Molecular dynamics simulation of the room-temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate

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Abstract

Room-temperature ionic liquids (RTILs) due to their unique properties and solvent capabilities have been motivating an extraordinary growth on experimental and theoretical investigations. Many RTILs have been developed to fulfill specific applications and therefore this class of compounds has been termed “designer solvents”. Therefore, to accomplish this purpose, the understanding of RTILs behavior at the atomistic level is needed. In this work a 5 ns NpT molecular dynamic simulation at $T = 300 \text{ K}$ and $p = 1.0 \text{ atm}$ was performed to investigate thermodynamical and structural properties of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate. All force field parameters but charges and geometries were taken from the OPLS-AA. The partial charges and geometry parameters were obtained at the \textit{ab initio} MP2/6-31g(d) level, with charges computed using the ChelpG procedure. This same level of theory was used to calculate energies for cation–anion interactions at several configurations to validate the force field parameters. The agreement between geometries and energies obtained with \textit{ab initio} and force field calculations is good. The value obtained for the liquid density, $1.178 \text{ g cm}^{-3}$, is close to the experimental data ($1.17 \text{ g cm}^{-3}$). The value estimated for the heat of vaporization, $\Delta H_{\text{vap}} \approx 413 \text{ kJ mol}^{-1}$, is larger than the ones usually observed for molecular liquids, which is in accordance with the very low vapor pressure observed for RTILs. Structural and dynamics properties, such as radial distribution function and mean square displacement were analyzed and are also in good agreement with data reported in the literature. Comparatively to the anion, the cation self-diffusion constant is larger despite the fact that it is heavier and bigger. Compared to the values observed for molecular liquids the self-diffusion constants obtained for cation and anions are about three orders of magnitude smaller.

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1. Introduction

Room-temperature ionic liquids (RTILs) are a new class of solvents with many unique and interesting properties, such as very low vapor pressure, no flammability, wide liquid range temperature, unusual solubility with organic and inorganic compounds and catalytic activity in some organic reactions. Many experiments have been demonstrating that organic solvents can be replaced by RTILs in a great number of different chemical reactions such as hydrogenation [1], hydroformulation [2], Heck [3], Diels-Alder [4], Friedel-Crafts [5], esterification [6] and dimerization of alkenes [7]. An interesting RTILs solvent property which is potentially useful towards industrial applications is the possibility of recycling without affecting the reaction yield. However, despite the experimental and theoretical efforts, a clear understanding of the connections between structure and properties of ionic liquid has not yet been achieved. To fill this gap, computer simulations are valuable tools to improve the comprehension about this class of liquids.

Aimed to investigate relationships between structure and thermodynamical properties of the RTIL 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM] + [BF₄]⁻), Fig. 1, the necessary force field was developed combining parameters taken from the OPLS-AA force field with

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geometries and charges obtained at the MP2/6-31g(d) level of theory. The procedures used to obtain the force field parameters are described below.

2. Force field parameters

Following standard formalism the force field includes intramolecular interactions such as bond stretching, \( U_{\text{stretch}} \), angle bending, \( U_{\text{bend}} \), dihedral torsion, \( U_{\text{tor}} \), was well as Lennard–Jones, \( U_{\text{LJ}} \), and Coulombic, \( U_{\text{Coulomb}} \), interactions:

\[
U = U_{\text{stretch}} + U_{\text{bend}} + U_{\text{tor}} + U_{\text{LJ}} + U_{\text{Coulomb}}.
\]

(1)

The functional forms of these potentials are, respectively,

\[
U_{\text{stretch}} = \sum K_i (r - r_{eq})^2
\]

(2)

\[
U_{\text{bend}} = \sum K_i (\theta - \theta_{eq})^2
\]

(3)

\[
U_{\text{tor}} = \sum \frac{\theta}{\text{dihedrals}} \sum C_n (\cos(\phi - 180)\\n^{n})
\]

(4)

\[
U_{\text{LJ}} = \sum_{i<j} \left\{ 4q_i q_j / r_{ij}^2 - \left( \sigma_{ij} / r_{ij} \right)^6 \right\}
\]

(5)

\[
U_{\text{Coulomb}} = \sum_{i<j} \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}.
\]

(6)

