



Molecular dynamics simulations of temperature-dependent structures and dynamics of ethylammonium nitrate protic ionic liquid: The role of hydrogen bond



Yiping Huang^a, Guobing Zhou^a, Yunzhi Li^a, Zhen Yang^{a,*}, Man Shi^a, Xueping Wang^a, Xiangshu Chen^{a,*}, Fei Zhang^a, Wei Li^b

^a College of Chemistry and Chemical Engineering, Jiangxi Inorganic Membrane Materials Engineering Research Center, Jiangxi Normal University, Nanchang 330022, People's Republic of China

^b School of Chemistry and Chemical Engineering, Key Laboratory of Mesoscopic Chemistry of the Ministry of Education, Institute of Theoretical and Computational Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

ARTICLE INFO

Article history:

Received 27 January 2016

In final form 27 March 2016

Available online 31 March 2016

Keywords:

Protic ionic liquid

Hydrogen bond

Diffusion

Ion-pair dissociation

Molecular dynamics simulation

ABSTRACT

Molecular dynamics simulations have been employed to systematically investigate the structure and dynamics properties, hydrogen bond (HB) dynamics of protic ionic liquid (IL) ethylammonium nitrate (EAN) in the temperature range between 300 K and 400 K. The simulation results demonstrate clearly that the temperature almost has little influence on the structures of EAN IL, whereas the translational and the rotational motions of both cations and anions become much faster at higher temperatures. Furthermore, both anions and cations are found to display an obvious sub-diffusive behavior. These changes can be attributed to the temperature-dependent HB strength between the cations and the anions, where the strength of HBs decreases significantly with increasing temperature. Accordingly, the ion-pair association/dissociation dynamics decreases considerably with increasing temperature. Therefore, our simulations reveal at a molecular level that the HBs interactions play an essential role in determining the dynamics properties of protic ILs.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In the past decades, ionic liquids (ILs) have received increasing attention due to their unique properties such as near-zero vapor pressure, high thermal conductivity and thermal stability, non-flammability, high conductivity and so on [1–5]. More importantly, the physical and chemical properties of ILs can be easily tailored by changing the combinations of cations and anions [6–10], which is promising in the molecular-level design and preparation of desired ILs with specific properties. To exploit such an approach, the understanding of interactions between cations and anions in ILs is very necessary. It is well-known that the cation–anion interactions mainly include the electrostatic and van der Waals interactions, as well as hydrogen bonds (HBs), where experimental observations of the HBs in ILs are often fraught with enormous difficulties owing to its localized and directional characters [11–13]. Especially in protic ILs, the proton transfer from the Brønsted acid

to the Brønsted base, resulting in the presence of proton-donor and proton-acceptor sites so that the three-dimensional HB network can be built in protic ILs like in water [14,15].

Experimentally, Ludwig and co-workers [12,13,16–21] have used far-IR spectroscopy to extensively probe the cation–anion interaction strength in the imidazolium-based aprotic ILs and protic ILs. They found that the HB contribution to the total interaction energy increases from 33% for the aprotic IL [C₄mim][NO₃] (i.e., 1-butyl-3-methylimidazolium nitrate) to 53% for the protic IL [PrAm][NO₃] (i.e., propylammonium nitrate) [17]. Meanwhile, increasing HB contributions can fluidize ILs, resulting in lower melting points, viscosities, and enthalpies of vaporization [12,13,16–19]. This is because the introduction of strong and localized directional HB can distort the charge symmetry of system, leading to the existence of “defects” in the electrostatic network of ILs [12,13,16–20]. Noack et al. [22] and Endo et al. [23] have revealed by IR, Raman, and NMR spectroscopies, that the methylation in the C2 position of the cation ring in imidazolium-based aprotic ILs strongly disrupts the HB interaction between cations and anions, causing significant changes in their melting and freezing points. Miran et al. [24] have provided experimental evidence

* Corresponding authors.

E-mail addresses: yangzhen@jxnu.edu.cn (Z. Yang), cxs66cn@jxnu.edu.cn (X. Chen).

for that the HB strength plays an important role in determining the ionicity of protic ILs decreasing significantly with temperature, in contrast to the independence of ionicity on temperature in aprotic ILs. Based on above experimental observations, therefore, the HB interaction between cations and anions in ILs should be as essential as both electrostatic and van der Waals interactions, especially in aprotic ILs.

On the other hand, theoretical calculations have been proven to be a convenient method to explore the HB properties in ILs at a molecular level up to now [25–38]. For example, Hunt and co-workers [25–27] have investigated the electronic properties of gas-phase aprotic [C₄mim]Cl (1-butyl-3-methylimidazolium chloride) ion pair at the B3LYP, MP2, and CCSD(T) levels. They revealed that the methylation in the C2 position of the cation ring is expected to decrease the HB strength between cation and anion but is unexpected to reduce the entropy of system. Then, they attributed the increase in viscosity and melting point of [C₄mim]Cl IL to the hypothesis that the loss effect in HB is outweighed by that in entropy [27]. Although static quantum chemistry calculations can offer a deep understanding of the original nature of HBs in various ILs at a molecular level, the relevant HB dynamics and temperature effects are not taken into account. Alternatively, molecular dynamics (MD) simulation with proper force fields can directly describe ion and HB dynamics as well as the entropy effects since the dynamics and temperature have been included in a direct way. Currently, a large number of MD simulations have been used to investigate the structures, dynamics, and HBs in the imidazolium-based aprotic ILs [30–38]. For example, the MD results proposed by Kirchner and co-workers [31] have confirmed that the methylation in the C2 position of the cation ring can restrict the free movement of the Cl[−] anion, leading to an increase in melting point. Zhao and co-workers [32] reported that the strength HB in [C₄mim][PF₆] (i.e., 1-butyl-3-methylimidazolium hexafluorophosphate) IL are weaker than expected, which is due to the fast rotational motion of anions. As an important subset of the ILs, however, protic ILs have received little attention in previous MD studies [37,38]. In protic ILs, a unique distorted HB behavior was revealed by recent X-ray diffraction proposed by Song et al. [38] and a large-angle jump in HB dynamics was observed in the dielectric relaxation and femtosecond-IR spectroscopies of Hunger and co-workers [39]. Clearly compared to aprotic ILs, much more MD work is needed to understand the complex HB behavior of protic ILs and their relationship to the relevant structures and dynamics of cations and anions.

