SUPPORTING INFORMATION

Nano-segregation in Ionic Liquids:

Scorpions and Vanishing Chains

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Force field development.

The molecular force field used in this work is based on the function with the general form given in eq. (1), with the traditional decomposition of the potential energy, $u_{\alpha\beta}$, into covalent bond stretching, valence angle bending, torsion barriers around dihedral angles, and atom-atom pair-wise repulsive, dispersive, and electrostatic contributions. The Coulomb interactions are defined in terms of atomic point charges while the (12-6) Lennard-Jones potential describes the repulsive and dispersive terms. Together they act either between sites in different molecules or between sites in the same molecule separated by three or more bonds. A scaling factor of 0.5 is applied to the Lennard-Jones and Coulombic interactions when sites in the same molecule are exactly three bonds apart.

$$
\begin{aligned}
u_{\alpha,\beta} = {} & \sum_{ij}^{\text{bonds}} \frac{k_{ij}}{2}\left(r_{ij} - r_{0,ij}\right)^2 + \sum_{ijk}^{\text{angles}} \frac{\theta_{ij}}{2}\left(\theta_{ijk} - \theta_{0,ijk}\right)^2 \\
& \sum_{ijkl}^{\text{dihedrals}} \sum_{m=1}^{4} \frac{\mathrm{V}_{m,ijkl}}{2}\left[1 - (-1)^m \cos\left(m\phi_{ijkl}\right)\right] + \\
& \sum_{ij}^{\text{nonbonded}} \left\{ 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}} \right\} \quad (1)
\end{aligned}
$$

The Coulomb interactions were modeled by partial charges positioned at the center of mass of each atom. These interactions that describe the electrostatic forces acting on each ion are calculated ab initio at the MP2 theoretical level using a quite large basis set, cc-pVTZ(-f). The point charges are calculated from the electron density using the CHelpG electrostatic surface potential methodology. [1] Intra-molecular terms related to covalent bonds and angles and also non-bonded terms related to repulsive and dispersive interactions were taken directly from the AMBER/OPLS data set. [2] In cases where the parameters from the OPLS-AA/AMBER force field could not be transferred, *ab initio* calculations were performed using the Gaussian package. [3] The development of a set of parameters capable of describing the torsions of articulated molecules or ions includes the *ab initio* calculation for a given dihedral angle of the compound of the corresponding torsion energy profile, the calculation by molecular dynamics of that same torsion energy profile considering only non-bonded interactions in an isolated molecule or ion and the fitting of the dihedral angle parameters (V1 to V3 in eq.(1)) to the difference between the profiles obtained by *ab initio* and MD. The simulation procedure employed in this case consisted of a series of MD quench runs on the isolated $[C_1OC_2OC_1mim]^+$ cation during 10000 timesteps of 0.5 fs under canonical ensemble conditions at 10, 1, 0.1, and 0 K. The dihedral angles being studied were constrained at the desired values by the addition of very steep harmonic terms. This method provides very accurate torsion energy profiles in a consistent manner, thus the parameters obtained are transferable along a family of molecules or ions. It has been explain in detail in previous publications. [4]

TABLE 1: Force field parameters for the [$C_1OC_2OC_1$mim]$^+$ cation. The parameters are the result of ab initio and MD calculations performed in the present study.

atoms	Q (e)	ε (kJ mol^{-1})	σ (nm)
CR	-0.06	0.29288	0.355
NAE	0.02	0.71128	0.325
CWE	-0.08	0.29288	0.355
C1E	0.28	0.27614	0.350
H1E	0.06	0.12552	0.250
O	-0.35	0.58615	0.290
CSE	0.14	0.27614	0.350
HCE	0.03	0.12552	0.250
Dihedrals	V_1 (kJ mol^{-1})	V_2 (kJ mol^{-1})	V_3 (kJ mol^{-1})
CWE-NAE-C1E-O	1.0136	-2.3950	1.3588
NAE-C1E-O-CSE	-10.653	-10.004	6.5813

Molecular dynamics and structure factors.

