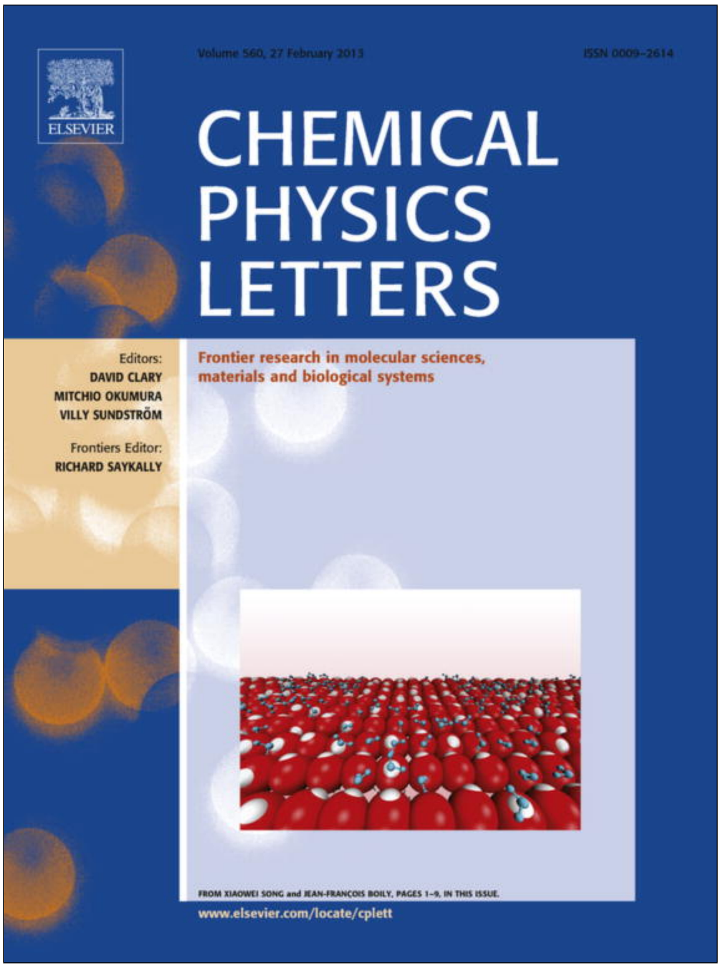
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Hydrogen-bond rich ionic liquids with hydroxyl cationic tails

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ABSTRACT

To investigate if the amphiphilic feature exhibited in ionic liquids (ILs) with nonpolar cationic tails still exists in ILs with polar tails, by performing molecular dynamics simulations for 1-(8-hydroxyoctyl)-3-methyl-imidazolium nitrate (C_{OH}) and 1-octyl-3-methyl-imidazolium nitrate (C_8), we found that, in C_{OH}, cationic tail groups can no longer aggregate to form separated nonpolar tail domains, instead hydroxyl groups form a rich number of hydrogen bonds with other groups, indicating that the hydroxyl substituent changes the IL system from an amphiphilic liquid to a polar liquid. Due to the large amount of hydrogen bonds, C_{OH} has slower dynamics than C_8.

Ionic liquids (ILs) are very promising in many areas of industrial applications [1–3]. A systematic understanding of the relation between IL structure and physical properties is essential for their efficient usage in those applications. Several molecular dynamics (MD) simulations [4–7] discovered a nanoscale spatially heterogeneous structure in ILs with an intermediate alkyl cationic tail length (about 6–12 carbon groups), which was supported by many experimental observations (see, e.g., Refs. [8–16]). The spatially heterogeneous structure is formed by the nonpolar tail domains ascribed to tail aggregation separated by the continuous polar network composed of anions and cationic head groups. Among its many fundamental meanings, this amphiphilic feature is especially important for understanding the performance of ILs with other chemical compounds, such as water [17–24] and gas molecules [25–28]. In recent couple of years, more and more researchers have been extending their attentions to another categories of ILs—those with polar cationic tails [29–38]. In particular, Pensado et al. [36] studied the surface properties of imidazolium ILs with hydroxyl (OH) tail groups by MD simulations and found that the hydroxyl groups make the liquid interface less organized. Although experimental studies have already revealed that hydroxyl groups make ILs less ordered [30], strengthen interionic interactions [32], and increase the polarity, hydrophilicity, and hydrogen-bonding capability [35], until now no systematic investigations have been conducted on the microscopic structure of bulk ILs with hydroxyl tails and associated mechanism which consistently explains the experimental observations. Moreover, it is very important to see if the amphiphilic feature still exists when the cationic tail changes from nonpolar to polar.

