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Nanoscale Tail Aggregation in Ionic Liquids: Roles of Electrostatic and van der Waals Interactions*

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Abstract *Nanoscale spatial heterogeneity in ionic liquids is formed by the aggregation of cationic tail groups. The electrostatic interactions between polar groups and the collective van der Waals interactions between nonpolar tail groups both contribute to the formation of tail domains, but the degrees of their contributions were unknown. In this work, by applying a strong external electric field to effectively overpower the electrostatic interactions between polar groups, we have determined that the tail aggregation is majorly attributed to the electrostatic interactions and the van der Waals interactions only have minor influence on the spatial heterogeneity phenomenon of ionic liquids.*

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1 Introduction

Ionic liquids are perspective next generation "liquids by design"[1] with very wide applications in many areas. The discovered spatial heterogeneity phenomenon,[2–4] which has been verified to be truly of nanoscale,[5] is important for understanding the physical properties of ionic liquids and developing systematic design methods for ionic liquids. The spatial heterogeneity in ionic liquids is formed by continuous polar network of anions and cationic head groups and nonpolar domains of cationic tail groups separated by the polar network. The formation of nonpolar tail domains may be attributed to two types of intermolecular interactions: i) the electrostatic interactions — the nonpolar tail groups "passively" gather together due to the steric repulsion from the continuous polar networks and ii) the van der Waals (VDW) interactions — the tail groups "actively" aggregate due to the attraction of the collective VDW interactions between tail groups.

The roles of different interactions in determining the structure and dynamics of ionic liquids are unknown and difficult to be determined by experiment. However, determining which one contributes more is of fundamental importance to the studies and applications of ionic liquids. For example, by carrying out molecular simulations, Jeong and coworkers[6] indicated that the structure of ionic liquids is mainly determined by electrostatic interactions and their relaxation dynamics in glassy states is dominated by the VDW interactions. Furthermore, Padua and coworkers[7–8] proposed that the segregation of the nonpolar domains is energy driven. That is, they are excluded from the cohesive network of positive and negative charges. On the other hand, Seduraman and coworkers[9] studied the nano-domains in guanidinium-based ionic liquids and proposed that the aggregation of the long alkyl chains is dominated by attractive VDW interactions. A more detailed microscopic mechanism is required to better understand the roles of electrostatic and VDW interactions in the formation of nanoscale spatial heterogeneity in ionic liquids.

In this work, we examine the effectiveness of these two contributions to the tail domain formation by means of molecular dynamics (MD) simulations. A strong external electric field is applied to the ionic liquid systems with various cationic side chain lengths to effectively overpower the electrostatic interactions between ions. In this way, the electrostatic interactions are suppressed by the external electric field and the role of collective VDW interactions with various strengths given by nonpolar side chains is clearly seen. Our results indicate that the tail aggregation is mainly attributed to the electrostatic interactions and the VDW interactions between tail groups have minor influence on the spatial heterogeneity of ionic liquids. These results can also be justified by the fact that the strength of electrostatic interactions is approximately one order of magnitude higher than that of VDW interactions, according to our simulation data (see Table 1). In addition, on average, the VDW energy increases 0.13 eV for each additional C_2H_4 group in one molecule but the

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electrostatic energy remains almost the same for different side-chain length systems, which is consistent with a previous cohesive energy calculation.[10] The energies of the C_2 system are different from others, because the side chains are so short that the VDW forces become repulsive to balance the attractive electrostatic interactions. These data suggest that the electrostatic energy dominates in ionic liquids and thus the nonpolar tail groups tend to aggregate to avoid the disruption of the continuous polar network. Besides the investigation of interactions, the studies of the structural, dynamical, and thermodynamical properties of ionic liquid systems with various side chain lengths under an external electric field is also very important for the applications of ionic liquids in electrochemical devices with charge transport reactions,[11] such as lithium batteries,[12–13] solar cells,[13–14] fuel cells,[13,15] and double-layer capacitors.[13,16]

Table 1 Average potential energies of electrostatic (U_{EL}) and VDW (U_{VDW}) interactions of the system (512 ion pairs) under different external electric fields E. The unit for the potential energies is eV and that for the electric field is N/C.

