Room-Temperature Ionic Liquids: Excluded Volume and Ion Polarizability Effects in the Electrical Double-Layer Structure and Capacitance

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We study structures of room-temperature ionic liquids at electrified interfaces and the corresponding electrical double-layer capacities using a self-consistent mean-field theory. Ionic liquids are modeled as segmented dendrimers and the effective dielectric constant is calculated from the local distribution of ions to accommodate the excluded volume and the local dielectric screening effects. The resulting camel-shaped capacitance curve is further analyzed in terms of the thickness of alternating layers and the polarization of ions at electrified interfaces.

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Room-temperature ionic liquids are typically composed of bulky cations and anions of unequal size. Recent studies suggest that ionic liquids form alternating layers at air-liquid surfaces and at charged interfaces [1]. At a charged interface the coion and counterion self-order in alternating layers and the overall thickness of layers depends on the electrostatic potential of the electrode. The typical size of each layer is of the order of a molecular length, generating a large electrostatic potential field. It is intriguing that the average density or the "envelope" of alternating layers of ionic liquids bear a strong resemblance to the electrical double-layer (EDL) structure commonly found in aqueous electrolytes, i.e., a compact (Stern) layer of counterions and specifically adsorbed ions, and a diffuse layer further towards the bulk [2]. Although studies of the EDL in aqueous electrolyte solutions are numerous, similar studies in ionic liquids have only recently been undertaken [1]. Some modelling studies of the interfacial structure of ionic liquids have been carried out at a molecular level by implementing molecular dynamics simulations [3,4]. Recent analytical predictions on the EDL structure based on mean-field approximations have been developed by solving the Poisson-Fermi equation with or without applying compressibility constraint on ions [5,6]. However, despite these advances, our understanding of the structure of ionic liquids at electrified interfaces is far from complete. Among the most exciting experimental result that needs further studies is the differential capacitance curve of an ionic liquid system which reaches a maximum around the point of zero charge (PZC)—the opposite behavior to that seen in an aqueous electrolyte solution [7]. Here, we study the EDL capacitance in ionic liquids based on a detailed molecular model of ionic liquids and a novel use of local (effective) dielectric constant of ionic liquids in our model system.

In general, the EDL capacitance reflects the extent to which the electrostatic potential at the interface is screened by the ions that accumulate there. A better screening is reflected by a higher capacitance value. This parameter provides valuable information about the thickness of the EDL and the composition and polarization of ions at the interface. However, explaining the shape of the differential capacitance curve in ionic liquids is difficult for many reasons, not the least of which is the need to determine the behavior of multiple ionic layers, which are in total no more than a few nanometers thick. For example, to fit experimental results from reflectometry measurements correctly, one needs good *a priori* assumptions about the orientation and coordination of ionic liquids at the thin interface. The best results are provided when these assumptions are based on a first-principles molecular model. Consequently, we used a numerical self-consistent mean-field theory (SCMFT) to model the structure of room-temperature ionic liquids at electrified interfaces and to predict qualitatively the corresponding electrical properties such as the EDL capacitance.

The SCMFT is a powerful first-principles molecular modelling technique for studying physical and thermodynamic properties of systems at equilibrium [8]. An essential component of the SCMFT methodology is a self-consistent iterative procedure for minimizing the free energy of the system. In principle, the SCMFT model goes beyond the Gouy-Chapman approach for several reasons: (i) all ions have volume and thus they experience nonideal interactions, which SCMFT is able to approximate, (ii) ions typically have internal conformational degrees of freedom (similar to surfactants and polymers) which can be accounted for efficiently using a Markov approximation in SCMFT, (iii) when the local dielectric constant is a function of the molecular distribution (as in ionic liquids), it is necessary to account for the polarizability of the molecules, (iv) one can choose the suitable compressibility relationship for the system using SCMFT. While not necessary, it is usual to choose the system to be incompressible. For ionic liquids, this choice is important because a dense packing of ions is an essential ingredient. The suc-

