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Disordering and Reordering of Ionic Liquids under an External Electric Field

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The previous study (Wang and Voth, *J. Am. Chem. Soc.* **2005**, 127, 12192) has shown that the nonpolar alkyl cationic tail groups of ionic liquids can aggregate and form nanoscale spatial heterogeneity. To facilitate applications of ionic liquids under nonequilibrium conditions, it is of great interest to see how this spatial heterogeneity of ionic liquids changes when an external electric field is applied. The nonequilibrium molecular dynamics simulations indicate that, when the external electric field strength increases, the ionic liquid structure is first disordered from spatially heterogeneous to spatially homogeneous, and is then reordered to nematic-like. Accordingly, both the ionic self-diffusion and the system volume increase in the spatially homogeneous region and decrease in the nematic-like region. This is understood by the competition between the external electric field and the electrostatic interactions between ions.

In many applications, such as fuel cells,¹ propellants,² and electrowetting,³ ionic liquids work in nonequilibrium states under an external force. Understanding the structural properties of ionic liquids in nonequilibrium states will greatly facilitate those applications.

The previous simulation studies^{4–6} have shown that the nonpolar alkyl cationic tail groups of ionic liquids can aggregate and form nanoscale spatial heterogeneity. It is interesting to see how this spatial heterogeneity changes when an external electric field is applied. In this work, nonequilibrium molecular dynamics (MD) simulations have revealed a disordering and reordering process of structural change of ionic liquids. With increasing field strength, the aggregation of cationic tail domains is attenuated, since the external electric field effectively screens the electrostatic interactions between the polar cationic head groups and anions. At the same time, the ions are more aligned along the direction of the driving electric field. Consequently, the ionic liquid structure is disordered from spatially heterogeneous to spatially homogeneous, and is then reordered to nematic-like. Corresponding to their structural change, self-diffusion as well as system volume of ionic liquids first increases and then decreases with increasing strength of the applied electric field.

The effective force coarse-graining (EF-CG) method⁷ was successfully applied to developing transferable models for XMIM⁺NO₃[−] ionic liquids.⁸ For convenience, the ionic liquid systems are denoted by C_n, where *n* is the number of carbon groups on the alkyl side chain. The atomistic molecular structure of C₁₂ is shown in Figure 1, and its coarse-grained model is shown in Figure 2a: the nitrate anion has been coarse-grained as site D, the aromatic ring of the cation as site A, the methyl group on the end of the alkyl chain as site E, and the methylene groups on the alkyl chain and the other methyl group as other CG sites. An equilibrated configuration of the C₁₂ system with 512 ion pairs was taken from the CG MD simulation reported

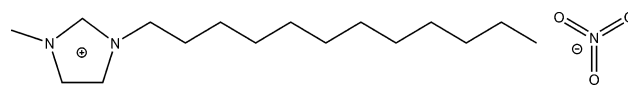


Figure 1. Atomistic molecular structure of C₁₂ containing a nitrate anion (right) and an imidazole-based cation (left) with an alkyl side chain having 12 carbon groups.

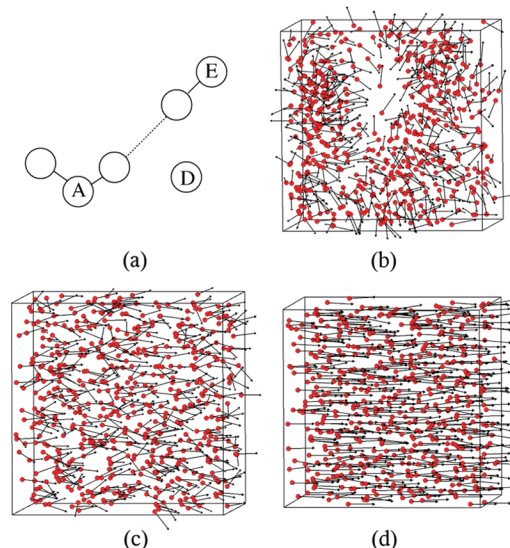


Figure 2. (a) Coarse-grained model of XMIM⁺NO₃[−]. The cationic head group is coarse-grained as CG site A, the cationic tail group as site E, and the anion as site D. (b) Snapshot of C₁₂ under an external electric field of 10⁸ N/C. (c) Snapshot of C₁₂ under an external electric field of 2 × 10⁹ N/C. (d) Snapshot of C₁₂ under an external electric field of 10¹⁰ N/C. In parts b–d, the red spheres represent CG sites E, and each arrow points from site E to site A in the same molecule. The direction of the external electric field is from left to right.

in ref 8. With a static external electric field *E* applied to the *X* direction of this system, a nonequilibrium constant *NPT* CG MD simulation was first performed by using the DL_POLY

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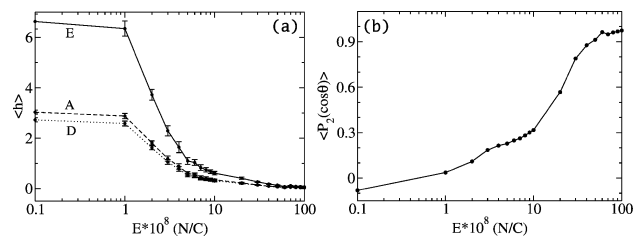


Figure 3. (a) Average reduced heterogeneity order parameters vs external electric field for CG sites A (head), D (anion), and E (tail), respectively. The error bars represent standard deviations. (b) Average second Legendre polynomials quantifying the cationic orientation with respect to the direction of the external electric field.

program⁹ at $T = 400$ K and $P = 1$ atm for 10^7 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.

