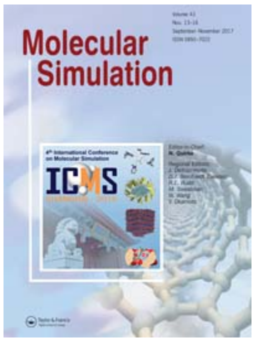

Molecular Simulation

ISSN: 0892-7022 (Print) 1029-0435 (Online) Journal homepage: http://www.tandfonline.com/loi/gmos20

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To cite this article: Rui Shi & Yanting Wang (2017) Surface structure of ionic liquids under an external electric field, Molecular Simulation, 43:13-16, 1295-1299, DOI: 10.1080/08927022.2017.1332412

To link to this article: http://dx.doi.org/10.1080/08927022.2017.1332412

MOLECULAR SIMULATION, 2017
VOL. 43, NOS. 13–16, 1295–1299
https://doi.org/10.1080/08927022.2017.1332412

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Surface structure of ionic liquids under an external electric field

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ABSTRACT

Surface structure and properties play an important role in many applications of ionic liquids (ILs). ILs can form unique surface structures that are very different from the bulk. In imidazolium-based ILs, for example, polar groups form ordered layer structure, while cationic alkyl chains are bundled together and point out from the surface. In many applications, ILs work under an external electric field. However, the effect of external electric field on the surface structure of ILs is still not clear. Here by using coarse-grained molecular dynamics simulation, we found that an electric field as strong as 1 V/nm is required to alter the surface structure of 1-dodecyl-3-methylimidazolium nitrate. Under a strong external electric field, layered structure disappears, and instead a sparser, more homogeneous and less orientationally ordered surface develops.

ARTICLE HISTORY
Received 13 February 2017
Accepted 13 May 2017

KEYWORDS
Ionic liquids; surface; molecular dynamics simulation; electric field

1. Introduction

Room temperature ionic liquids, briefly known as ionic liquids (ILs), are usually liquids at room temperature that consist solely of ions. Because of their unique physical and chemical properties, ILs have attracted widespread interest in both academia and industry [1,2]. Beside the bulk properties, surface (interface) structure of ILs plays a crucial role in many applications, such as multiphase catalytic reactions [3] and electrolytes [4]. Surface structure not only determines the wetting behaviour of ILs, but also directly participate in many catalysis and energy storage processes. At a small scale, in particular working with nanomaterials, ILs show much larger surface area than in macroscopic phase and as a result their performance can be significantly affected by the surface structure.

Due to the break of symmetry at the interface, ILs can form unique surface structures that are very different from the bulk. Both experiments [5–7] and simulations [8–10] have shown that ILs can form layered structures extending into the bulk by several nanometers with cationic alkyl chains bundled together and pointing away from the surface. In many applications, ILs work under external electric fields, such as lithium battery [11], fuel cells [12] and supercapacitors [13]. Although it has been extensively studied how an electric field changes the bulk structure of ILs [14–17], its influence to the surface structure of ILs is still unclear. In this paper, by using coarse-grained (CG) molecular dynamics simulation, we studied the effect of a static electric field on the surface structure of an IL prototype, 1-dodecyl-3-methylimidazolium nitrate ($[C_{12}mim][NO_3]$) and showed that an electric field as strong as 1 V/nm is required to tune its surface structure. Under a strong external electric field, ordered layer structure breaks, and instead a sparser, more homogeneous and less orientationally ordered structure develops at the IL surface. The knowledge of the effect of electric field on the surface structure may provide useful infromation for efficiently tuning the surface morphology and properties of ILs, and thus further improve the performance of ILs in many applications.

2. Computational methods

The effective force coarse-graining (EF-CG) method [18,19] has been successfully applied to modelling 1-alkyl-3-methylimidazolium nitrate ILs. In this study, the surface structure of 1-dodecyl-3-methylimidazolium nitrate was investigated. One $[C_{12}mim][NO_3]$ ion pair was coarse-grained into 15 CG sites, as shown in Figure 1. The imidazolium ring was coarse-grained into site A, the methyl head group site B, the methyl tail site T, the methylene group connected to the imidazolium ring site M, the nitrate site D, and others site C.

The total potential energy of the EF-CG model is described by

$$V = V_b + V_{nb}, \tag{1}$$

where the bonded interactions are given by

$$V_b = \sum_{\text{bonds}} k_b (r - r_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} [A_1(1 + \cos(\phi)) + A_2(1 - \cos(2\phi)) + A_3(1 + \cos(3\phi))], \tag{2}$$

The non-bonded interactions V_{nb} include Coulomb and effective van der Waals (VDW) potentials. The former is characterized by the point partial charges on the CG sites and the latter is defined by tabulated arrays generated by utilizing the EF-CG methodology. The details of the EF-CG model for $[C_{12}mim][NO_3]$ can be found in ref [18].