In this Letter, we perform all-atom MD simulations for 1-(8-hydroxyoctyl)-3-methyl-imidazolium nitrate (denoted as C_{OH}), and compare the results with those for 1-octyl-3-methyl-imidazolium nitrate (denoted as C_8). The molecular structures of C_{OH} and C_8 are shown in Figure 1. We selected the C_8 system to study because it is a typical one forming nonpolar tail domains. Our results indicate that, only by replacing one of the hydrogen atoms on the terminal methyl group with a hydroxyl group, the IL system can no longer form nonpolar tail domains. Instead, the hydroxyl tails have a very large probability to be around anions, cationic head groups, and other hydroxyl groups to form a rich amount of hydrogen bonds, which leads to slower dynamics of C_{OH} than C_8.

Both C_8 and C_{OH} IL systems were simulated with the GROMACS MD simulation package [39] by employing the AMBER 94 force field [40]. The details of the force field are given in the Supplemental material associated with this Letter. Despite the fact that a nonpolarizable force field leads to slower dynamics than experiment [41–43], it is still adopted in this Letter for modeling simplicity and computational efficiency. Our qualitative conclusions still hold since we compare the results of C_{OH} with C_8 and the conclusions are drawn upon comparisons of relative values rather than absolute values precisely comparable to experiment. For each system, 512 ion pairs were uniformly located on the lattice positions of a very large cubic simulation box. A simulated annealing procedure was performed from temperature $T = 2000$ K down to 1500, 1000, 800, 600, and 400 K with a constant *NPT* MD simulation at pressure $P \sim 100$ atm for 1 ns at each temperature. The last configuration further went through another constant *NPT* MD simulation at $P = 1$ atm and $T = 400$ K for 1 ns to determine the system density in equilibrium. The simulation box size was then fixed to perform a constant *NVT* simulated annealing procedure from $T = 1000$ K down to 400 K with a temperature interval of 200 K and a simulation time of 1 ns at each temperature. Finally, the equilibrated configuration went through a constant *NVT* simulation at $T = 400$ K for 10 ns to sample 1000 evenly distributed instantaneous configurations. The simulation time step was 2 fs for all MD simulations.

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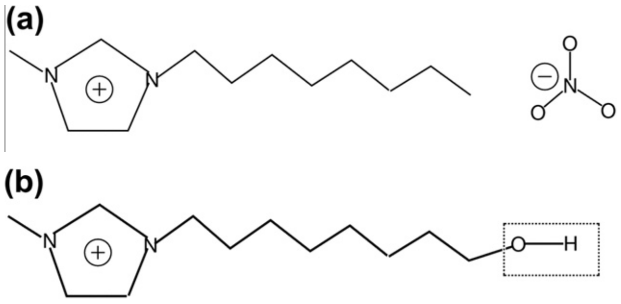

Figure 1. Molecular structures of C_8 and C_{OH}. Both systems have the same nitrate anion and the cation of C_{OH} (b) only differs from the cation of C_8 (a) by replacing one of the terminal hydrogen atoms with a hydroxyl group.

All-atom MD simulations were performed at $T = 400$ K for C_8 and C_{OH} IL systems. The simulation box sizes in equilibrium are 5.95 and 5.90 nm, corresponding to the densities of 1.04 and 1.13 g/cm^3 for C_8 and C_{OH}, respectively. The random snapshots for the two IL systems in equilibrium are drawn in Figure 2. For C_8, due to the repulsion by the polar groups (anions and head groups) [44] which form a continuous polar network, the alkyl tails aggregate and form separated nonpolar tail domains [4,6,45]. For C_{OH}, since the terminal OH groups are also polar, they are not repulsed by the polar groups to aggregate. Instead, they distribute all over the space and are not obviously separated from anions and cationic head groups.

