystalline structure containing the 1,2,3-trialkyl-imidazolium cations with a suitable anion could be selected from the database.

The crystalline structures studied by MD simulation were those of ammonium, pyridinium, and guanidinium methyl-sulfonate ( $[NH_4][C_1SO_3]$ ,<sup>18</sup>  $[C_5H_5N][C_1SO_3]$ ,<sup>19</sup>  $[GuH][C_1SO_3]$ <sup>20</sup>), 1,3-dimethylimidazolium methyl-sulfate ( $[C_1mim][C_1SO_4]$ <sup>17</sup>), guanidinium ethyl- and butyl-sulfonate ( $[GuH][C_2SO_3]$ ,<sup>20</sup>  $[GuH][C_4SO_3]$ <sup>20</sup>), and 1-(1-(ethoxycarbonyl)ethyl)-3-methylimidazolium bistriflamide,  $[C_{200c}C_{1im}][Ntf_2]$ .<sup>16</sup> These choices reflect on one hand the small amount of structures containing the desired cations and anions but also the fact that, in these compounds, they are all paired with counterions already parametrized by the present force field for ionic liquids, namely, 1-alkyl-3-methylimidazolium<sup>1</sup> cations and pyridinium<sup>2</sup> or bistriflamide<sup>13</sup> anions, or contained in the more general OPLS framework (guanidinium or ammonium<sup>33</sup>).

The objective of the simulations in the crystalline phase is to test the performance of the force field in predicting both the crystal density and its structural parameters such as the dimensions and director angles of the crystalline unit cell.

The simulation boxes and initial configurations were setup by taking into account the dimensions and occupancy of the unit cells of each crystalline structure given by the CSD data. In most cases, the unit cells of the crystals are too small to accommodate a sufficiently large cutoff distance. To overcome this problem, several cells were stacked together to form a sufficiently large simulation box that allows cutoff distances longer than 10 Å. Long-range corrections were applied to the Lennard-Jones interactions beyond those distances, and the Ewald method was implemented to take into account the long-range character of the electrostatic interactions. Since the overall size of the simulation box is defined by the dimension and director angles 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 and the cutoff were sufficiently large to avoid any finite-size effects, including distortions caused by spurious long-range corrections. The results presented in Table 2 correspond to simulations performed with the larger cutoff distances. The runs were performed using

**TABLE 2: Comparison of Simulated Crystal Structures with Experimental Data from the Cambridge Structural Database (CSD)**

	[NH <sub>4</sub> ][C <sub>1</sub> SO <sub>3</sub> ]	[C <sub>5</sub> H <sub>6</sub> N][C <sub>1</sub> SO <sub>3</sub> ]	[GuH][C <sub>1</sub> SO <sub>3</sub> ]	[C <sub>1</sub> mim][C <sub>1</sub> SO <sub>4</sub> ]	[GuH][C <sub>2</sub> SO <sub>3</sub> ]	[GuH][C <sub>4</sub> SO <sub>3</sub> ]	[C <sub>2</sub> oocC <sub>1</sub> im][Ntf <sub>2</sub> ]
CSD code	FASJUE <sup>a</sup>	QOQVOH <sup>b</sup>	WETNEO <sup>c</sup>	UJOSER <sup>d</sup>	WETNOY <sup>c</sup>	WETNUE <sup>c</sup>	IZUZAEd
space group	12 (C 2/m)	33 (P n a 21)	12 (C 2/m)	19 (P 21 21 21)	12 (C 2/m)	60 (P b c n)	14 (P 21/n)
ion pairs/box	400	192	400	288	320	216	96
stacked cells	5 × 5 × 4	3 × 4 × 4	4 × 5 × 5	6 × 4 × 3	4 × 5 × 4	3 × 3 × 3	3 × 4 × 2
cutoff/Å	16.0	16.0	16.0	16.0	16.0	16.0	16.0
T/K	298	173	298	173	298	298	223
ion pairs/cell	4	4	4	4	4	8	4
<i>a</i> <sub>exp</sub> /Å	7.4993	11.0853	12.778	6.2418	12.793	14.733	13.170
<i>a</i> <sub>sim</sub> /Å	7.6381	10.8371	12.135	6.5956	12.038	13.786	12.966
<i>b</i> <sub>exp</sub> /Å	7.2882	8.1425	7.342	9.747	7.398	12.278	8.539
<i>b</i> <sub>sim</sub> /Å	7.3999	8.3841	6.981	9.494	6.968	13.126	8.237
<i>c</i> <sub>exp</sub> /Å	9.2342	8.453	9.998	15.951	11.172	12.314	17.453
<i>c</i> <sub>sim</sub> /Å	8.8214	8.742	9.678	16.025	11.362	11.793	17.072
$\delta abc$ % <sup>e</sup>	2.7	2.8	4.6	2.8	4.7	5.9	2.5
$\alpha_{exp}$ /(deg)	90	90	90	90	90	90	90
$\alpha_{sim}$ /(deg)	90.01	90.00	90.02	90.02	90.07	90.03	89.68
$\beta_{exp}$ /(deg)	93.341	90	126.96	90	128.06	90	107.50
$\beta_{sim}$ /(deg)	87.34	90.00	123.97	89.94	123.22	90.01	106.45
$\gamma_{exp}$ /(deg)	90	90	90	90	90	90	90
$\gamma_{sim}$ /(deg)	90.00	90.00	89.99	90.50	89.83	90.01	90.45
<i>V</i> <sub>exp</sub> /Å <sup>3</sup>	503.85	762.985	749.493	970.44	832.519	2227.5	1871.91
<i>V</i> <sub>sim</sub> /Å <sup>3</sup>	498.2	794.3	687.2	1003.4	804.2	2133.9	1903.7
$\rho_{exp}$ mol dm <sup>-3</sup>	13.183	8.705	8.862	6.844	7.978	5.964	3.548
$\rho_{sim}$ mol dm <sup>-3</sup>	13.332	8.363	9.666	6.620	8.260	6.225	3.489
$\delta\rho$ %	1.1	-4.1	8.3	-3.4	3.4	4.2	-1.7