	C_2		C_6		C_8		C_{10}		C_{12}	
E	U_{EL}	U_{VDW}	U_{EL}	U_{VDW}	U_{EL}	U_{VDW}	U_{EL}	U_{VDW}	U_{EL}	U_{VDW}
0	–2475	34.0	–2336	–135	–2332	–199	–2335	–260	–2344	–326
10^2	–2475	33.8	–2336	–135	–2331	–200	–2332	–263	–2340	–331
10^4	–2474	33.7	–2336	–135	–2330	–200	–2333	–261	–2343	–328
10^6	–2474	34.0	–2336	–135	–2330	–200	–2332	–261	–2345	–328
10^8	–2474	36.1	–2335	–135	–2328	–200	–2331	–262	–2339	–331

2 Method

The effective force coarse-graining (EF-CG) method[17] was successfully applied to developing transferable models for $\mathrm{XMIM}^+/\mathrm{NO}_3^-$ ionic liquids which has been verified to be able to rebuild the structure of ionic liquids effectively and accurately.[5] The atomistic molecular structure and CG model are shown in Fig. 1. The CG strategy was: the nitrate anion was coarse-grained as site D, the aromatic ring of the cation as site A, the methyl group at the end of the alkyl chain as site E, the methylene groups on the alkyl chain and the other methyl group as other CG sites. For convenience, the ionic liquid systems are denoted by C_n, where n is the number of carbon groups on the alkyl side chain. Larger n corresponds to stronger VDW interactions from tail groups.

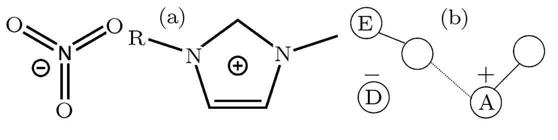

Fig. 1 (a) Atomistic molecular structure of $\mathrm{XMIM}^+/\mathrm{NO}_3^-$ ionic liquids containing a nitrate anion (left) and an imidazole-based cation (right). (b) Coarse-grained model of $\mathrm{XMIM}^+/\mathrm{NO}_3^-$.

The previous nonequilibrium CG MD simulations[18] for C_{12} indicated that, with increasing external electric field strength E, due to the effective overpowering of the electrostatic interactions between the polar cationic head groups and anions by the external electric field, the ionic liquid structure is disordered from spatially heterogeneous ($E \sim 0$–10^8 N/C) to spatially homogeneous ($E \sim 10^9$ N/C), and is then reordered to nematic-like ($E \sim 10^{10}$ N/C). However, it is unclear how the electrostatic and VDW interactions involve in that structural change. In this work, the same simulation procedure was applied to ionic liquid systems with various side chain lengths, so that the electrostatic interactions can be effectively canceled out by the external electric field and the influence of VDW interactions becomes observable. An equilibrated configuration of the C_n ($n = 2$, 6, 8, 10, or 12) system with 512 ion pairs was taken from the previous CG MD simulations.[5] With a static external electric field E applied to the X direction of the system, a nonequilibrium constant NPT CG MD simulation was first performed by using the DL_POLY program[19] at $T = 400$ K and $P = 1$ atm for 10^6 steps with a time step of 4 fs to allow the system to reach its steady state. With the average system size determined from this NPT run, a constant NVT production run at $T = 400$ K was performed for 10^6 steps. A total of 1000 configurations were evenly sampled during the production run. Although the C_4 system was not studied in this work due to the lack of its EF-CG model,[5] our conclusions should not be varied by the results of the C_4 system.

3 Results and Discussions

The change of the spatial heterogeneity in ionic liquids with respect to the strength of an external electric field was quantified by the reduced heterogeneity order parameter (HOP).[20] For a given configuration in this study, the HOP is defined for CG sites E as

$$\hat{h} = \frac{1}{N_{\rm s}} \sum_{i=1}^{N_{\rm s}} \sum_{j=1}^{N_{\rm s}} \exp(-r_{ij}^2/2\sigma^2), \tag{1}$$

where r_{ij} is the distance between sites i and j corrected with the periodic boundary conditions, and $\sigma = L/N_{\rm s}^{1/3}$ with L the side length of the cubic simulation box and $N_{\rm s}$ the total number of sites. The HOP value can be shifted to have a reduced HOP $h = \hat{h} - \hat{h}_0$, where $\hat{h}_0$ is the HOP for an ideally homogeneous system with $N_{\rm s}$ sites. The reduced HOP takes a value around 0 when the system is close to being homogeneous, and a larger value when the site distribution is more heterogeneous.