The radial distribution functions (RDFs) for cationic tail groups with cationic head groups, anions, and other tail groups in C_8 and C_{OH} systems, respectively, as well as the OH–OH RDF in C_{OH}, are plotted in Figure 3. Here 'head' is defined as the center-of-geometry (COG) position of the cationic head ring, 'anion' the COG of the whole anion, 'tail' the position of the last carbon atom on the cationic tail, and 'hydroxyl' the position of the oxygen atom in the hydroxyl group. As can be seen from Figure 3a, the first peak of the C_{OH} tail–tail RDF greatly drops down to around 1 from more than 2.5 for C_8, demonstrating that the tail groups do not aggregate in C_{OH}. In contrast, in Figure 3b, the first peak of the tail-anion RDF greatly increases from less than 1 for C_8 to more than 2 for C_{OH}, indicating that, in the C_{OH} system, the tail groups have a much larger probability to be around anions and form hydrogen bonds. In Figure 3c, the higher first peak of the tail-head RDF suggests that the terminal OH groups also form some hydrogen bonds with the cationic head groups. The RDF for hydroxyl groups in Figure 3d is almost 1 for $r > 5$ Å, indicating that the OH groups are almost randomly distributed with respect to each other. The small peak at $r \sim 3$ Å corresponds to the hydrogen bonds formed between the terminal OH groups.

The hydrogen bonds in the two IL systems were then identified according to the criterion that a hydrogen bond A–H…B should have the distance between atoms A and B shorter than 3.5 Å and simultaneously have the angle between AH and AB smaller than 30° [46]. The average numbers of hydrogen bonds formed in the two IL systems are listed in Table 1. In C_{OH}, about two thirds of hydrogen bonds are formed between anion and hydroxyl, and a small number of hydrogen bonds are formed between head and hydroxyl as well as between two hydroxyl groups. Both systems have certain numbers of hydrogen bonds formed between anions and head groups, and C_{OH} has fewer because the hydrogen binding sites in some cations are already occupied by terminal hydroxyl groups and therefore unavailable for forming hydrogen bonds with

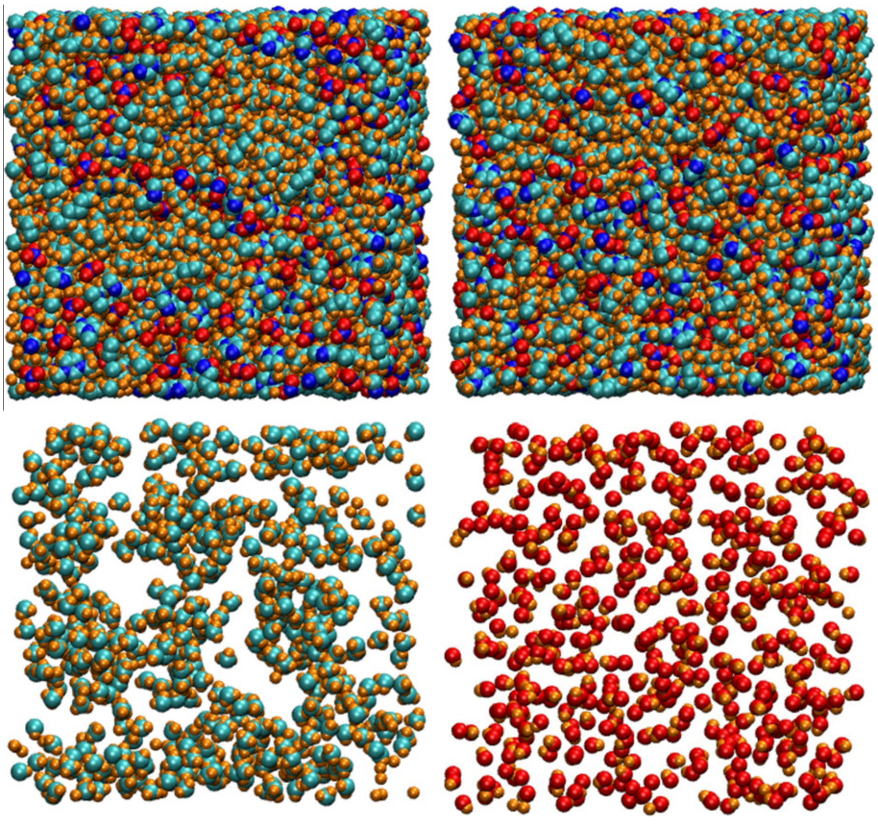

Figure 2. Random snapshots of C_8 (left column) and C_{OH} (right column). First row: all atoms; second row: terminal groups (CH_3 for C_8 and OH for C_{OH}) only. Carbon atoms are colored with cyan, nitrogen blue, oxygen red, and hydrogen gold.