cess of a molecularly realistic SCMFT model for ionic liquids strongly depends on how accurate the size and shape, the flexibility, and the various chemical moieties are modeled. This means detailed molecular structures such as chain branching should be accounted for. The SCMFT model provides a direct comparison to experimental systems and enables us to link the structure of ionic liquids at the electrified interface to the corresponding EDL capacitance. The system of interest is thus composed of ionic liquids adjacent to a charged solid surface. A periodic boundary condition is applied to the two sides perpendicular to the surface, whereas a Neumann boundary condition is used on the side opposite to the surface to reflect bulk properties. In SCMFT, one can deconvolute the electrostatic and steric contributions in the free energy formulation. The total free energy F per unit volume V of the system reads,

$$
\begin{aligned}
\frac{F}{Vk_BT} &= \frac{f_+}{N_+} \ln\left(\frac{Vf_+}{Q_+}\right) + \frac{f_-}{N_-} \ln\left(\frac{Vf_-}{Q_-}\right) + f_v \ln f_v \\
&+ \frac{1}{V} \int \left[\frac{1}{2}\sum_{i,j}\chi_{ij}\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})\right]d\mathbf{r} \\
&- \frac{1}{V} \int \left[\sum_i w_i(\mathbf{r})\varphi_i(\mathbf{r}) + \lambda(\mathbf{r})\left(1 - \sum_i \varphi_i(\mathbf{r})\right)\right. \\
&\left. + \frac{1}{2}\sum_i e\nu_i\varphi_i(\mathbf{r})\psi(\mathbf{r})\right]d\mathbf{r}
\end{aligned}
\tag{1}
$$

where the first to the third terms are the mixing entropy; the fourth term is the mixing enthalpy based on the Flory-Huggins formulation [9]; the fifth term comes from the local mean-field interactions; the sixth one is an extra contribution due to an incompressibility constraint; and the seventh term is the electrostatic (Coulombic) contribution.

Since ionic liquids are composed of bulky ions, each ion here is modeled as a chain of segments of a particular order. The connectivity of every segment in each chain is accounted for using a freely jointed chain model and the statistical weights of all possible conformations are found using the Edwards diffusion equation [10]. In addition to the freely jointed chain, a small amount of monomeric void (10^{-4} of the total fraction) is introduced as a volume-filling segment to accommodate densely packed ionic liquids. We refer the readers to Refs. [8] for further details. The indices $+$, $-$, and v in Eq. (1) represent the cation and the anion of ionic liquids, and the uncharged monomeric void, respectively; f_+, f_-, and f_v are the total (volume) fraction of cation, anion, and void; N_+ and N_- are the lengths of the cation and the anion; Q_+ and Q_- are the partition function of the cation and the anion; the indices i and j refer to the segment types; $w_i(\mathbf{r})$ is the potential of mean force of segment i at point $\mathbf{r}$; $\varphi_i(\mathbf{r})$ is the corresponding volume fraction of segment i; $\lambda(\mathbf{r})$ is the Lagrange multiplier at $\mathbf{r}$; ν_i is the valence of segment i; $\psi(\mathbf{r})$ is the electrostatic potential at $\mathbf{r}$; χ_{ij} is the interaction parameter between

segment i and segment j. To minimize the free energy, the first order derivation of the free energy F with respect to the order parameters $w_i(\mathbf{r})$ and $\varphi_i(\mathbf{r})$ are set equal to zero, subject to the incompressibility constraint $\sum_i \varphi_i(\mathbf{r}) = 1$ at all $\mathbf{r}$. The local electrostatic potential $\psi(\mathbf{r})$ is obtained by solving the Poisson equation, i.e., $\epsilon_0\nabla[\epsilon_r(\mathbf{r})\nabla\psi(\mathbf{r})] = -\sum_i e\nu_i\varphi_i(\mathbf{r})$, where the local dielectric constant $\epsilon_r(\mathbf{r}) = \sum_i \epsilon_{r,i}\varphi_i(\mathbf{r})$, and $\epsilon_{r,i}$ is the relative dielectric constant of segment i. After a certain number of iterations, the free energy converges to an optimum value when the mean-field potential and the volume fraction of ions are self-consistent.