<sup>a</sup> Reference 18. <sup>b</sup> Reference 19. <sup>c</sup> Reference 20. <sup>d</sup> Reference 17. <sup>e</sup>  $\delta abc$  represents the average absolute deviation of the sum of the lattice constants,  $|(a_{sim} - a_{exp})/3a_{exp} + (b_{sim} - b_{exp})/3b_{exp} + (c_{sim} - c_{exp})/3c_{exp}|$ .

**TABLE 3: Comparison of Simulated Liquid Densities with Experimental Data<sup>a</sup>**

	[C <sub>5</sub> oocC <sub>1</sub> im][Ntf <sub>2</sub> ]	[C <sub>5</sub> oocC <sub>1</sub> im][C <sub>8</sub> SO <sub>4</sub> ]	[C <sub>4</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ]	[C <sub>2</sub> C <sub>1</sub> im][C <sub>1</sub> SO <sub>3</sub> ]	[C <sub>4</sub> C <sub>1</sub> im][C <sub>1</sub> SO <sub>4</sub> ]
<i>T</i> /K	298	298	298	293	293
$\rho_{exp}$ /mol dm <sup>-3</sup>	2.888	2.723	3.274	6.005	4.852
$\rho_{sim}$ /mol dm <sup>-3</sup>	2.96	2.56	3.32	5.92	4.76
$\delta\rho$ %	2.3	-6.2	1.2	-1.4	-1.9

	[C <sub>2</sub> C <sub>1</sub> im][C <sub>2</sub> SO <sub>4</sub> ]	[C <sub>2</sub> C <sub>1</sub> im][C <sub>2</sub> SO <sub>4</sub> ]	[C <sub>2</sub> C <sub>1</sub> im][C <sub>2</sub> SO <sub>4</sub> ]	[C <sub>2</sub> C <sub>1</sub> im][C <sub>4</sub> SO <sub>4</sub> ]	[C <sub>2</sub> C <sub>1</sub> im][C <sub>6</sub> SO <sub>4</sub> ]	[C <sub>2</sub> C <sub>1</sub> im][C <sub>8</sub> SO <sub>4</sub> ]
<i>T</i> /K	391	332	293	293	293	293
$\rho_{exp}$ /mol dm <sup>-3</sup>	5.010	5.143	5.261	4.495	3.968	3.463
$\rho_{sim}$ /mol dm <sup>-3</sup>	5.01	5.17	5.23	4.45	3.86	3.40
$\delta\rho$ %	0.1	0.4	-0.6	-1.1	-3.0	-1.8

<sup>a</sup> Reference 34.

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 0.2 ns, followed by production times of at least 0.4 ns. These simulation times were found to be appropriate since the runs are started from an “equilibrated” configuration (the equilibrium crystalline structure), and it was observed, by inspection of the corresponding thermodynamic properties, that the relaxation is complete well before the end of the equilibration period.

The simulation results for each crystal are given in Table 2. The densities of all crystals except those based on the guanidinium cation are predicted with an accuracy better than 4.1%. It is important to notice that (i) the deviations are of the same order of magnitude as those obtained by us or other authors when comparing the performance of their (unrefined) ionic liquid 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 force field or calculated ab initio, i.e., none was adjusted to match the kind of experimental data, and (iii) in some cases, experimental ionic liquid density results from

different sources also exhibit deviations in the 2–4% range, reflecting in some cases the difficulty of using consistently pure ionic liquids or the existence polymorphism.