On the basis of the radial distribution functions shown in Figure 6 of ref 8, the strength of the internal electric field caused by other ions around an ion is estimated to be in the order of 10^9 N/C. As shown in Figure 2b, an applied electric field $E = 10^8$ N/C does not noticeably alter the equilibrium structure of the ionic liquid. The cationic tail groups (red spheres) still aggregate and form separate tail domains, while the cationic head groups (arrow heads) form a continuous polar network. This “spatially heterogeneous region” exists roughly up to $E \approx 10^9$ N/C, when the ionic liquid structure is analogous to the one in equilibrium. With a stronger electric field of 2×10^9 N/C applied (Figure 2c), which is comparable to and effectively screens the electrostatic interactions between the head groups and the anions, the continuous polar network is destroyed and the correlations of ion movements are attenuated. Correspondingly, the tail groups can no longer form separate domains. In this “spatially homogeneous region” ranging from $E \approx 10^9$ to 6×10^9 N/C, the ionic liquid structure resembles the structure of a simple liquid. With an electric field as strong as 10^{10} N/C applied (Figure 2d), the ions are forced by the dominating external field to line up along the *X* direction, forming a nematic-like liquid crystal structure.

The change of the spatial heterogeneity of ionic liquids with respect to the strength of an external electric field was quantified by the reduced heterogeneity order parameter (HOP).¹⁰ As plotted in Figure 3a, the degree of the system spatial heterogeneity keeps almost no change up to $E \approx 10^8$ N/C and then drastically drops down until about 10^9 N/C. The spatial heterogeneity is almost nondetectable at 10^{10} N/C, as indicated by the zero values of all reduced HOPs.

The degree of cationic alignment along the *X* direction is quantified by the average of the second Legendre polynomial $\langle P_2(\cos \theta) \rangle = (3 \cos^2 \theta - 1)/2$, 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 with respect to the external electric field, as plotted in Figure 3b, indicate that the cationic alignment along the *X* direction increases monotonically with the applied electric field. The increase becomes more rapid in the spatially homogeneous region from $E \approx 10^9$ to 6×10^9 N/C.

The two-dimensional self-diffusion constants of ions perpendicular to the external electric field are calculated and plotted in Figure 4a. Because diffusion is accelerated this coarse-grained system, this plot only provides qualitative information without numerical accuracy. In the spatially

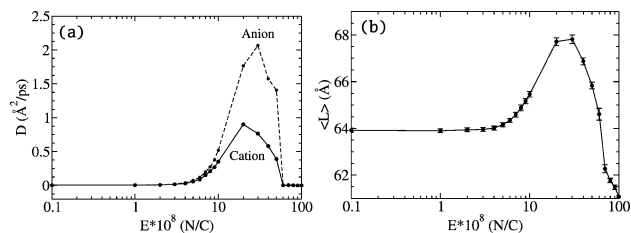


Figure 4. (a) Two-dimensional self-diffusion constants of cations and anions perpendicular to the external electric field. (b) Average side lengths of the cubic simulation box representing the system volume.

heterogeneous region, the diffusion is slow due to the strong collective ionic interactions. In the spatially homogeneous region, because the electrostatic interactions between ions are effectively screened by the external electric field, both cations and anions diffuse much faster. When the external electric field is larger than 6×10^9 N/C, the ions are more constrained to move along the *X* direction, so the diffusion perpendicular to the *X* direction is greatly suppressed.

The average side lengths of the cubic simulation box representing the system volume are shown in Figure 4b. 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 aligned along the *X* direction, so the system volume becomes smaller than the one in the spatially heterogeneous region.

In summary, with increasing external electric field, the ionic liquid structure changes from spatially heterogeneous to spatially homogeneous, and then to nematic-like. An electric field weaker than 10^9 N/C does not noticeably alter the equilibrium structure, and the cationic tail groups still aggregate to form separate domains. The dynamic and thermodynamic properties are analogous to those in equilibrium. When the external electric field is comparable to the electrostatic interactions between cationic head groups and anions (10^9 to 6×10^9 N/C), the electrostatic interactions between ions are effectively screened, and the system resembles a simple liquid with more freely moved ions and a larger system volume. With an even stronger electric field applied, the external field dominates the electrostatic interactions between ions, so the ions are aligned along the direction of the applied electric field. The nematic-like system diffuses very slowly with a smaller system volume than the one in equilibrium. This work forms a basis for further theoretical work of ionic liquids in nonequilibrium states. It also provides a theoretical framework for the experimental investigations and the applications of ionic liquids under external driving fields.

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