We performed a series of calculations to study the structure of pure ionic liquids at charged interfaces with the following modelling details. The cation and the anion are modeled as dendrimers with four branches (Fig. 1). We consider they are generic representation of ionic liquids with similar size orders and well-hidden charged groups, such as phosphonium cation and BF_4^- or PF_6^- anion. The void is modeled as an uncharged monomer. For simplicity, we consider the variation of the volume fraction of ions only in the direction perpendicular to the surface. This approximation implies that the volume fraction of ions is homogeneous throughout each plane parallel to the surface. We chose the size of a segment to be 3 Å; the size of the system was chosen such that the bulk properties are reached within the boundaries of the modeled system; $\epsilon_{r,A} = \epsilon_{r,B} = 10$, $\epsilon_{r,P} = \epsilon_{r,N} = 30$, $\epsilon_{r,v} = 1$, and $\epsilon_{r,S} = 10$ (S refers to the surface); $\chi_{AB} = 1$ represents an adequate repulsion between uncharged segment A of cation and B of anion. The choice of the dielectric constants is as such that the (static) dielectric constant of the ionic liquid in the bulk is realistic (of the order of 11) [11].

The surface charge σ_0 and the total differential capacitance C are plotted as functions of the surface potential ψ_0 in Fig. 2. The capacitance C is calculated from the first derivative of σ_0 with respect to ψ_0, i.e., $C = \frac{\partial \sigma_0}{\partial \psi_0}$ [12]. The bell-shaped capacitance curve obtained from a uniform dielectric constant of segments, i.e., $\epsilon_{r,A} = \epsilon_{r,P} = \epsilon_{r,B} = \epsilon_{r,N} = 11$, is displayed here for comparisons. The $\sigma_0(\psi_0)$
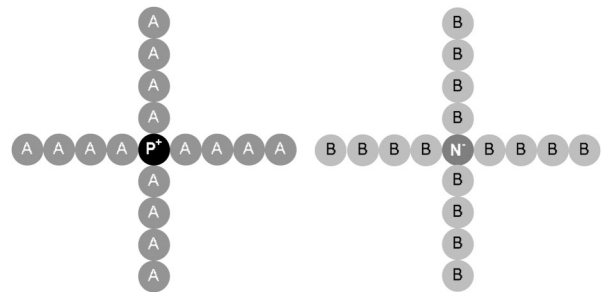

FIG. 1. Schematic of the dendrimeric structure of cation (left panel) and anion (right right) used in the model. The cation is composed of a positively charged segment P and four neutral segments A per branch, whereas the anion consists of a negatively charged segment N and four neutral segments B per branch.
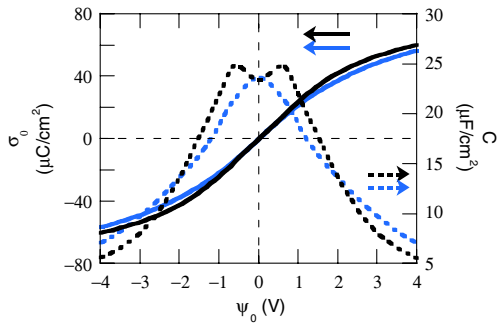
FIG. 2 (color online).   Full line: plot of the surface charge σ_0 as a function of the surface potential ψ_0 for a pure ionic liquid system. Dashed line: plot of the corresponding capacitance curve C. The black and the blue curves are results with and without an effective dielectric constant, respectively. The quasilinear regime of $\sigma_0(\psi_0)$ is in the region of $-0.8\text{V} \lesssim \psi_0 \lesssim 0.8\text{V}$, within which the capacitance curve (black) has a camel-like shape.