For each ionic liquid studied, we started from low-density initial configurations composed of 350 ion pairs for [C_1OC_1mim][Ntf_2], 300 ion pairs for [$(C_1OC_1)_2$mim][Ntf_2], 250 ion pairs for [$(C_1OC_1)_3$mim][Ntf_2] and [C_9mim][Ntf_2], 320 ion pairs for [C_3mim][Ntf_2] and 275 ion pairs for [C_6mim][Ntf_2]. The variation in number of ion pairs in each ionic liquid reflects the need to obtain simulations boxes with similar size (*ca* 5 nm). The boxes were equilibrated in isothermal-isobaric ensemble conditions for 700 ps at 298 K using the Nosé-Hoover thermostat and isotropic barostat with time constants of 0.5 and 2 ps, respectively. Five sucessive equilibration runs were performed interspersed with temperature anealling steps. Further simulation runs of 1.5 ns each were used to produce equilibrated systems at the studied temperature. At least six consecutive runs were used in order to avoid any ergodicity problems. Electrostatic interactions were treated using the Ewald summation method considering six reciprocal-space vectors, and repulsive-dispersive interactions were explicitly calculated below a cutoff distance of 1.6 nm (long-range corrections were applied assuming the system has an uniform density beyond that cutoff radius).

The total static structure factor, $S(q)$, was calculated from: [5]

$$S(q) = \sum_i \sum_j S_{ij}(q) \tag{2}$$

$$S_{ij}(q) = \frac{\rho_o x_i x_j b_i(q) b_j(q) \int_0^R 4\pi r^2 \left[g_{ij}(r) - 1 \right] \frac{\sin(qr)}{qr} \frac{\sin(\pi R)}{\pi r / R} dr}{\left(\sum_i x_i b_i(q) \right)^2} \tag{3}$$

were $S_{ij}(q)$ is the partial static structure factor between atoms types i and j (e.g. carbon's, hydrogen's and nitrogen's), calculated from the corresponding Fourier transform of the partial radial distribution function $g_{ij}(r)$; r is the distance; q is the scattering vector; $\tilde{n}_o$ is the average atom number density; R is the cutoff used in the calculation of $g_{ij}(r)$, established to half of the size of the one side of the cubic simulation box; x_i and x_j are the atomic fraction of i and j; and $b_i(q)$ and $b_j(q)$ are the coherent bound neutron scattering length of the corresponding atom type, interpolated from recommended values in the International Tables for Crystallography. [6] The term $\frac{\sin(\pi R)}{\pi r / R}$ is a Lorch type window function [7] and was added to eq. 3 to reduce the effect of using a finite cutoff in the radial distribution function calculation.

As shown in eq. 3, the computed partial static structure factors essentially depend on the radial distribution function (RDF) between the different atomic types in the simulation box. Therefore, several tests were performed to determine the ideal conditions for their computation. The first test was the effect of the histogram spacing. The results shown that as $q \rightarrow 0$, $S(q)$ values can be significantly altered, leading to uncharacteristic results. In fact, because q = 2ð/r, if, for example, $R = 2$ nm then only values of $q > 3.1$ nm^{-1} have physical meaning. In this case, it was found that consistent results, regardless the cutoff used in the $g_{ij}(r)$ calculation, were obtained by applying a spacing of 0.001 nm. As previously referred, because q = 2ð/r, a carefully choice of R is required. From the example above, if an eventual peak exists for $q < 3.1$ nm^{-1} then the RDF will not contain any information about its existence. On the other hand, because the computation time scales with the simulation box size, the use of extremely large simulation boxes to accommodate big cutoffs has to be considered with caution. In your case a the RDF's were computed with cutoff's of 2.5 nm, since allowed a good relation between computation time and the range of analyzed q values. Finally, the hypothesis of excluding the determination of RDF's including hydrogen's was also tested, in the attempt to improve the calculation times. In fact, the coherent bound neutron scattering lengths of the hydrogen atoms are very close to zero and, therefore, have a small effect on $S(q)$, spatially for high q values. [6] The obtained results shown that the exclusion of these partial structure factors leads to a small variation in the intensity of $S(q)$ for $q < 0.06$ nm.

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