



The effect of dispersion interactions on the structure and performance of electrical double layer of ionic liquids



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ABSTRACT

A classical density functional theory has been used to study the structure and phase behavior of the electrical double layer of a dense ionic liquid. The model for IL consists of a trimer cation (with a charged head and two neutral segments) and a monomer anion. The effect of dispersion interactions on the density profile and differential capacitance curve has been investigated. Increasing the contribution of dispersion interactions leads to a camel-shape differential capacitance curve. In the case of bell-shape curve, the maximum of the differential capacitance increases with decreasing the dispersion forces. These observations are related to the depletion or accumulation of ions near electrode with zero or low surface charge density.

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1. Introduction

An interfacial region called electrical double layer is formed when a charged electrode is immersed in an electrolyte. Some experimental and theoretical studies carried out to understand structure and performance of electric double layers for applications in energy storage devices [1–3]. Recently, room temperature ILs have been considered as a promising electrolyte in electrical double layer capacitors (EDLC) because of their unique properties such as low volatility, low melting point, high thermal stability and low toxicity [4,5]. Due to their high ionic concentration, low dielectric constant and steric interactions, understanding performance of ILs at room temperature with charged interfaces in electrical double layer (EDL) requires the use of an advanced approach. One of the modern theories is the classical density functional theory (DFT) [6–10], which may successfully incorporate steric effects and strong electrostatic correlations for an inhomogeneous ILs.

The most important property of an electrical double layer is differential capacitance. A number of theoretical studies have been reported to understand the electrolyte/electrode interface behavior. Jiang et al. [11] considered EDL including hard sphere ions in the vicinity of a planar charged surface and studied the effect of ion size and concentration on the differential capacitance using DFT. It was found that at low ionic concentrations the curve of differential capacitance as a function of surface potential (electrode surface charge density) has two maxima,

and a minimum of the camel shape curve occurs at zero surface potential. At high ionic concentrations the model produce a bell shape capacitance curve in which it's maximum coincide with zero surface potential. Using modified Poisson-Boltzmann theory and simulation, Lamperski et al. [12] obtained analogous results for a restricted primitive model. Moreover, the experimental capacitance curves involving room temperature ILs showed both camel-shape and bell-shape [13–18]. To explain these experimental observations, Fedorov et al. [19] performed Monte Carlo (MC) simulations for three different IL double layers having the same anion modeled as a negatively charged spherical segment and differing in the cation shape. The cation was made of one charged segment (monomer), or two touching segments (dimer), or three touching segments (trimer), in which the dimer and trimer cations had a charged head and a neutral tail. A bell shape capacitance curve was obtained for the monomer cations, whereas a camel shape was obtained for the dimer and trimer cations. The authors related the observed camel shape curve to the neutral tail of cations in which neutral segments act as latent voids which can be replaced by positive segments. It was concluded that this rearrangement leads to the camel shape curve.

The DFT calculations and MC simulations for the monomer and dimer cations by Henderson et al. [20–23] showed that the shape of capacitance curve depends on the electrolyte charge concentration. The results showed that the influence of neutral tails on the behavior of capacitance is a secondary effect. In these theoretical works, the dispersion interactions were disregarded, while the MC simulation performed by Trulsson et al. [24] showed that dispersion interactions play a significant role in the occurrence of camel shape capacitance curve.

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In this work, for a dense IL, we aim to systematically investigate the influence of dispersion forces on the EDL structure and the performance of differential capacitance curve using DFT calculations. The model IL for this study consists of trimer cations (each has a charged head and two neutral segments) and monomer anions. In addition, in the absence of chain connectivity we obtained a symmetric IL model and compared its structure and behavior with our asymmetric model. The model parameters are consistent with the thermodynamic properties of ILs.

2. Theory

It is assumed that the IL is composed of an anion and a cation, in which the anion is treated as a charged spherical segment and the cation is modeled as a chain composed of a charged head and a neutral tail of three tangentially bonded spherical segments. All segments interact with each other through a square-well (SW) potential

$$\phi^{SW} = \begin{cases} +\infty & r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases} \quad (1)$$

where σ is diameter of spherical segment, r is the distance between segment centers and $\lambda\sigma$ determines the range of the attractive interaction of depth $-\varepsilon$. These parameters are assumed to be the same for all segments in an IL. The electrostatic interaction between charged segments separated by a distance r is given by

$$\phi_{ij}^{el}(r) = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r} \quad (2)$$

where q_i and q_j are charge of interacting particles, ϵ_0 is the permittivity of vacuum and ϵ_r is relative dielectric constant. The quantity ϵ_r for ILs was set at 12.5 based on the literature reports [25].

The model parameters (σ , ε and λ) must be consistent with the thermodynamic properties of a typical room temperature ILs. For this purpose, in the frame work of an ionic based on statistical associating fluid theory for potentials of variable range (SAFT-VR) [26] equation of state (EOS), we calculated the parameters by means of fitting the model predictions to experimental $p\rho T$ data of $[C_6mim][BF_4]$ over a wide temperature and pressure ranges. The optimized parameters are:

$\sigma = 4.15 \times 10^{-10}$ m, $\frac{\varepsilon}{k_B} = 651$ K and $\lambda = 1.49$, where k_B is the Boltzmann constant. In our previous works [27–29] the SAFT approach having rigorous physical foundation can successfully describe bulk properties of ILs. In the ionic based SAFT-VR EOS used in the present work, the excess Helmholtz energy for the bulk region is defined as

$$A^{ex} = A^{mono} + A^{chain} + A^{ion} \quad (3)$$

where A^{mono} represents monomer term, which includes repulsive and dispersive contributions, A^{chain} is the chain contribution to the free energy [30] and A^{ion} is the contribution due to the ion-ion interaction, which may be obtained from the solution of Ornstein-Zernicke equation for the restricted primitive model with the mean-spherical approximation (MSA) [31] given by [32]

$$\frac{A^{ion}}{Nk_B T} = -\frac{3\chi^2 + 6\chi + 2 - 2(1 + 2\chi)^{\frac{3}{2}}}{12\pi\rho\sigma^3} \quad (4)$$

where $\chi = \kappa\sigma$, in which κ is the inverse of the Debye screening length defined by.

$$\kappa^2 = \frac{1}{\epsilon_0\epsilon_r k_B T} \sum_{j=1}^2 \rho_j q_j^2 \quad (5)$$

In the classical DFT the grand potential of an inhomogeneous system can be written as a function of density distribution. For the equilibrium density profile, this potential reaches a minimum value. The equilibrium

density profile for the system including IL near charged surface using the variation principle was obtained by

$$\frac{\delta\Omega[\rho_c(\mathbf{R}), \rho_a(\mathbf{r})]}{\delta\rho_c(\mathbf{R})} = \frac{\delta\Omega[\rho_c(\mathbf{R}), \rho_a(\mathbf{r})]}{\delta\rho_a(\mathbf{r})} = 0 \quad (6)$$

where $\rho_c(\mathbf{R})$ is the cation density, \mathbf{R} denotes the position of the constituent segments and $\rho_a(\mathbf{r})$ is density of anion. The grand potential $\Omega[\rho_c(\mathbf{R}), \rho_a(\mathbf{r})]$ is given by

$$\Omega[\rho_c(\mathbf{R}), \rho_a(\mathbf{r})] = F^{id}[\rho_c(\mathbf{R}), \rho_a(\mathbf{r})] + F^{ex}[\rho_c(\mathbf{R}), \rho_a(\mathbf{r})] + \int [V_{ext,c} - \mu_c] \rho_c(\mathbf{R}) d\mathbf{R} + \int [V_{ext,a} - \mu_a] \rho_a(\mathbf{r}) d\mathbf{r} \quad (7)$$

where V_{ext} is the external potential. The ideal contribution to the free energy functional is given by

$$F^{id}[\rho_c(\mathbf{R}), \rho_a(\mathbf{r})] = k_B T \int [\ln \rho_c(\mathbf{R}) - 1] \rho_c(\mathbf{R}) d\mathbf{R} + \int \rho_c(\mathbf{R}) V_b(\mathbf{R}) d\mathbf{R} + k_B T \int [\ln \rho_a(\mathbf{r}) - 1] \rho_c(\mathbf{R}) d\mathbf{R} \quad (8)$$

where $V_b(\mathbf{R})$ is the total bonding potential for tangentially connected segments, which satisfies the expression [33]

$$\exp[-\beta V_b(\mathbf{R})] = \prod_{j=1}^{m_c-1} \delta(|\mathbf{r}_{j+1} - \mathbf{r}_j| - \sigma) / 4\pi\sigma^2 \quad (9)$$

where $\delta(r)$ is the Dirac delta function and $\beta = \frac{1}{k_B T}$.

The excess Helmholtz free energy functional F^{ex} is given by

$$F^{ex} = F^{hs} + F^{disp} + F^{chain} + F^C + F^{el} \quad (10)$$

where F^{hs} is the hard sphere contribution, F^{disp} represents dispersion interactions, F^{chain} is the chain connectivity contribution, F^C takes into account direct Coulombic interactions and F^{el} represents the free energy due to electrostatic correlations.

Using White-Bear version [34] of Rosenfeld's fundamental measure theory (FMT) [35], the hard-sphere repulsion term is given by

$$\beta F^{hs} = \int f^{hs}(\{n_\alpha(\mathbf{r})\}) d\mathbf{r} \quad (11)$$

where f^{hs} , the reduced free energy density given by

$$f^{hs} = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \mathbf{n}_{V1} \cdot \mathbf{n}_{V2}}{1 - n_3} + n_2^3 \frac{(1 - \xi^2)^3 n_3 + (1 - n_3)^2 \ln(1 - n_3)}{36\pi n_3^2 (1 - n_3)^2} \quad (12)$$

in which

$$\xi(\mathbf{r}) = \frac{|\mathbf{n}_{V2}(\mathbf{r})|}{n_2(\mathbf{r})} \quad (13)$$

and f^{hs} is expressed as a function of six weighted densities, $n_\alpha(\mathbf{r})$,

$$n_\alpha(\mathbf{r}) = n_{\alpha\alpha}(\mathbf{r}) + n_{\alpha a}(\mathbf{r}) = \int \rho_s(\mathbf{r}') w_s^{(\alpha)}(\mathbf{r} - \mathbf{r}') d\mathbf{r}' + \int \rho_a(\mathbf{r}') w_a^{(\alpha)}(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \quad (14)$$

where $\rho_s(\mathbf{r})$ is the total segment density of cation molecule including neutral and positive segments, the subscripts $\alpha = 0, 1, 2, 3$ and $\alpha = V1, V2$ denote scalar and vector weight functions, respectively:

$$w^{(2)}(r) = \delta\left(\frac{\sigma}{2} - r\right) \quad (15)$$

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