The average reduced HOPs for the tail groups (CG sites E) are plotted in Fig. 2(a). In the heterogeneous region, longer side-chain systems have larger HOP values, indicating stronger tail aggregation. Nevertheless, for all systems, the degree of the system spatial heterogeneity keeps almost no change up to $E \approx 10^8$ N/C, then significantly drops down until about 10^9 N/C. The spatial heterogeneity is almost non-detectable at 10^{10} N/C, as indicated by the zero values of all reduced HOPs. Unlike the longer-chain systems, the reduced HOP of C_2 remains a small value, indicating that the C_2 system is much more homogeneous because the side chains are too short to aggregate. For longer-chain systems, in spite of the difference in the strength of the VDW interactions given by side chains with different lengths, the tail groups in all systems disperse at the same external field strength, when the collective electrostatic interactions between cationic head groups and anions are effectively overpowered. This indicates that the electrostatic interactions are the major cause of the tail aggregation and that the VDW interactions have negligible influences to the global structure of ionic liquids.

The degree of cationic alignment along the X direction is quantified by the average of the second Legendre polynomials

$$S = \langle P_2(\cos\theta) \rangle = \langle (3\cos^2\theta - 1)/2 \rangle, \tag{2}$$

where θ is the angle between the X axis and the vector connecting CG sites A and E in the same molecule. The average second Legendre polynomials S with respect to the strength of the external electric field are plotted in Fig. 2(b). In the heterogeneous region, all systems roughly take an S value close to zero, showing no orientational asymmetry of cations. The non-vanishing S value of C_{12} might be attributed to the finite-size effect of the relatively small simulation box with respect to the long side chain of C_{12}. In the homogeneous region, the S value is larger for a longer-chain system, because a cation with a longer side chain exhibits a smaller tilt angle, given the same vertical fluctuation distance. In the narrow transition region from homogeneous to netmatic-like around $E \approx 5 \times 10^9$ N/C, the above trend reverses because the stronger VDW interactions of cations in a longer-chain system make the cations more difficult to line up along the direction of the external electric field. In the nematic-like region, except C_2, S almost reaches its highest value of 1, indicating highly ordered alignment of cations along the X direction. The cationic side chains of C_2 are so short that its directional fluctuations of cations are hardly eliminated by the external electric field. Correspondingly, its S value, although significantly increases at $E = 3 \times 10^9$ N/C, can only reach an average value between 0.3 and 0.4 in the nematic-like region. The difference of cationic alignment demonstrates that the local structure of ionic liquids is sensitive to the strength of the VDW interactions.

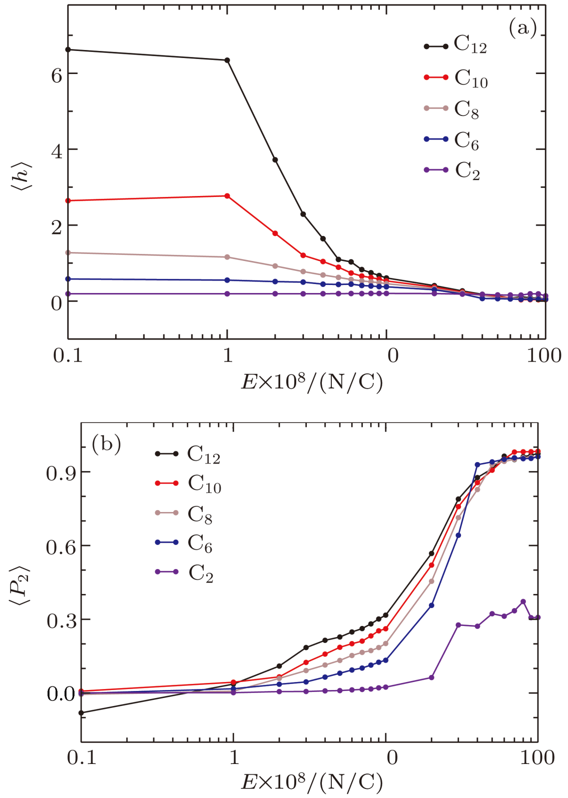

Fig. 2 (a) Average reduced heterogeneity order parameters of the cationic tail groups (CG sites E) vs. external electric field. (b) Average second Legendre polynomials quantifying the cationic orientation with respect to the direction of the external electric field.

