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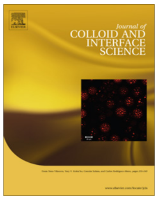

Density functional theory study of the capacitance of single file ions in a narrow cylinder

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It is a pleasure for us to dedicate this article to Darsh Wasan, who has served so well as the Editor-in-Chief of this journal and, at the same time, has had a distinguished career as a university administrator, and as an outstanding teacher and research scientist. At times, we are inclined to believe that there is a set of identical triplets, all posing to be one person. In any case, one or three, Darsh Wasan is a fine human being and good friend. We are glad that he is lightening his load.

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ABSTRACT

The differential capacitance of a model organic electrolyte in a cylindrical pore that is so narrow that the ions can form only a single file is studied by means of density functional theory (DFT). Kornyshev (2013), has studied this system and found the differential capacitance to have only a double hump shape (the so-called camel shape) whereas other geometries show this behavior only at low ionic concentrations that are typical for aqueous electrolytes. However, his calculation is rather approximate. In this DFT study we find that the double hump shape occurs only at low ionic concentrations. At high concentrations, the capacitance has only a single hump. Kornyshev considers a metallic cylinder and approximately includes the contributions of electrostatic images. Electrostatic images are not easily incorporated into DFT. As a result, images are not considered in this study and the question of whether Kornyshev's result is due to his approximations or images cannot be answered. Simulations to answer this question are planned.

1. Introduction

Supercapacitors based on electric double layer expansion show great potential as an energy storage device due to their large power density, high capacitance, and sustainable life cycles [1,2]. Recent developments in the nanostructured electrode materials [3,4] largely improved the performance of the supercapacitors due to their high specific surface area. In these materials, the characteristic sizes of the pores are comparable to the size of the electrolytes, namely, only single file or single layer of electrolyte ions may enter the pores.

Kornyshev [5] has published an intriguing article in which he studied the dependence of the capacitance of the double layer formed by a system of organic electrolyte ions in a cylindrical pore that is so narrow that the ions can form only a single row. This geometry is shown in Fig.1. We consider first the case where all the ions have the same diameter but do report some results for differing diameters. In the equal diameter case, to have a single file, the cylinder diameter, $D = 2a$, and ion diameter, d, must obey $d \leqslant 2a \leqslant 2d$. The system is open in the sense that the ionic concentration inside the pore is determined by that the concentration of ions in a reservoir with which the ions in the cylinder are in equilibrium. In this article, when we give a value for the concentration of the organic electrolyte, it is to be understood that this is the concentration of the organic electrolyte ions in the reservoir. Kornyshev devised an interesting Ising-like lattice theory to describe this system. The Ising theory rests upon a lattice with nearest neighbor interactions and a binary proposition (occupied or unoccupied sites or a similar proposition). It is a bit of a stretch to apply this to a fluid with long range coulombic interactions but it is not an impossibility. Additionally, he considers a metallic cylinder wall and takes into account, albeit very approximately, electrostatic images. According to his theory, the differential capacitance of this system as a function of the surface potential always has the shape of two humps, at least for the range of parameters that he studied. The two hump shape is often referred to as a "camel" shape.

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However, this is not a fully satisfactory term since only bactrian camels have two humps; dromedary camels have a single hump. We find it more satisfactory to describe the shape of the capacitance curve as having a single-hump (or a bell) shape or a double-hump shape. Kornyshev's result is interesting because it contrasts with experience with single-surface double layers using modified Poisson–Boltzmann (MPB) theory [6], Monte Carlo (MC) simulations [7], and density functional theory (DFT) [8]. Earlier theoretical studies all show that the capacitance has a two-hump shape at only low ionic concentrations but that, as the concentration increases, the minimum between the two humps fills in and becomes a maximum. The capacitance has a bell shape or single-hump shape at higher concentrations. The question naturally arises whether the persistent double hump capacitance curves predicted by Kornshev is a feature of his Ising-like approximation or of image effects or a feature of the single file geometry. Thus, it seems worthwhile to examine this single file cylindrical ion system by means of a more realistic approximation to determine whether single-hump as well as double-hump capacitance curves could be found for single file ions in a cylindrical pore.

2. Model

We consider a cylindrical pore of diameter $D = 2a$ containing ions that are in equilibrium with a reservoir. The ions are treated as charged hard spheres. The diameter and charge of the cations are d_+ and Z_+e, and those corresponding to anions are d_- and Z_-e, with e being the magnitude of the elementary charge and Z_i **is** the ion valence. There are no solvent molecules in our model. The model is appropriate for an organic electrolyte with the solvent represented by a dielectric continuum.

