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Poly(a)morphic portrait of the electrical double layer in ionic liquids

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ABSTRACT

In this paper we present a unified view on charge-driven structural transitions in the electrical double layer in ionic liquids and summarise molecular-scale mechanisms of the ionic liquid structural response to the surface charge.

1. Introduction

Charge/voltage driven structural transitions in the electrical double layer (EDL) in ionic liquids (ILs) have recently attracted large interest in experimental [1–6], theoretical [7] and computational [8–14] communities due to the importance of this subject for a variety of IL applications [15,16].

Bazant et al. [7] suggested that general trends in structural transitions in ILs upon surface charging are determined by the crossover between the over-screening and the crowding regime in the EDL structure. In a recent modelling work [11] it was shown that this crossover corresponds to a structural transition from a multilayer (intermediate charges) to an overcrowded structure (high charges; superposition of two or more counter-ion layers) through the formation of a monolayer structure at a certain charge density value. Recently in Ref. [14] it has been suggested that these trends may be universal and are expected to be found in many IL systems (see also [17]). However, this hypothesis is based on theories and models that do not take into account molecular-scale effects of ion geometry and heterogeneous partial charge distribution across the IL molecules, and overall it remains unclear whether the conclusions from the Refs. [7,11,14] are not effects of an oversimplified view on ILs.

Here we make the next step towards rationalising general mechanisms of charge-driven interfacial structural transitions in ILs by investigating and comparing structural behaviour of three different coarse-grained IL models [18,19,11] with the behaviour of a fully atomistic model of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]) [20].

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2. Methods

2.1. Simulations

All simulations were performed using the classical Molecular Dynamics (MD) method in the *NVT* ensemble at a temperature of 350 K with the Gromacs 4.5.5 software [21]. The simulation setups (equilibration, length of simulations, system parameters and computational methods) were overall the same to the ones used in our previous works: Ref. [20] (fully atomistic model of [BMIm][BF_4]) and Refs. [11] (coarse-grained models).

2.1.1. Coarse-grained simulations

The models represented IL ions as charged Lennard-Jones spheres [18,11]. Three different models of IL were chosen, with the cation-to-anion diameter (d_{LJ}) ratios of 1 : 1 (large anion – LA), 1 : 0.8 (medium anion – MA) and 1 : 0.5 (small anion – SA) with constant d_{LJ} (Cation) = 1.0 nm.

The simulated systems represent IL ions confined between two model electrodes [18,19,11]. The electrodes consist of 2500 Lennard-Jones spheres with a diameter (d_{LJ}) of 0.22 nm that are arranged on a square lattice with a size of 11 nm × 11 nm, in *x* and *y* directions. The distance between the electrodes was chosen to be 54 nm, 36 nm and 24 nm for the LA, MA and SA systems, respectively. The ion pair number was fixed in all simulations to be equal 1050.

2.1.2. Fully atomistic simulations

The system consisted of two rigid graphene slabs with dimensions of 3.408 nm by 3.4433 nm separated by a distance of 10.4 nm. 374 [BMIm][BF_4] ion pairs were placed between these surfaces and equilibrated. The OPLS-AA force field was used together with partial charges taken

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from Ref. [22] for the IL. The charges were screened by a factor of 0.79 to account for electronic polarisability [20].

2.2. Analysis

As in Refs. [11,14], we define a unified κ -scale, where the surface charge density (σ) is normalised by the maximum charge density that can be stored in a densely packed counter-ion monolayer ($\theta_{\text{Ion}}^{\text{max}}$):

$$\kappa_{\text{Ion}} = \left|\frac{\sigma}{\theta_{\text{Ion}}^{\text{max}}}\right|. \tag{1}$$

Below we use the κ-scale for generalised analysis with a focus on the regions $0 < \kappa_{\text{Anion}} < 1$ and $0 < \kappa_{\text{Cation}} < 2$, where κ_{Cation} corresponds to the negative surface charge density values ($\sigma < 0$) and κ_{Anion} corresponds to the positive values ($\sigma > 0$).