Equilibrium bond lengths, \( r_{eq} \), angles, \( \theta_{eq} \), and dihedral angles, \( \phi_{eq} \), were obtained from \textit{ab initio} calculation at the MP2/6-31g(d) level. All force constants \( (k_i, k_\theta) \) and parameters \( (\sigma_i, \varepsilon_i) \) for Lennard–Jones interactions were taken from sites with similar chemical environmental in the OPLS-AA force field [8]. In Eq. (5) \( r_{ij} \) is the distance between atoms \( i \) and \( j \) and, as a usual procedure for the OPLS force field, parameters \( \sigma_{ij} \) and \( \varepsilon_{ij} \) for site \( i \) site \( j \) interaction were calculated using the geometric mean combining rule. Parameters needed to calculate the Ryckaert–Bellemans coefficients, \( C_n \), were obtained from the OPLS-AA force field and the 1–4 interactions were considered in the usual way. The partial charges needed to calculate Coulomb interactions were obtained with \textit{ab initio} MP2/6-31g(d) using the ChelpG [9] methodology implemented in the GAUSSIAN 94 package [10]. All bond equilibrium distances and stretching constants \( k_i \) are showed in Table 1. Selected angles and their force field constants \( k_\theta \) are given in Table 2 and Lennard–Jones parameters and partial charges are displayed in the Table 3. Using the force field defined above cation, anion and cation–anion pairs geometries were optimized and compared with the ones obtained at the \textit{ab initio} MP2/6-31g(d) level. The root mean square deviations (RMSD) were calculated and are presented in Table 4. To further test the force field parameterization energies of some arbitrarily chosen cation–anion pairs configurations were calculated at the MP2/6-31g(d) level and compared with the ones obtained using the force field defined above. The results are displayed in Table 5. As a general trend, the force field results in Tables 4 and 5 are in good agreement with the \textit{ab initio} ones, giving confidence to the force field parameters proposed here.

3. Simulation details

Molecular dynamics simulations of ionic liquid [BMIM][BF_4] were performed using the GROMACS 3.1.4 package [11,12] with the following protocol: (a) the simulations were carried out in the NpT ensemble; (b) a Berendsen thermostat [13] was used to maintain the temperature \( T = 300 \text{ K} \) and a Berendsen pressure coupling

---

Table 1

<table>
<thead>
<tr>
<th>Bond</th>
<th>( r_{eq} ) (nm)</th>
<th>( K_i ) (kJ mol(^{-1})nm(^{-1}))</th>
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</thead>
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<tr>
<td>N1–C3</td>
<td>0.13428</td>
<td>399420.7</td>
</tr>
<tr>
<td>N1–C4</td>
<td>0.13754</td>
<td>357552.7</td>
</tr>
<tr>
<td>N1–C7</td>
<td>0.14781</td>
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</tr>
<tr>
<td>N2–C3</td>
<td>0.13441</td>
<td>408631.7</td>
</tr>
<tr>
<td>N2–C5</td>
<td>0.13753</td>
<td>343317.6</td>
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<tr>
<td>N2–C6</td>
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<td>282190.3</td>
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<tr>
<td>C3–H9</td>
<td>0.10810</td>
<td>307311.1</td>
</tr>
<tr>
<td>C4–C5</td>
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<td>435427.2</td>
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<tr>
<td>C4–H10</td>
<td>0.10805</td>
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<td>284702.4</td>
</tr>
<tr>
<td>C6–H15</td>
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<td>284702.4</td>
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<tr>
<td>C6–H16</td>
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</tr>
<tr>
<td>C7–C8</td>
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<td>224412.5</td>
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<td>C7–H17</td>
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<td>284702.4</td>
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<td>C8–C12</td>
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</tr>
<tr>
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<td>C12–H21</td>
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<tr>
<td>C13–H23</td>
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</tr>
<tr>
<td>B–F</td>
<td>0.14227</td>
<td>50000.0</td>
</tr>
</tbody>
</table>

The atom labels are in accord with Fig. 1.
[13] kept the pressure $p = 1$ atm; (c) the initial configuration was obtained by randomly disposing 125 [BMIM][BF$_4$] ion pairs in a cubic box whose initial dimensions were chosen to match the experimental density [14] of 1.17 g cm$^{-3}$. Standard periodic boundary conditions and the minimum image convention were applied. A cut off distance of 1.7 nm was used and corrections for Coulomb interactions beyond cut off were performed using the Particle Mesh Ewald (PME) [15,16]. After the equilibration process a trajectory with 5 ns was generated.

4. Results and discussion

The root mean square deviations (RMSD) calculated using geometries obtained with MP2/6-31g(d) and the proposed force field are presented in Table 4. The small RMSD values demonstrate that the force field is able to reproduce molecular structures in good agreement with $ab$ initio optimizations. The structures of the isolated cation and anion obtained in both calculations are very similar but, as shown in Fig. 2, the cation–anion distance obtained with the force field, 3.40 Å, is larger than the value, 3.02 Å, calculated at the MP2/6-31g(d) level of theory. Regarding molecular liquids, the comparison between experimental and theoretical values for liquid density is a relevant criterion to validate the force field parameterization. With a similar purpose, the density values obtained with the MD simulation along the 5 ns trajectory are presented in Fig. 3. The average value obtained, 1.178 g cm$^{-3}$, is in very good agreement with the experimental data, 1.17 g cm$^{-3}$. Therefore, the packing in the liquid state was not affected by the differences observed between $ab$ initio and force field cation–anion distances presented in Fig. 2.