Molecular dynamics simulations were performed by using the DL_POLY package [20] to study the surface structure of

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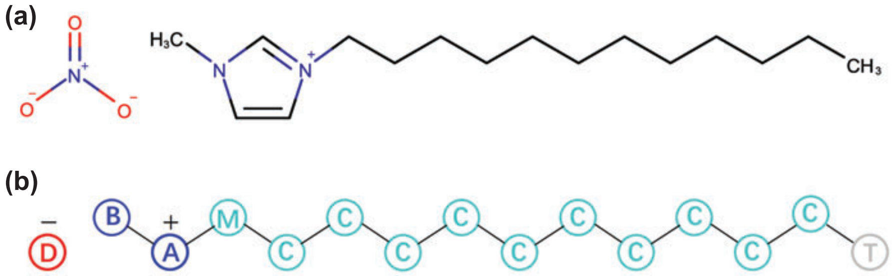

Figure 1. (Colour online) (a) Atomistic molecular structure and (b) coarse-grained model of $[C_{12}mim][NO_3]$.

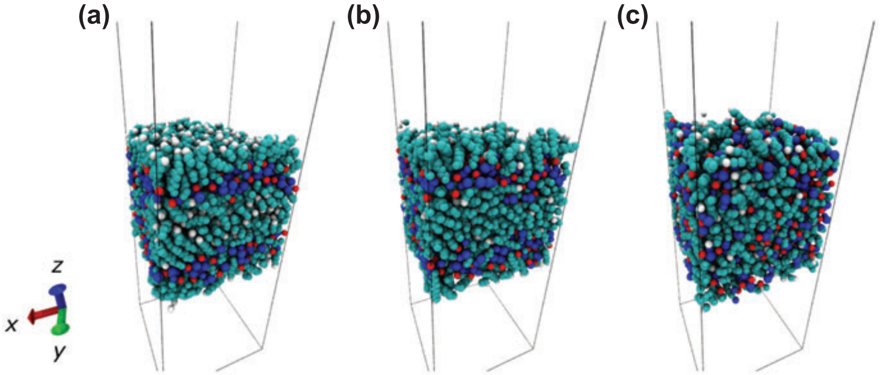

Figure 2. (Colour online) Snapshots of $[C_{12}mim][NO_3]$ surface under an external electric field of (a) 0, (b) 0.1, and (c) 1.0 V/nm. In (a–c) blue spheres represent cationic head groups A and B, white spheres are methyl tail T, red ones are nitrate D, and cyan spheres represent other groups.

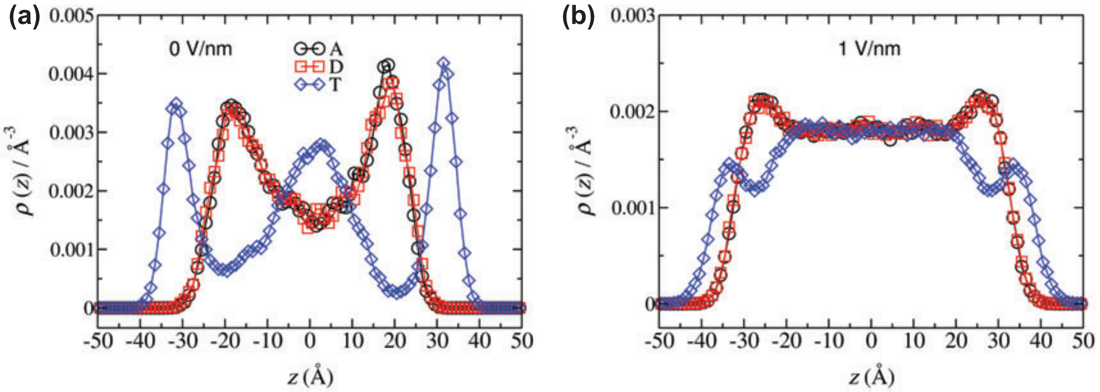

Figure 3. (Colour online) Number density of groups A, D and T along the z-axis under an external electric field of (a) 0 and (b) 1.0 V/nm.