Because the monolayer structure is characterised by smearing of oscillations in the electrostatic potential $\phi(z)$ -profiles [11,14], the value of ($\theta_{\text{Ion}}^{\text{max}}$) was extracted from the simulation results at the point of surface charge that corresponds to a linear potential drop. The potential drop at $\kappa_{\text{Ion}} = 1$ can be roughly approximated as:

$$\phi_{\text{ML}} = \frac{d}{\epsilon}\theta_{\text{Ion}}^{\text{max}}, \tag{2}$$

where $\theta_{\text{Ion}}^{\text{max}} \approx e\frac{q_{\text{Ion}}}{r_{\text{Ion}}^2}$, d is the distance between the surface and the monolayer charge planes, r_{Ion} is ionic radius, q_{Ion} is ionic charge, e is elementary charge, and ϵ is permittivity of the monolayer structure. $\theta_{\text{Ion}}^{\text{max}}$ was found to be the same for all three coarse grain-systems ($+16\ \mu\text{C/cm}^2$) in accordance with the fact that the cation model is the same in all systems. This value equals to the density of one cation per 1 nm^2 of the surface that corresponds to the dense coverage of the surface by the cations. $\theta_{\text{Anion}}^{\text{max}}$ values were found to be -68, -26 and $-16\ \mu\text{C/cm}^2$ for the systems with small, medium and large anions, respectively. These values also correspond to the dense coverage of the surface by the anions. For the atomistic model of [BMIm][BF_4], $\theta_{\text{Anion}}^{\text{max}}$ is $-100\ \mu\text{C/cm}^2$, $\theta_{\text{Cation}}^{\text{max}}$ is $+\ 38\ \mu\text{C/cm}^2$.

The restructuring process at different charge densities can be illustrated with the use of parameter λ that for an i-th ion layer at surface is defined as the normalised excess of charge in this layer [14]:

$$\lambda_i = \kappa_{\text{Ion}} \times \left(\left|\frac{\text{cn}_Q(z_i)}{\sigma}\right| - 1\right), \tag{3}$$

where z_i corresponds to an extremum or to a step height on the normalized cumulative charge density profiles ($-\text{cn}_Q(z)/\sigma$-profiles) in the i-th interval between the two successive interception points $|\text{cn}_Q(z)/\sigma| = 0$. In the analysis below we consider only the λ parameter of the first ion layer (λ_1), therefore the index i is omitted.

The κ_{Ion} –scale represents a universal analogue of dimensionless "reaction coordinate" for the EDL restructuring process in response to the surface charge. Analysis of the dependence of λ on κ_{Ion} allows to study the evolution of the EDL structure in terms of the charge excess. Namely, an increase of the charge excess in the first interfacial layer (λ_1) manifests formation of a multilayer EDL structure, while the decrease of the charge excess indicates the vanishing of the multilayer EDL structure towards the formation of the monolayer structure at $\kappa_{\text{Ion}} = 1$.

3. Results

Fig. 1 presents the dependency of the IL ion number density ρ_N from the distance to the electrode z and κ_{Ion} in the form of $\rho_N(z,\kappa)$ contour maps. These maps illustrate charge-dependent layering of cation (light, red) and anion (dark, blue) for the coarse-grained (left, MA) and the atomistic (right) model IL systems.