To this end, a series of molecular dynamics simulations have been carried out to explore structures, dynamics, HBs of a protic IL at different temperatures. A prototype protic IL of ethylammonium nitrate (EAN) is considered here because of its simple structure and water-like properties. In this work, we mainly focus on the temperature-dependent HB properties and their relationship with the relevant structures, translational and rotational motions as well as ion-pair association/dissociation dynamics of both EA⁺ cations and NO₃[−] anions. Our paper is arranged as follows. In Section 2, we first present the details of simulation methods. Then, the simulation results will be discussed and analyzed in Section 3. Finally, several brief conclusions will be summarized in Section 4.

2. Simulation details

In this work, an all-atom OPLS model developed recently by Acevedo and Tirado-Rives [40,41] was employed for the EAN IL, where the nonbonded interactions were described by the combination of electrostatic and Lennard–Jones (L–J) interactions. All L–J parameters and partial atomic charges used in this work were summarized and listed in Table S1 of Supplementary Data. Then,

the mixed L–J parameters, including the collision diameter σ_{ij} and the well depth ϵ_{ij} , were derived from self-parameters using the mixing rule of geometric mean. First, a bulk EAN system with 512 pairs of EA⁺ cations and NO₃[−] anions, was arranged within a cubic simulation cell of 53.0 × 53.0 × 53.0 Å³. Then, a series of MD simulations have been carried out for the bulk EAN system in isothermal-isobaric ensemble (NPT) with different temperatures (300, 325, 350, 375, and 400 K) and the pressure of 1.0 atm. For each temperature, an NPT MD simulation of 10 ns was first performed for equilibration, and then another NPT MD simulation of 50 ns was performed for data analysis with the trajectories stored every 100 fs. After equilibration, the dimension of simulation box for each direction is in the range from 40.97 to 41.63 Å. During all NPT MD simulations, the bond length of EA⁺ cations and NO₃[−] anions was fixed through the RATTLE algorithm for the reason of computational economy. The Newton's equations of motion were integrated by using the velocity-Verlet algorithm with a time step of 2 fs, and the periodic boundary condition was used in all three directions. The cutoff distance of nonbonded interactions was set to 12 Å, and the long-range electrostatic interactions were calculated by using the particle-mesh Ewald (PME) method [42]. Both the temperature and pressure were controlled by using the Berendsen algorithm with coupling times of 0.2 and 4.0 ps, respectively. In addition, another NPT MD simulation of 2 ns following the above final configuration was performed to calculate the continuous HB dynamics. The trajectories stored every 5 fs instead of 100 fs, which is short enough to accurately calculate continuous HB dynamics. In this work, all NPT MD simulations were performed by using the Tinker 6.1 code [43].

3. Results and discussion

Based on our simulation, the radial distribution functions (RDFs), anion-anion g_{aa} , cation-cation g_{cc} , and cation-anion g_{ca} at different temperatures are first presented in Fig. 1. It can be observed expectedly from Fig. 1 that the first peak of g_{ca} curve is always higher and narrower than those of g_{aa} and g_{cc} curves regardless of temperatures, because of the strong interactions of electrostatic attractions and HBs between cations and anions. Meanwhile, the first peak height of each g_{aa} curve is found to be obviously lower than that of the corresponding g_{cc} curve at each temperature, suggesting the attractive interactions among anions are weaker than those among cations. Similar structure properties can be also found for other ILs in the previous work [44,45]. Such difference may result partly from different sizes between cations and anions. The larger cations have stronger repulsive steric interactions so that the cation-cation contact distance becomes larger. In other words, the electrostatic repulsions among cations are weaker than those among anions. Accordingly, we can see from the insets of Fig. 1a and b that the first peaks of g_{aa} curves locate at around 5.0 Å compared to 5.6 Å in the g_{cc} curves. More recently, Ludwig and co-workers [46–48] have further revealed the presence of cooperative HB interactions between cations in protic ILs, which can overcome the repulsive electrostatic forces between cations. Meanwhile, it should be noted that there is no CH₃–NO₃[−] HBs in bulk EAN IL at different temperatures, as shown in the RDFs Fig. S1a of Supplementary Data. In addition, the temperature is found to have a little influence on the structures of EAN IL in the range from 300 K to 400 K, as shown in the insets of Fig. 1. Unlike the HBs, both the electrostatic and the van der Waals interactions in ILs are mainly determined by the distances among ions. Therefore, the temperature-independent RDF curves in Fig. 1 mean that the electrostatic and the van der Waals interactions between ions almost keep constant as the temperature increases.

Download English Version:

<https://daneshyari.com/en/article/5372997>

Download Persian Version:

<https://daneshyari.com/article/5372997>

[Daneshyari.com](https://daneshyari.com)