The results for guanidinium-based crystals are not encouraging but in fact reveal the sensitivity of the model in detecting ill-parametrized ions (a similar situation occurred in the first article of this series when the Lennard-Jones OPLS-AA parameters of the chloride anion had to be reparametrized because they had been obtained from aqueous solution data, very distant from the conditions of a chloride anion in a molten-salt environment). The problem with the guanidinium cation lies in the parametrization of the hydrogen atoms that exhibit a null interaction diameter (like in the OPLS-AA models for water or the ammonium ion) and cause the simulations to yield crystalline structures more dense than the experimental X-ray studies. Probably the delocalization of the positive charge between the three nitrogen atoms plus the central carbon atom (all sp<sup>2</sup> atoms, unlike in the cases of ammonia or water) demand a different parametrization. Since only derivatives of the guanidinium anion where the problematic hydrogen atoms are replaced by alkyl chains are used as components of ionic liquids, we decided not to perform any kind of reparametrization in this case. Nevertheless, future work in the field must take this

problem into account when dealing with the modeling of hydrogen atoms in guanidinium or similar cations.

**Liquid Densities.** Nine ionic liquids with known density and containing at least one of the cations or anions under discussion were selected from the literature. These include 1-(pentoxycarbonyl)methyl-3-methylimidazolium bistriflamide and octylsulfate ( $[\text{C}_5\text{oocC}_1\text{im}][\text{Ntf}_2]$  and  $[\text{C}_5\text{oocC}_1\text{im}][\text{C}_8\text{SO}_4]$ ),<sup>34</sup> 1-butyl-2,3-dimethylimidazolium bistriflamide ( $[\text{C}_4\text{C}_1\text{im}][\text{Ntf}_2]$ ),<sup>35</sup> 1-ethyl-3-methylimidazolium methyl-sulfonate, ethyl-sulfate, butyl-sulfate, hexyl-sulfate and octyl-sulfate ( $[\text{C}_2\text{C}_1\text{im}][\text{C}_1\text{SO}_3]$ ,  $[\text{C}_2\text{C}_1\text{im}][\text{C}_2\text{SO}_4]$ ,  $[\text{C}_2\text{C}_1\text{im}][\text{C}_4\text{SO}_4]$ ,  $[\text{C}_2\text{C}_1\text{im}][\text{C}_6\text{SO}_4]$ , and  $[\text{C}_2\text{C}_8\text{im}][\text{C}_1\text{SO}_4]$ ),<sup>35,36</sup> and 1-butyl-3-methylimidazolium methyl-sulfate ( $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ ).<sup>35</sup>

All ionic liquids were represented by 250 ion pairs. Cutoffs were taken at 16 Å for short-range Lennard-Jones interactions, with appropriate tail corrections, and the long-range Coulombic forces were handled by Ewald sums. Nosé-Hoover thermostats and barostats were activated to maintain the desired temperature and pressure, with time constants of 0.1 and 0.5 ps, respectively.

The equilibration period in the liquid-phase simulation runs is very important. Like in previous publications, different approaches were used to ensure that the ergodicity of the simulation was properly attained: Initially, the ions are placed at random in the simulation box, at very low density, and the equilibration starts by a short relaxation of a few picoseconds at 1 K in the microcanonical ensemble to allow internal modes to relax. Then, an equilibration period is imposed at the final temperature of the simulation, followed by the activation of the thermostat and barostat (isobaric–isothermal-ensemble). Alternatively, other simulations of the same system were allowed to evolve from initial configurations based on the expanded structure of an analogous ionic crystal. Another method to ensure the ergodicity of the simulation is to perform several temperature annealing cycles or to scramble/unscramble the two components (ions) of the system by switching off and on the electrostatic charges. The equilibration was considered successful only after stable and consistent results over periods of at least 100 ps. The production runs took at least 400 ps and were made in ( $N$ ,  $p$ ,  $T$ ) conditions, under a pressure of 1 bar and at a temperature matching that of a liquid density reported in the literature. Simulation and relevant experimental data are presented in Table 3. In all cases except that involving the pentoxycarbonyl imidazolium octylsulfate ionic liquid, the liquid densities were predicted with within 3% uncertainty. It is hard to pinpoint the cause of discrepancy in the above-mentioned system since, coincidentally, it contains two ions parametrized in the present force field that, when combined with other counterions (bistriflamide and 1-ethyl-3-methylimidazolium), yielded densities with much lower deviations relative to the experimental values (cf. Table 3, columns 1, 2, and 11). As stressed above, the agreement of simulated densities with experiment could eventually be improved by fine-tuning some of the parameters on a case-by-case basis. In our previous reports on force-field development for ionic liquids, we concluded that it was difficult to attribute the sign of the deviations to a certain cation family or anion and could not devise a strategy to improve the results in a general and transferable manner.

For instance, in the case of systems containing alkylsulfate or sulfonate anions in the solid phase, it would be easy to slightly increase the (systematically lower) density of the simulated systems in order to agree with the experimental data by changing the corresponding OPLS Lennard-Jones parameters of the oxygen atoms, but that would probably destroy the agreement

between the liquid densities in similar systems. Therefore, we continue to think that an accuracy of around 3% in liquid densities is reasonable and justified by the generality and transferability of the present model and by the consistent use of the OPLS-AA repulsive and dispersive terms in systems where the amount of reliable and systematic thermodynamic data is still limited.

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**Supporting Information Available:** a file containing the complete parametrization of the force-field, with all the ions studied up to the present date, is available as Supporting Information.

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