$[C_{12}mim][NO_3]$. An equilibrated configuration containing 512 $[C_{12}mim][NO_3]$ ion pairs in a $64 \times 64 \times 64$ Å^3 cubic box was taken as the initial configuration. Two IL/vapour interfaces were generated by elongating the z axis of the simulation box to 192 Å (see Figure 2). Simulations were carried out in the *NVT* ensemble and the Nosé-Hoover thermostat was employed to stabilize the temperature at 400 K. A cutoff of 14 Å was applied for van der Waals and Coulomb interactions in the real space. The original Ewald sum method [21] was empolyed to treat the long-range Coulomb interactions. Since the EF-CG model of the IL not only accelerates the dynamics of the system, but also effectively enhances the sampling in the phase space, a 2-ns simulation time has been found to be long enough to equilibrate or sample the system.[10] After applying an electric field E along the z-axis, the system was equilibrated for 2 ns and then followed by another 2-ns production run with a timestep of 4 fs.

In our previous work [17] on the effect of an electric field on the bulk structure of ILs, we found that at $E < 0.1$ V/nm, there were almost no detectable structural changes; at $E = 1.0$ V/nm, obvious structural changes were observed; at 0.1 V/nm $< E <$ 1.0 V/nm, only small and gradual structural changes can be seen, due to the gradually enhanced competition between internal and external electric fields. The same mechanism can also be applied to IL surfaces. Two field strengths of 0.1 and 1.0 V/nm were chosen in this work to study the structural change of IL surface under an external electric field. Other field strengths in between are expected to induce detectable but qualitatively similar structural changes and therefore not demonstrated in this work.

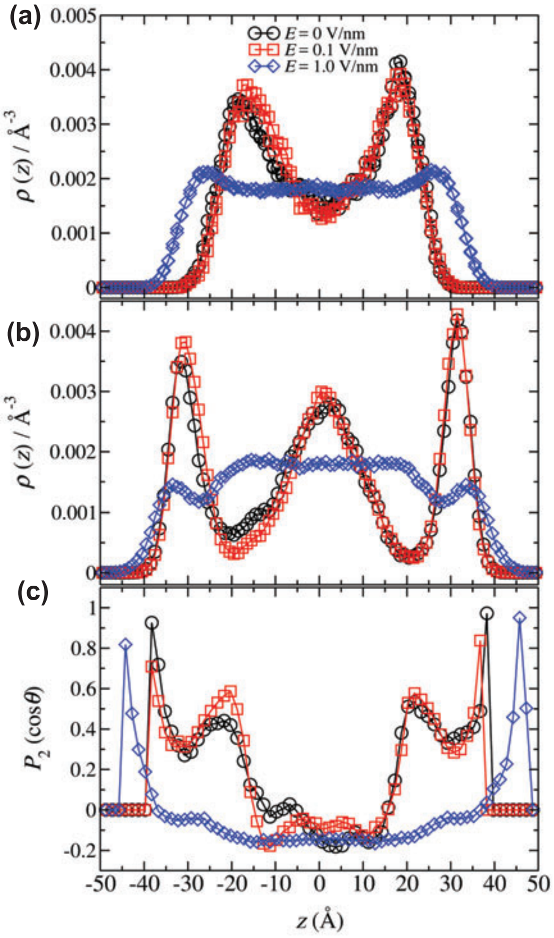

Figure 4. (Colour online) Number densities of (a) cationic head group A and anion D, and (b) cationic tail group T along z axis at different field strengths. In panel (a) the number densities of cationic head groups A (solid line) and D (broken line) are almost overlapped. (c) Orientational order of alkyl chains along z axis at different field strengths.

3. Results and discussion

A snapshot of [C_{12}mim][NO_3] surface structure in absence of an electric field from our simulations is shown in Figure 2(a). We can clearly see that the polar cationic head group A and anion D stay close to each other and form two layers underneath the surface which is almost fully covered by the cationic alkyl chains, in aggrement with previous experimental [5–7] and simulation [8–10] results. Figure 2(b) shows the surface structure of [C_{12}mim][NO_3] under an external electric field of 0.1 V/nm. It can be seen that the surface structure nearly keeps the same features with that in absence of an electric field, indicating that an electric field of 0.1 V/nm may not be able to change the surface structure of [C_{12}mim][NO_3]. When we increase the applied electric field to 1.0 V/nm, the surface layers are totally destroyed by the applied field and the system exhibits a more homogenous surface, as shown in Figure 2(c).

In order to study quantitatively the effect of an external electric field on the surface structure of [C_{12}mim][NO_3], we calculated the number density of different groups along the z-axis (field direction). Figure 3(a) shows the number density of group A (circle), D (square) and T (diamond) in absence of an electric field with $z = 0$ defined as the middle of the simulation box. We note that the cationic head group A takes a positive partial charge, anion D has a negative partial charge and tail group T is charge neutral. In consistence with the snapshot shown in Figure 2(a), we can clearly see a double-layer structure formed by cationic head group A and anion D (two peaks at $z \approx \pm 20$ Å). Groups A and D stay close to each other due to their strong Coulomb attractions, so the number density profiles of A and D are almost identical. It is worth noting that cationic head group A and anion D form continuous polar network, instead of seperated layers, as indicated by the considerable density profile between two peaks. The density profile of cationic tail group T at $E = 0$ also confirms our observation in Figure 2(a) that the cationic alkyl chains either expose to the vacuum on the surface or fill the space between polar layers in the bulk.