Structural change is generally associated with dynamical change. To exclude ionic drifting driven by the electric field, the two-dimensional self-diffusion constants of cations perpendicular to the external electric field are calculated and plotted in Fig. 3(a). They have little change in the heterogeneous region, but drastically increase in the homogeneous region and are greatly suppressed in the nematic-like region. Compared to the longer-chain systems, the overall change of C_2 shifts to smaller E values, since very little VDW interactions between the cationic tail groups allow the ions of C_2 to be more mobile and more sensitive to the external electric field. For all systems, longer-chain systems diffuse slower at E weaker than the peak values, because in the simple liquid region, stronger collective VDW interactions between cationic tail groups make the liquid system more viscous. On the other hand, at E stronger than the peak values, when the systems change from homogeneous to nematic-like, since stronger tail-group VDW interactions make the ordering more difficult, longer-chain systems diffuse faster, coincident with the structural change in the transition region around $E \approx 5 \times 10^9$ N/C seen in Fig. 2(b). The diffusion results indicate that the VDW interactions have a noticeable influence on dynamic properties of ionic liquids.

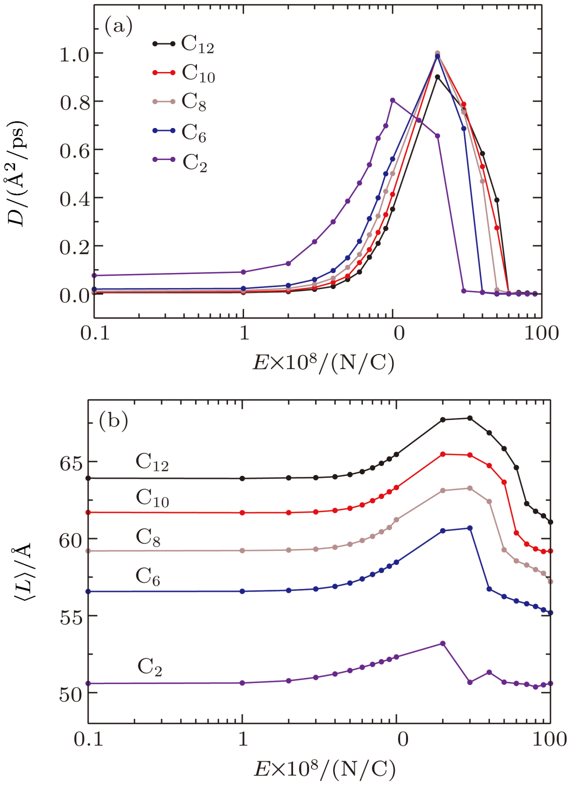

Fig. 3 (a) Two-dimensional self-diffusion constants of cations perpendicular to the external electric field. (b) Average side lengths of the cubic simulation box representing system volume.

The average side lengths of the cubic simulation box representing the system volumes are shown in Fig. 3(b). A longer-chain system has a larger volume due to more atoms on the cationic tails. For each system, the system volume increases very slowly in the spatially heterogeneous region. In the spatially homogeneous region, when the spatial correlation of ions is reduced, the system volume becomes larger. In the nematic-like region, the ionic orientations are ordered along the X direction, so the system volume becomes smaller than the one in the spatially heterogeneous region. This indicates that thermodynamic properties of ionic liquids seem to be insensitive to the difference of the collective VDW interactions between the cationic tail groups.

4 Conclusions

In summary, the roles of electrostatic and VDW interactions in determining the spatial heterogeneity in ionic liquids formed by the aggregation of cationic tail groups are examined with nonequilibrium CG MD simulations. An external electric field is applied to the ionic liquid systems with various side chain lengths. Our simulation results indicate that the electrostatic interactions are the major cause of the tail aggregation. That is, the nonpolar cationic tail groups aggregate mainly due to the steric repulsion from the continuous polar networks formed by anions and cationic head groups. On the other hand, the collective VDW interactions between cationic tail groups have a strong influence on the local structure and dynamical properties of ionic liquids. This understanding advances our knowledge of the importance and special roles of electrostatic and VDW interactions in determining properties of ionic liquids and is anticipated to help better select and design ionic liquids to meet specific requirements of a wide range of applications. Besides, this work and other emerged theoretical studies[18,21] are to enhance our understanding of the behavior of ionic liquids under external forces and help the electrochemical applications[13,22] of ionic liquids.

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