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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 $T = 300$ K and $p = 1.0$ 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 *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 *ab initio* and force field calculations is good. The value obtained for the liquid density, 1.178 g cm^{-3}, is close to 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 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.

Keywords: Room-temperature ionic liquids; 1-Butyl-3-methylimidazolium tetrafluoroborate; Molecular dynamics

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], hydroformilation [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 ($[\text{BMIM}]^+[\text{BF}_4]^-$), Fig. 1, the necessary force field was developed combining parameters taken from the OPLS-AA force field with

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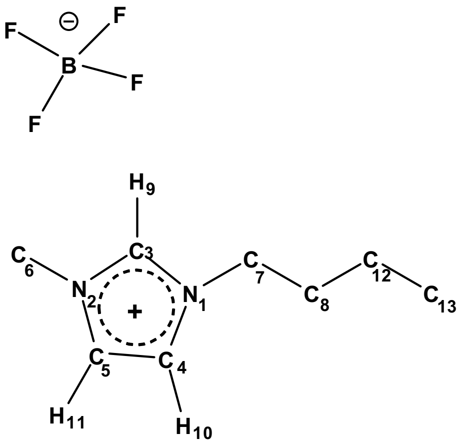

Fig. 1. Structure and atomic labeling of 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM]^+[BF_4]^-$) ion pair. The hydrogen atoms from methyl and butyl groups were omitted.

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_{stretch}, angle bending, U_{bend}, dihedral torsion, U_{torsion}, was well as Lennard–Jones, U_{LJ}, and Coulombic, U_{Coulomb}, interactions:

$$U = U_{\text{stretch}} + U_{\text{bend}} + U_{\text{torsion}} + U_{\text{LJ}} + U_{\text{Coulomb}}. \tag{1}$$

The functional forms of these potentials are, respectively,

$$U_{\text{stretch}} = \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2 \tag{2}$$

$$U_{\text{bend}} = \sum_{\text{angles}} K_\theta (\theta - \theta_{\text{eq}})^2 \tag{3}$$

$$U_{\text{torsion}} = \sum_{\text{dihedrals}} \sum_{n=0}^{5} C_n (\cos(\phi - 180)^n) \tag{4}$$

$$U_{\text{LJ}} = \sum_i \sum_{i<j} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \right\} \tag{5}$$

$$U_{\text{Coulomb}} = \sum_{i<j} \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}. \tag{6}$$

Equilibrium bond lengths, r_{eq}, angles, θ_{eq}, and dihedral angles, ψ_{eq}, were obtained from *ab initio* calculation at the MP2/6-31g(d) level. All force constants (k_r, k_θ) and parameters (σ_i, ε_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 σ_{ij} and ε_{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 *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_r are showed in Table 1. Selected angles and their force field constants k_θ 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 pair geometries were optimized and compared with the ones obtained at the *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 *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 $T = 300$ K and a Berendsen pressure coupling

Table 1
Optimized bond lengths and their respective, Eq. (2), force field constants

Bond	r_{eq} (nm)	K_r (kJ mol^{-1} nm^{-1})
N1–C3	0.13428	399420.7
N1–C4	0.13754	357552.7
N1–C7	0.14781	282190.3
N2–C3	0.13441	408631.7
N2–C5	0.13753	343317.6
N2–C6	0.14696	282190.3
C3–H9	0.10810	307311.1
C4–C5	0.13722	435427.2
C4–H10	0.10805	307311.1
C5–H11	0.10806	307311.1
C6–H14	0.10899	284702.4
C6–H15	0.10892	284702.4
C6–H16	0.10900	284702.4
C7–C8	0.15236	224412.5
C7–H17	0.10934	284702.4
C7–H18	0.10934	284702.4
C8–C12	0.15293	224412.5
C8–H19	0.10966	284702.4
C8–H20	0.10965	284702.4
C12–C13	0.15264	224412.5
C12–H21	0.10965	284702.4
C12–H22	0.10965	284702.4
C13–H23	0.10936	284702.4
B–F	0.14227	500000.0

The atom labels are in accord with Fig. 1.