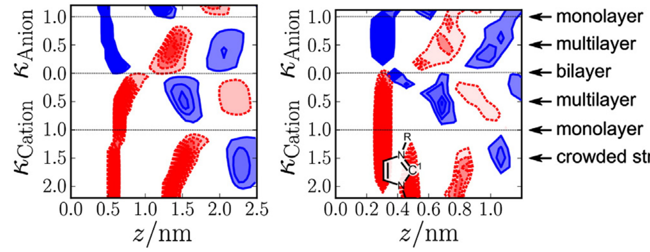

Fig. 1. The figure presents the ion number density $\rho_N(z,\kappa)$ contour maps that illustrate charge-dependent layering of cation (light, red) and anion (dark, blue) for the MA (left) and the [BMIm][BF_4] (right) models.The contour interval equals to ρ_{bulk}, the first contour starts at 1.5 ρ_{bulk} (MA) and 2.5 ρ_{bulk} ([BMIm][BF_4]), and the $\rho_N(z,\kappa)$ peaks are cut at $7\rho_{\text{bulk}}$ to facilitate the visual analysis. For [BMIm][BF_4] the positions of the IL anions and cations are assigned to the centres of C^1 and B atoms respectively; the picture of [BMIm]$^+$ indicates that the lamination of the $\rho_N(z$, Cation) at large κ_{Cation} values is due to the presence of parallel and perpendicular (shown) orientation of the aromatic ring in the first cationic layer at high surface charges.

Although the compared IL models are quite different from each other, in both cases the contour maps reveal similar features of the IL structural response to the surface charge that are described below.

As can be seen, the vertical ridges of high ion number density divide the interfacial region into distinct regions of ion accumulation. We refer to the region of counter-ions accumulation closest to the electrode, as the *first* layer. Counter-ions $\rho_N(z,\kappa)$ in the first layer grows upon surface charging while counter-ions become pressed against the surface due to the strong electrostatic attraction. Differently, in the subsequent layer the $\rho_N(z,\kappa)$ grows until some saturation at $\kappa_{\text{Ion}} \approx 0.5$ and then decreases until $\kappa_{\text{Ion}} = 1.0$. The dotted horizontal lines point to the areas of practical absence of layering around $\kappa_{\text{Ion}} = 1.0$ (Fig. 1).

To facilitate comparison of *different* IL systems, in Fig. 2, we plot λ versus κ_{Ion} for cationic and anionic layers. As can be seen, the evolution of the EDL structure upon surface charging is qualitatively the same for all coarse-grained and atomistic models. This implies that the main mechanisms of ion accumulation at the surface are governed mostly by electrostatic interactions and sterical effects. Yet, despite of the apparent *general* similarity seen in Figs. 1 and 2, there is a lamination of the $\rho_N(z$, Cation) at large κ_{Cation} due to the presence of both parallel and perpendicular orientation of the [BMIm]$^+$ ring in the first cationic layer.

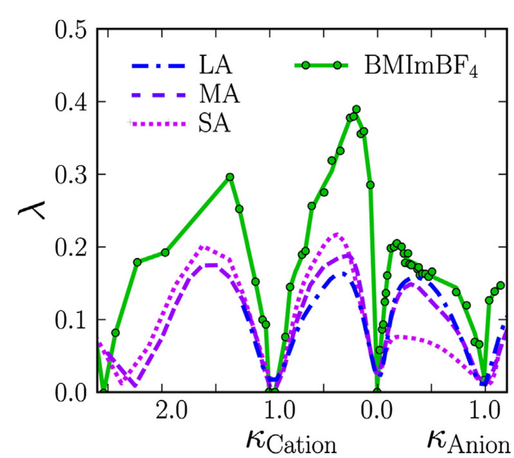

Fig. 2. Variation of the normalised charge excess in the first interfacial layer (λ) with κ_{Ion} for the four model ILs studied in this work. The figure illustrates the overall similarity of the charge-induced EDL restructuring in these *different* model ILs. The κ_{Ion} values of 1.0 correspond to the $\theta_{\text{Ion}}^{\text{max}}$ values of the charge density σ. λ minimum at $\kappa_{\text{Cation}} \approx 2.3$ indicates the formation of a crowded layer of cations which accommodates more counter-ions that is expected from a superposition of two dense monolayers; that happens due to the squeezing and reorientation of the cations in the strong electric field at these high charges.