In Fig. 4 the partition of intermolecular energies into to Coulomb and Lennard–Jones interactions is presented. As expected, the ionic nature of the particles involved is revealed by the predominance of the Coulomb contribution.
tions. The mean energy values due to Lennard–Jones interaction is $-8812.14 \text{ kJ mol}^{-1}$ and the Coulomb short and long range interactions are, respectively, $-17,369.6 \text{ kJ mol}^{-1}$ and $-25,565.9 \text{ kJ mol}^{-1}$. Therefore, the total Coulomb contribution to the cohesion energy, $-42,935.5 \text{ kJ mol}^{-1}$, is almost five times greater than the Lennard–Jones interactions. The total cohesion energy obtained can be used to estimate the heat of vaporization $\Delta H_{\text{vap}}$ of this ionic liquid assuming that $\Delta H_{\text{vap}} = -E_{\text{cohesion}} + RT$, where $E_{\text{cohesion}}$ is the total cohesion energy per particle (anion–cation dimer), $R$ is the gas constant and $T$ the temperature. A value $\Delta H_{\text{vap}} \approx 413 \text{ kJ mol}^{-1}$ was obtained, therefore justifying the very low vapor pressure of this ionic liquid. As a guide for comparison, the heat of vaporization of liquid water at this same temperature is $\Delta H_{\text{vap}} \approx 41 \text{ kJ mol}^{-1}$.

The radial distribution functions (RDF) obtained for this ionic liquid are shown in Fig. 5. One can observe in this figure a strong periodic profile in the RDF, extending over the range of the simulation box length, which is in agreement with the overwhelming contribution of long range Coulomb interactions to the cohesion energy, presented in Fig. 4. In the cation–cation interaction, there are two peaks, one in 0.8 nm and other in 1.4 nm. Two peaks are
also observed in the anion–anion correlation at 0.7 and 1.3 nm, respectively. These peaks positions are 0.1 nm shorter compared to the ones observed in the cation–cation RDF. The systematic distance of 0.6 nm between the positions of the first and second picks can be associated to solvation shells for both cation and anions. In RDF obtained from the cation–anion correlation there is a sharp peak at 0.45 nm and a broader second peak at 1.0 nm. Again, it is interesting to note that these peak positions are separated by almost 0.6 nm. Therefore, the features observed in the RDFs indicate that [BMIM][BF₄] ionic liquid has a well organized structure with strong counter ions interactions. The RDF data obtained in this work are in good agreement with the results reported by Andrade et al. [17].

To further address the structural characteristics of this ionic liquid, RDFs due to correlations between the positively charged hydrogen sites H9, H10 and H11 of [BMIM⁺] and [BF₄⁻] fluorine atoms were calculated and are presented in Fig. 6. The well defined peaks at 0.25 nm in Fig. 6 indicate strong interaction between these sites. Moreover, the well defined positions and sharpness of these distributions indicate that these correlations can be associated to hydrogen bond like interactions between the ionic pairs. In each RDF, a second peak near 0.44 nm

![Fig. 5. Radial distribution function involving cation–cation, anion–anion and cation–anion interactions. The reference sites are the nitrogen N1 for cation and the Boron atom for the anion.](image1)

![Fig. 6. Radial distribution functions from correlations between sites H9, H10 and H11 of imidazolium ring and fluorine atoms.](image2)
is due to interactions of the reference Hydrogen site with the remaining fluorine atoms of [BF₄]⁻ ion. As presented in Table 3, the Lennard–Jones parameters and charges of H9, H10 and H11 hydrogen sites are similar. Nevertheless, one observes in Fig. 6 some differences in the amplitude of the RDFs obtained, indicating that the strongest interaction involved the H9 hydrogen site. Similar results were observed and reported in several imidazolium derived cation simulations [18–24]. Two peaks in the H9-F RDF are observed at distances in the interval 0.6–0.9 nm, and can be attributed to correlations with second shell anions. The RDF data presented in Fig. 6 are in good agreement with experimental and simulation results reported elsewhere [25].