relationship, when the effective dielectric constant is taken into account (black curve), basically consists of two regimes: a quasilinear regime at low electrostatic potentials and a nonlinear regime at high potentials [13]. In the quasilinear regime, the electrode's surface is still not yet fully saturated by counterions, whereas the counterions saturate the electrode's surface and accumulate further away from the surface in the nonlinear regime [cf. Fig. 3(a)]. In both regimes, the surface charge is overcompensated or overscreened by the counterions in a similar mechanism to one described in Ref. [4]. Moreover, the capacitance is symmetric with the minimum value at PZC and maxima at $\psi_0 \approx \pm 0.8\text{V}$. This camel-shaped capacitance curve is not unique to ionic liquids. It was first observed decades ago in the study of aqueous solutions of NaI, NaF, KPF_6, and KBF_4 at Au or Ag electrodes where a specific (nonelectrostatic) adsorption occurs [14]. Arguably, the primary cause for such a capacitance curve in ionic liquids may be different, as highlighted by Kornyshev in his recent theoretical paper [5]. He concluded that camel-shaped capacitance curves can be obtained when ions are considered to have finite sizes (beyond the Poisson-Boltzmann model which assumes

they are point charges). We confirm this point here using the SCMFT, in which the excluded volume effect is incorporated by modelling ions as segmented dendrimers with a sufficient repulsion between uncharged segments A and B in the branches of each cation and anion. However, we found that the excluded volume effect is not the only cause. By considering the effective dielectric constant of ionic liquids as a function of the local segment density, we found that the polarizability of ions at the interface is another key factor that contributes to the camel-shaped capacitance curve. In the supporting information [15], we show that the Kornyshev's analytical approach actually allows some local fluctuations of the dielectric screening.

The camel-shaped capacitance curve can be further analyzed from the perspective of the potential dependence of the structure of ionic liquids at the interface. This structure-property relationship is elaborated as follows: (1) Within the quasilinear regime of $\sigma_0(\psi_0)$, the capacitance increases with the surface potential and the maxima of the capacitance curve can be used to define the boundaries of this regime ($-0.8\text{V} \lesssim \psi_0 \lesssim 0.8\text{V}$ as shown in Fig. 2). A more compressed (thinner) EDL leads to higher capacitance values. For qualitative analyses, we show alternating layers with the corresponding profile of potential field and dielectric constant at four different surface potentials in Fig. 3. Following the trend of these profiles, one can conclude that at the points where the capacitance reaches its maximum values ($\psi_0 \approx -0.8\text{V}$, 0.8V), the electrode's surface is saturated with counterions. In between these two points, some coions can still be found at the surface. At large applied potentials [$\psi_0 \lesssim -0.5\text{V}$ in Fig. 3(c)], the charged segment of the counterions is primarily located at the electrode's surface, causing a higher dielectric constant value there. One can assume the alternating layers of positive and negative charges as a series of capacitors where the corresponding capacitance C is obtained from $1/C = \sum_l 1/C_l$, where C_l is the capacitance of layer l. Based on this representative formula, the capacitance of the EDL in ionic liquids is determined by a nontrivial balance between the thinning (thickening) of each layer and the decreasing (increasing) polarization. A higher capacitance value can be a result of thinner layers
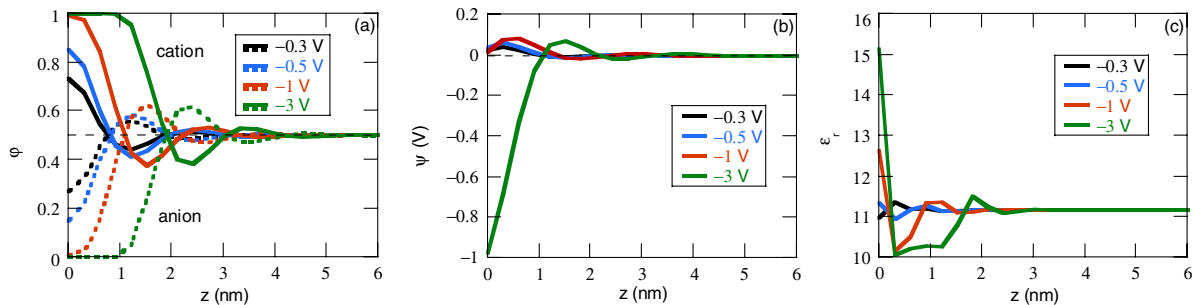