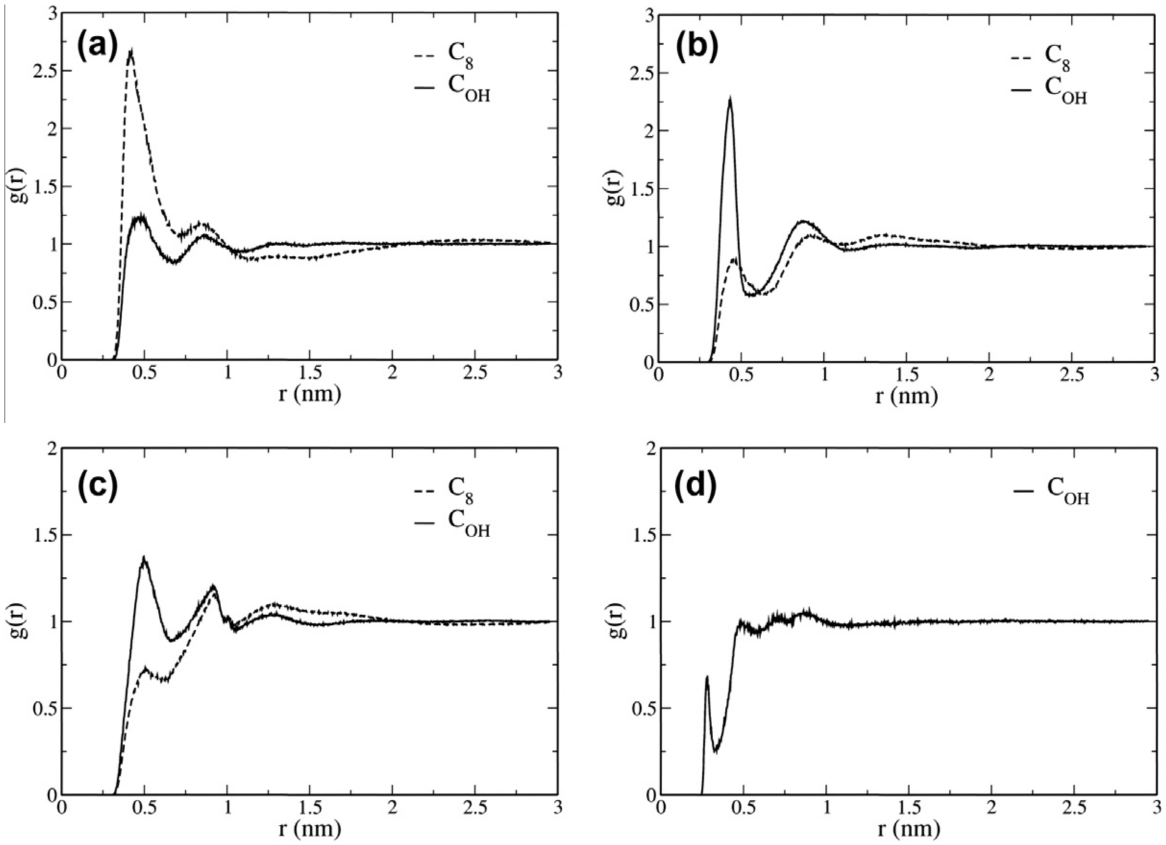

Figure 3. Radial distribution functions for (a) tail–tail, (b) tail-anion, (c) tail-head, and (d) OH–OH.

Table 1
Numbers of hydrogen bonds in C_8 and C_{OH} systems.

Hydrogen bond	C_8	C_{OH}
Head-anion	378.74 ± 17.93	287.40 ± 20.90
Anion-OH	–	498.63 ± 7.63
Head-OH	–	31.73 ± 5.43
OH–OH	–	17.98 ± 3.82

anions. The majority of hydrogen bonds in C_{OH} are formed between anions and OH groups because (1) terminal OH groups are strong hydrogen-bond donors; (2) one anion has three oxygen atoms and each oxygen is a strong hydrogen-bond acceptor. Moreover, the total number of hydrogen bonds formed by OH in C_{OH} ($\sim$547) is larger than the number of OH groups (512), indicating that some OH groups form more than one hydrogen bonds by having the hydrogen atom as a hydrogen-bond donor and simultaneously the oxygen atom as a hydrogen-bond acceptor.

The spatial distributions of anions (represented by the nitrogen atom) around cationic terminal groups are drawn in Figure 4. It is clear that anions have a very large probability to distribute around the terminal of the cationic tail in C_{OH} (Figure 4b), but have almost no chance to approach the nonpolar cationic tail in C_8 (Figure 4a).