Insights on the ionic liquid structure can be also obtained by investigating the three dimensional probability density distribution of anions center of mass, \( \rho(X, Y, Z) \), around a cation coordinate origin. This origin was defined by the interception of two perpendicular vectors: one connecting the sites N1 and N2, and the other passing through the site C3 and bisecting the C5–C4 bond. The distributions obtained are presented in Fig. 7. The orange color isosurfaces were calculated assuming a probability density \( \rho(X, Y, Z) = 0.060 \text{ Å}^3 \) and represents the region of higher probability to find anions. This surface enclosures the C3–H9 bond above and below the plane of imidazolium ring and its shape and position are in good agreement with

![Fig. 7. Probability distribution of [BF₄]⁻ centers of mass around [BMIM]⁺. Yellow and orange isosurface corresponds, respectively, to a density level of 0.018 Å⁻³ and 0.060 Å⁻³. Hydrogen atoms from methyl and butyl groups were omitted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 8. Average mean square deviations (MSD) for [BMIM]⁺ and [BF₄]⁻ ions.](image)
other ionic liquids results available in the literature [25,20]. The distance between the isosurface and the cation center of mass is around 0.45 nm, in agreement with the peak obtained using ESP partial charges but different force fields (AMBER [30] and OPLS-AA [8]) are again very close. Nevertheless, in the simulations performed with the same force field parameters, but using partial charges obtained with different methodologies, large differences are observed in the calculated self-diffusion constants. The strong influence of charges on the values of dynamic properties is in accord with the overwhelming contribution of the Coulombic potential to the cohesion energy, as already shown in Fig. 4. These observations stress the need of investigating the influence of partial charges in calculation of structural and thermodynamical properties of RTILs. Such investigations must take into account the level of \textit{ab initio} theory as well as basis set size effects in the calculation.

5. Conclusions

This paper reports a force field for the ionic liquid [BMIM]$^+$[BF$_4^-$] obtained using OPLS-AA force field parameters and charges calculated at the MP2/6-31g(d) level using the ChaelpG methodology. The ions geometries were also calculate at this \textit{ab initio} level. Geometries and energies of [BMIM]$^+$[BF$_4^-$] dimers calculated with MP2/6-31g(d) and force field were compared and the accord is good. The value obtained for the liquid density using Molecular dynamics (MD), 1.178 g cm$^{-3}$, is in very good agreement with the experimental data, 1.17 g cm$^{-3}$. The value estimated for the heat of vaporization, $\Delta H_{\text{vap}} \approx 413$ kJ mol$^{-1}$, is in accord with the negligible vapor pressure of RTILs at $T = 300$ K. Radial Distributions functions show periodic structure between cations, anions and cations/anions. The RDFs also show strong interaction between cation ring hydrogen atoms and the fluorine atoms of [BF$_4^-$] anion. The displacements of ionic liquid species are smaller when compared with values observed for molecular liquids. The cations [BMIM]$^+$ spread out more than their counter ions. The results obtained for the self-diffusion constants are small if compared with the ones observed for molecular liquids. The cation and anion self-diffusion constants obtained are, respectively, $8.2 \times 10^{-12}$ m$^2$ s$^{-1}$ and $3.0 \times 10^{-12}$ m$^2$ s$^{-1}$. The experimental values for cation and anion in

<table>
<thead>
<tr>
<th>Table 6</th>
<th>Self-diffusion constants calculated with different force fields and point charge models</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d([\text{BMIM}]^+)/10^{-12}$ m$^2$ s$^{-1}$</td>
<td>$d([\text{BF}_4^-]/10^{-12}$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>This work$^a$</td>
<td>8.2</td>
</tr>
<tr>
<td>Morrow [21]</td>
<td>1.2</td>
</tr>
<tr>
<td>Liu [25]</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Experimental data for [BMIM]$^+$[PF$_6^-$] ionic liquid are also presented.

$^a$ As a guide for comparison, the self-diffusion constant reported in Gromacs benchmark [11,12] for water is near $10^{-9}$ m$^2$ s$^{-1}$, therefore, 3 orders of magnitude greater than the ones presented here.

$^b$ Self-diffusion values for [BMIM]$^+$ in the ionic liquid [BMIM]$^+$[PF$_6^-$]. The experimental data for [PF$_6^-$] reported by Tokuda et al. [33] is $4.0 \times 10^{-12}$ m$^2$ s$^{-1}$. Comparatively, the experimental value for the anion self-diffusion constant is lower, in qualitative accord with the theoretical results in this table.
[BMIM][PF₆] reported by Tokuda et al. [33] are, respectively, $6.8 \times 10^{-12} \text{ m}^2 \text{s}^{-1}$ and $4.0 \times 10^{-12} \text{ m}^2 \text{s}^{-1}$. Therefore, the cation is heavier and larger than anion but its self-diffusion constant is greater. This result is in agreement with well understood behavior of ionic solutions showing that the diffusion process depends on multiple factors such as volume, mass, cohesion energy and coordination numbers. It was observed a strong dependence between the results obtained for self-diffusion constants and the set of partial charge employed, with negligible influence of the others force field parameters. It is interesting to note that, as in Fig. 4 the Coulomb energy term is dominant, the cohesion energy is also affected by the set of partial charges used in the calculation. These facts point out that special care is needed to obtain point charges to implement ionic liquids force fields.

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