For a sufficiently long cylinder ($L \gg D$) such that the end effects are negligible, the ionic density profiles, i.e., ionic distributions, can be specified by a radial coordinate r. The separation of a pair of ions in the cylinder is given by the difference in their radial positions, r_{ij}, axial positions, z_{ij}, and polar angles, θ_{ij}. Since the ions are confined to the cylinder, the radial position of each ion must be less than a. The distance between the centers of the ions is denoted by R. The electrostatic interaction between the ions is given by

$$\beta U_{ij}(R) = l_B \frac{Z_i Z_j}{R}, \tag{1}$$

where $\beta = 1/(k_B T)$, k_B being the Boltzmann constant and T is the temperature (300 K). In Eq. (1), l_B is the Bjerrum length, defined by

$$l_B = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T} \tag{2}$$

where ε_0 is the vacuum dielectric constant or vacuum permittivity, ε is the relative dielectric constant, which we assumed to be 6.5 for a typical organic electrolyte. The resulting Bjerrum length is 8.55 nm. We have also considered other values of the Bjerrum length and concentration than those presented in this study. The behavior of the C_d–ψ_0 curve for these different values of l_B and concentrations is similar. For conciseness, these numerical results are not shown.

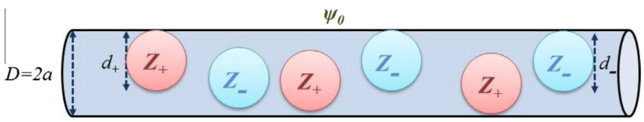

Fig. 1. Single file ions in a cylindrical pore electrode. The pore is infinitely long in the axial direction and **the fluid** is in equilibrium with a reservoir of ions at a specified constant concentration. The diameter of the cylinder is $D = 2a$ and ion diameters and charges of the cations and anions are d_+, d_-, Z^+e, and Z^-e, respectively. The surface of the cylinder is held at a constant electrical potential, ψ_0.

In our DFT calculations, the cylinder wall is maintained at a constant electrical potential, ψ_0. The cylinder is sufficiently narrow so that the ions form a single file, i.e., $d_i \leqslant 2a \leqslant d_i$. The pore confinement effect modeled as a hard-wall potential. In other words, the non-Coulomb external potential due to the presence of the wall is given by

$$V_i(r) = \begin{cases} 0, & r \leqslant a - d_i/2 \\ \infty, & r > a - d_i/2. \end{cases} \tag{3}$$

In our DFT calculations, we assume that the cylinder surface and the region outside the cylinder have the same dielectric constant as the interior of the cylinder. Thus, electrostatic images are not considered here. Kornyshev does consider images for a metallic cylinder wall. However, his treatment of images is rather approximate. The expression that he uses for the interaction between the ions presumes that each ion lies on the central axis of the cylinder. Although this appears to be a good approximation for a single ion pore, we cannot be sure how satisfactory it is given that the cylinder surface is also not far from the central axis and that the ions are also close to the cylinder surface and images. Also, the Ising-like theory used by Kornyshev is a further approximation. In any case, image effects are not easily incorporated into DFT [9]. In view of this, we feel it best make a study of image effects in the future using simulations or the modified Poisson–Boltzmann (MPB) equation [10], where images can be systematically incorporated.

3. Density functional theory

Density functional theory (DFT) is arguably the best theory for calculating the density profiles of particles near a wall. This is especially true for ions near an electrode. We have reported our DFT study of various ionic liquids near an electrode [8,11,12]. For model ionic liquids, the agreement with simulations is outstanding.

3.1. Ionic distribution functions

In the cylindrical geometry that we employ, Possion's equation for the ionic distributions is

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\psi(r)}{\partial r}\right) = -\frac{e}{\epsilon_0\epsilon}\sum_i Z_i\rho_i(r), \tag{4}$$

and the basic DFT expression for $\rho(r)$ is

$$\rho_i(r) = \rho_i^0 \exp\left[-\beta Z_i e\psi(r) - \beta\Delta\mu_i^{ex}(r)\right], \tag{5}$$

where $\rho_i(r)$ is the number density distribution function for the ions of species i, ρ_i^0 is **the** bulk number density, or concentration, of this species. The quantity μ_i^{ex} is the local excess chemical potential of species i. An explicit expression for μ_i^{ex} will be given in the following subsection. The boundary conditions for Poisson's equation are

$$\psi'(0) = 0, \tag{6}$$

and

$$\psi(a) = \psi_0, \tag{7}$$

where ψ_0 is the electric potential of the surface of the cylinder.

In our DFT calculation, we start with an initial guess for the density profile that is assumed to be uniform. The electric potential, $\psi(r)$ is calculated from Eq. (4) together with the above boundary conditions, Eqs. (6) and (7). With this new $\psi(r)$, we obtain a new set of ionic profiles. A Picard iteration is used and the iteration continues until the sum over the grid points of the differences between the old and new values of ρ_i is less than 10^{-6}. To ensure that the convergence is stable, we mix only a small fraction of the new profiles with the old profiles to form the next iterate.

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