Based on the above results, we summarize the four types of hydrogen bonds formed in C_{OH} and schematically illustrate them in Figure 5. When one of the hydrogen atoms on the nonpolar cationic terminal is replaced by a hydroxyl group, the cationic tails become polar and are not pushed by the polar groups to form separated nonpolar domains. Instead, the hydroxyl groups form hydrogen bonds with anions, cation head groups, and other hydroxyl groups. Most of the hydrogen bonds are formed between anions and hydroxyl groups because the hydrogen atoms of

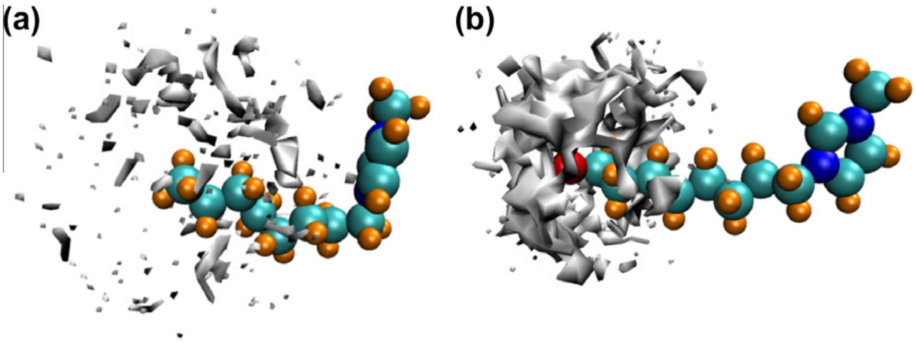

Figure 4. Spatial distributions of anionic nitrogen around cationic tail group in C_8 (a) and in C_{OH} (b). The isosurface value is three times the mean density of the system.

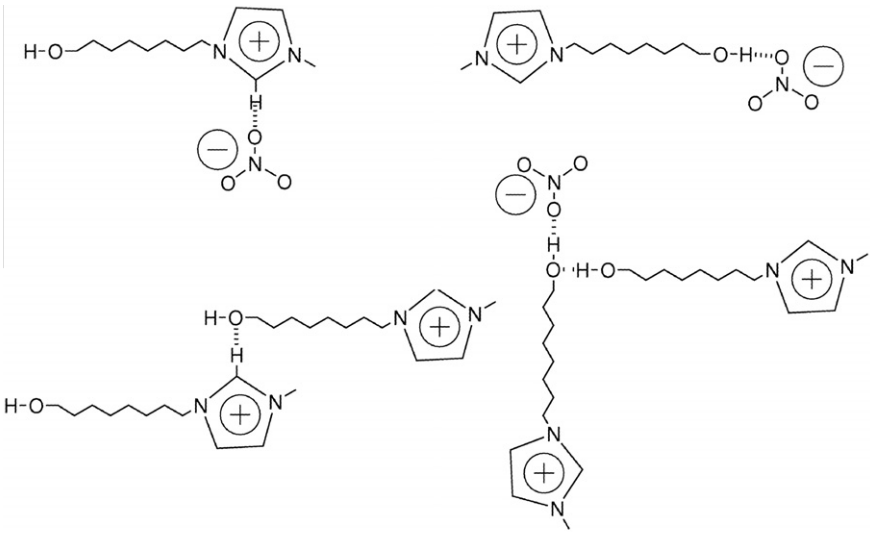

Figure 5. Schematic of the hydrogen-bond formation in C_{OH}: head-anion, head-hydroxyl, anion-hydroxyl, and hydroxyl–hydroxyl. The right-bottom figure shows one case when a hydroxyl group forms two hydrogen bonds simultaneously.

hydroxyl groups are strong hydrogen-bond donors and the three anionic oxygen atoms are strong hydrogen-bond acceptors. Consequently, although the difference between their molecular compositions is only one extra oxygen atom, C_{OH} is a polar liquid without the amphiphilic feature presented in C_8.

Different microscopic structures certainly lead to different dynamic properties. The mean square displacements (MSDs) of all ions in the two IL systems with respect to time t are plotted in Figure 6a. C_{OH} has a smaller MSD than C_8, and by fitting the MSD according to the Einstein relation MSD = 6 Dt, we obtain the diffusion coefficient for C_{OH} $D_{OH} = 0.59 \times 10^{-11}\ m^2/s$ and that for C_8 $D_8 = 1.06 \times 10^{-11}\ m^2/s$. The disappearance of nonpolar tail domains would allow the ions in C_{OH} diffuse faster, but the rich amount of hydrogen bonds overrides it and slows down the ion diffusion in C_{OH}.