In Figure 2(c), we have already shown that an external electric field of $E = 1$ V/nm can totally destroy the surface structure of [C_{12}mim][NO_3], which is confirmed in Figure 3(b). At $E = 1$ V/nm, the large oscillation of density along the z-axis almost disappears. Instead cationic head group A, tail group T and anion D all show homogeneous distribution from $z = -20$ to 20 Å. Polar groups A and D sightly accumulate at the surface and exhibit higher density than the bulk, due to the pulling of charge groups to the surface by the applied field. At $z \approx \pm - 35$ Å, tail group T shows small peaks, suggesting that some alkyl chains still keep pointing out of the surface, but with a much smaller density, compared to that at $E = 0$.

We have shown in Figure 2 that the surface layer structure survives at $E = 0.1$ V/nm. In order to further understand the effect of field strength on the surface structure of ILs, we compare the number density of polar groups A and D in Figure 4(a) and nonpolar group T in Figure 4(b) at different field strengths. Clearly, a moderate electric field of $E = 0.1$ V/nm turns out to be too weak to change the surface structure of [C_{12}mim][NO_3]. Since the intrinsic electric field in imidazolium-based ILs is in the order of 1 V/nm [22], an external field of $E = 1$ V/nm is needed to overpower the intrinsic field and thus alter the surface structure of ILs. At $E = 1$ V/nm, all groups A, D and T show wider density distributions than those in absence of an external electric field, indicative of a reduced density under the strong field, which can also be explained by the pulling effect of the applied field.

Finally, we compare the orientational order of the cationic alkyl chain along the z-axis at different field strengths in Figure 4(c). The orientational order parameter P_2 is defined as

$$P_2\left(\cos\theta\right) = \left\langle \frac{1}{2}\left(3\cos^2\theta - 1\right)\right\rangle, \tag{3}$$

where θ is the angle between the z-axis and the vector connecting CG sites M and T in the same molecule. P_2 quantifies the orientational order of the alkyl chain. $P_2 = 1$ indicates perfect alignment along the z-axis, whereas $P_2 = 0$ infers a totally random orientation. Figure 4(c) shows that at $E \leq 0.1$ V/nm, the alkyl chain has a high orientational order near the surface, while keeps a random orientation in the bulk. Moreover, the similar distributions of P_2 at $E = 0$ and 0.1 V/nm confirm again that a moderate electric field of 0.1 V/nm is too weak to change either the layered structure or the alkyl chain orientation. However, under a strong field of $E = 1$ V/nm, along with the breakdown of the surface layer structure, the alkyl chain loses its orientational order, and only a few chains on the outmost surface still keep a high orientational order, in consistence with our observation in Figure 2(c).

Because of their dual organic and ionic nature [23], ILs can form unique bulk stuctures, from nanoscale tail aggregation [24,25] to ionic liquid crystal [26], as a result of the competition between Coulomb and van der Waals interactions [15,26]. Similarly, the formation of the layered structure on IL surface can also be understood by the interplay of Coulomb and van der Waals interactions on the surface. Charged groups A and D tend to stay underneath, rather than to expose above the interface, in order to reduce the surface energy, due to their strong Coulomb attractions. As a result, polar groups form a continuous layered structure underneath the nonpolar alkyl chains. On the other hand, the alkyl chains are bundled together by the van der Waals force and point out of the IL surface, showing a high orientational order. When an external electric field becomes strong enough to compete with the intrinsic field in the order of 1 V/nm [22], the layered structure can be destroyed and instead a sparser, more homogeneous and less orientationally ordered surface develops.

4. Conclusions

In this article, we studied the effect of a static external electric field on the surface structure of 1-dodecyl-3-methylimidazolium nitrate by using coarse-grained molecular dynamics simulation. An electric field as strong as 1 V/nm is required to alter the IL surface, from an ordered layered structure with cationic alkyl chains pointing out of the surface to a sparser, more homogeneous and less orientationally ordered one. This finding advances our understanding of IL surface structures under an external electric field and may help to improve the performance of ILs in many applications.

Acknowledgements

YW also thanks the financial support through the CAS Interdisciplinary Innovation Team Project. The computations of this work were conducted on the HPC cluster of ITP-CAS.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This study was supported by the National Basic Research Program of China [973 program, grant number 2013CB932804]; National Natural Science Foundation of China [grant number 11421063].

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