FIG. 3 (color online).   (a) Profile of the volume fraction of cation and anion at the interface with different surface potential values. Beyond the quasilinear regime ($\psi_0 \lesssim -0.8\text{V}$) the electrode surface is saturated with counterions. (b) The corresponding profile of the diffuse electrostatic potential. (c) The corresponding profile of local dielectric constant ϵ_r.

and/or a larger interfacial polarization. Based on our modelling results, the thickness of the layers throughout the quasilinear regime is relatively the same and the alternating layers have a similar periodicity, whereas the local dielectric constants ϵ_r differ following the local distribution of molecular segments. Therefore, an increasing capacitance in the quasilinear regime must be caused by an increasing polarization of ionic liquids at the interface, as illustrated in Fig. 3 for the case of $\psi_0 = -0.3$V and -0.5V. (2) Within the nonlinear regime, the surface charge is less than a linear function of the surface potential. As shown in Fig. 2, the nonlinear regime is located at $\psi_0 \lesssim -0.8$V and $\psi_0 \gtrsim 0.8$V. In this regime, the interface is already saturated with counterions such that the EDL thickness grows with an increasing surface potential (cf. Fig. 3, $\psi_0 = -1$V, -3V). The physical interpretation of this trend lies in the fact that the energy needed to bring one counterion from the bulk to the surface increases more than linearly with an increasing surface charge. A thicker EDL overcomes the effect of an increasing polarization at the interface to lower the capacitance (cf. Fig. 3, $\psi_0 = -1$V, -3V). The scaling of the capacitance in the nonlinear regime is $C \propto |\psi_0|^{-0.8}$. As a comparison, the scaling for the bell-shaped capacitance curve is $C \propto |\psi_0|^{-0.6}$, which indicates that the effective dielectric constant plays an important role in determining the scale of the capacitance at the electrostatic potential "wings." Furthermore, both capacitance curves decay more rapidly than the analytical prediction of Kornyshev ($C \propto |\psi_0|^{-0.5}$) [5]. The difference in the scaling factors can be preliminarily attributed to the different modelling details, as highlighted in the supporting information [15].

An increasingly charged electrode in an aqueous electrolyte solution leads to a more effective screening of the electrostatic potential. The screening effect intensifies as the interface is more densely populated by counterions that replace electroneutral water molecules. As a result, the curvature of $\sigma_0(\psi_0)$ goes beyond linear in an aqueous electrolyte solution. At a first glance, the overall capacitance curve of the EDL in aqueous electrolytes seems to differ from that in ionic liquids. The capacitance curve in aqueous electrolytes usually reaches a minimum at PZC and increases monotonically with surface potential, whereas the capacitance curve in ionic liquids has a camel-like shape. Nevertheless, under similar premises both curves would have the same camel-like shape if similar potential limits could be attained. The maxima for the capacitance curve in aqueous electrolyte are predicted to occur at potentials beyond the electrochemical window of water, such that we never observed this camel-shaped capacitance curve in reality. To summarize, we model the structure of ionic liquids at electrified interfaces by implementing a molecularly realistic SCMFT model of ionic liquids. The model produces the alternating density profile of ionic liquids and is used to deduce measurable capacitance curves that have all the known camel-shaped

features, which are the results of an interplay between the excluded volume effect and the effective dielectric constant.

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[2] Throughout this article, the term aqueous electrolyte is used to refer to a general dilute or semidilute electrolyte solution in water where the ionic strength is still reasonably low and the nonelectrostatic adsorption of ions towards the surface of the electrode is minimum.

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[12] As pointed out in Ref. [6], the differential capacitance based on an equilibrium model can only be related to the experimental differential capacitance at very low frequencies. Nevertheless, since we are only interested in qualitative change in the capacitance curve, the use of differential capacitance here is still valid.

[13] Around the PZC—which in this case is located at $\psi_0 = 0$—the relationship between the surface charge and the surface potential appears to be linear and it is usually approximated by the well-known Debye-Huckel theory. However, it is clear from the capacitance curve that the surface charge actually has a point of inflection at the PZC. We thus categorize this region of low electrostatic potentials in a quasilinear regime.

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[15] See EPAPS Document No. E-PRLTAO-103-009939 for supporting information. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.