Since ions in ILs are usually trapped in the ion cages formed by their neighboring counterions in the first coordination shell, the dynamics of the two IL systems were also characterized by the lifetime of ion cage. The time correlation function of ion cage is defined as [47] $S(t) = \frac{\langle p(0)P(t)\rangle}{\langle p(0)\rangle}$, where $p(0)$ is unity if two counterions form a pair (distance less than 7 Å) at time 0 and zero otherwise, and $P(t)$ is unity if two counterions form a pair at time 0 and remain a pair continuously until time t and zero otherwise, and $\langle \ldots \rangle$ denotes the ensemble average over all ion pairs. Since, $S(t)$ considers all the ion pairs in the cage, it actually describes the dynamics of ion cage rather than an ion pair[48]. The calculated time correlation function curves for C_{OH} and C_8 are plotted in Figure 6b. Adopting the method descripted in ref [47], we estimated the lifetime of ion cage for C_{OH} to be 0.915 ns and that for C_8 to be 0.588 ns by fitting the curves by three weighted exponentials and integrating the fitted function from zero to infinity. Consistent with diffusion, ion cages in C_{OH} have a longer lifetime than those in C_8, corresponding to slower dynamics and in agreement with experimental observations that the hydroxyl-functionalization of ILs leads to higher viscosity [35].

In summary, we have performed all-atom MD simulations for the 1-(8-hydroxyoctyl)-3-methyl-imidazolium nitrate and 1-octyl-3-methyl-imidazolium nitrate. We found that the hydroxyl substituent on the cationic tail disallows the formation of separated nonpolar tail domains, consistent with the discoveries reported in Refs. [9,15,16,38]. Instead, the hydroxyl groups form a rich number of hydrogen bonds with anions, some with cationic head groups, and a few with each other. Due to the large amount of hydrogen bonds, the dynamics of the IL system with a hydroxyl terminal is slower than the one with an alkyl tail, characterized by the self-diffusion of all ions and lifetime of ion cages. Our suggested mechanisms based on the simulation results is consistent with and well explains the experimental observations

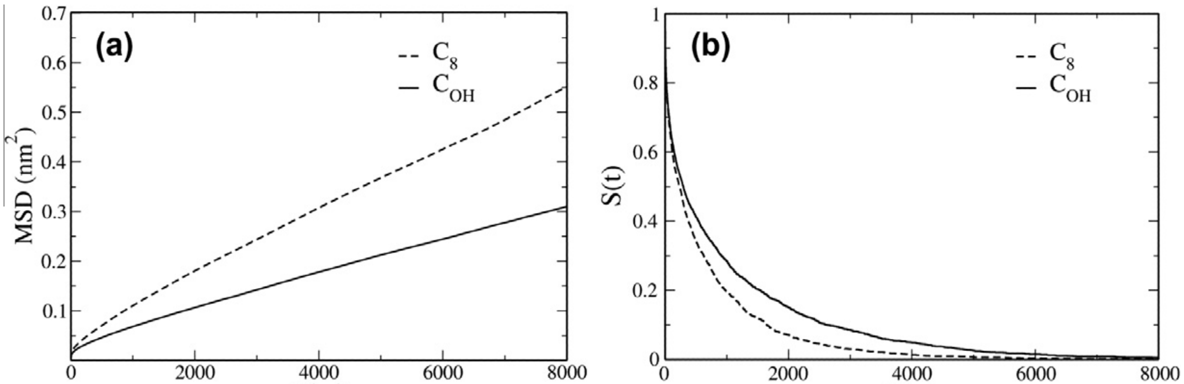

Figure 6. Mean square displacements (a) and time correlation functions of ion cages (b) of C_8 and C_{OH}.

[30,32,35,37]. Based on our results, we conclude that ILs with hydroxyl cationic tail groups are polar liquids without the amphiphilic feature presented in ILs with nonpolar cationic groups. Consequently, the physical properties of those two types of ILs are expected to be very different. For instance, their solubilities for various types of gas molecules may be very different, and their water mixtures should have totally different microscopic structures. Therefore, ILs with polar tails may be applied to cases in which ILs with nonpolar tails are not applicable, and thus extend the applicability of ILs in various applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2013.01.022.

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