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Structure of an electric double layer containing a 2:2 valency dimer electrolyte

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ABSTRACT

The structure of a planar electric double layer formed by a 2:2 valency dimer electrolyte in the vicinity of a uniformly charged planar hard electrode is investigated using density functional theory and Monte Carlo simulations. The dimer electrolyte consists of a mixture of charged divalent dimers and charged divalent monomers in a dielectric continuum. A dimer is constructed by two tangentially tethered rigid spheres, one of which is divalent and positively charged and the other neutral, whereas the monomer is a divalent and negatively charged rigid sphere. The density functional theory reproduces well the simulation results for (i) the singlet distributions of the various ion species with respect to the electrode, and (ii) the mean electrostatic potential. Comparison with earlier results for a 2:1/1:2 dimer electrolyte shows that the double layer structure is similar when the counterion has the same valency.

1. Introduction

We are pleased to dedicate this article to our friend and collaborator Darsh Wasan, to help celebrate his distinguished tenure as Editor-in-Chief of this journal. To be an exemplary editor is commendable. To combine this with a highly successful research career is exceptional but to combine both of these with a successful vice-presidency of an important university is truly outstanding.

An electric double layer is the name given to an inhomogeneous fluid system formed by a charged liquid (viz., an electrolyte, an ionic liquid, or a molten salt) in the vicinity of an electrode. Although the classical theory of the phenomenon [1–3] has been around for over a hundred years, the increasing relevance of the double layer in, for example, functioning of ion channels, DNA sequencing, and designing super-capacitors and lithium-ion batteries has continued to attract interest (see for example Refs. [4,5]) and requires a more accurate and modern theory.

The underlying model of the classical Gouy–Chapman–Stern (GCS) [1–3] theory of the electric double layer is the primitive model (PM) where the charged liquid consists of charged hard spheres in a uniform dielectric continuum (the solvent) characterized by its relative permittivity. In the restrictive case of the spheres having the same diameter, it is the restricted primitive model (RPM). The RPM and, to a lesser extent the PM double layers have been extensively studied for the better part of the last four decades through formal statistical mechanical approaches and numerical simulations and a great deal of knowledge about such systems has been acquired (see for example, the reviews [6,7]). The simulations have further established that the mean-field nature of the classical picture, for instance, neglect of the interionic correlations and ionic exclusion volume effects, is less than adequate in most situations.

In recent years experiments especially those involving differential capacitance (C_D) measurements have begun to expose the limitations of the PM double layer. For example, ionic liquid double layers manifest a variety of C_D versus electrode surface charge density σ behaviour [8–11], which can only be understood at best in rather broad terms using the RPM or the PM [12–23]. The primitive models necessarily introduce a shape symmetry in the constituent species of an electrolyte, which is probably not very realistic in the natural world. On the other hand, less simple models that have built-in asymmetry in ionic shape and/or size, molecules with off-centre charges might prove more useful in interpreting the experimental capacitance trends. By the same token complex models may prove too demanding theoretically. So the challenge is to

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be able to postulate more realistic models beyond the PM that are also amenable to theoretical treatment and/or numerical simulations. One such candidate is the dimer model of the electrolyte. Here, the cation is a dimer consisting of two tangentially tethered hard spheres one of which is positively charged and the other neutral, while the anion is a monomer, which is a negatively charged hard sphere. A related model is the trimer model with three touching, linearly aligned hard spheres with an end sphere being charged. Simulation studies on such models have been reported by Fedorov and Kornyshev [24], and Fedorov et al. [25], while the density functional theory (DFT) on the dimer model has been applied by Fedorov et al. [25], Wu et al. [26], Henderson and Wu [27], and Henderson et al. [28]. There is some practical relevance of the dimer model in that it can mimic the alkyl cation of some ionic liquids and has been used to represent tetraethylammonium (an ionic liquid) in a pore [29]. Furthermore, molecular dynamics (MD) simulation techniques have been performed on ionic liquids like imidazolium based on a trimer model consisting of a spherical anion and a cation formed by three coplanar connected spheres in the form of a triangle [30].

In a series of papers some of us have explored the dimer electrolyte model of the double layer using Monte Carlo (MC) simulations and/or the DFT in both ionic liquid regime [31] and electrolyte solution regime [32,33] for 1:1 valency systems. A more recent later work [34] delves into 2:1/1:2 asymmetric valency systems. The principal findings have been (i) significant differences in structure and capacitances relative to that with the spherically symmetric PM, (ii) a richer double layer structure when the counterions are non-spherical, (iii) asymmetry in the C_D versus σ plots that still show minimum–maximum transition at high salt concentrations, and (iv) similarity in double layer structure between systems where the counterion has the same valency. In the present paper we will continue to look at the dimer model but now for higher 2:2 valency situations. The use of DFT ought to be of interest since higher and/or asymmetric valencies are always a more stringent test of a theory.

2. Model and methods

We have treated here the dimer model of the double layer in planar symmetry, that is, the electrode is a uniformly charged, planar hard surface. The constituent spheres of the dimer cation and also the monomer anion all have the same diameter d. A relative permittivity ϵ_r specifies the continuum dielectric (solvent). The model used is exactly the same as in the earlier studies [29–33] excepting that the valencies of the cation and the anion are now +2 and −2, respectively. The MC simulation techniques and the DFT employed are the same as used in the previous papers [29,31–34] and will not be repeated here.

3. Results

All of the results presented here, except for a couple of exceptions, pertain to 2^+:2^- valency dimer electrolytes at temperature $T = 298$ K, $\epsilon_r = 78.5$ corresponding to a water-like solvent, and electrolyte concentration $c = 1$ mol/dm^3. The exceptions are two sets of MC simulations for 2^+:1^- and 1^+:2^- electrolytes, also at 1 mol/dm^3 and for a positive electrode, which were done for comparison purposes. In the rest of the paper we will refer to these electrolyte systems as 2:2, 2:1, and 1:2 systems with the understanding that the first index always refers to the valency of the dimer cation and the second index to the valency of the monomer anion. Following the usual custom, we will discuss the results in terms of the following reduced variables, viz.,

the reduced density

$$\rho_s^* = \rho_s d^3, \tag{1}$$

where ρ_s is the mean bulk number density of ion species s,

the reduced surface charge density

$$\sigma^* = \frac{\sigma d^2}{e}, \tag{2}$$

the reduced mean electrostatic potential

$$\psi^*(x) = e\beta\psi(x), \tag{3}$$

and the reduced temperature

$$T^* = \frac{4\pi\epsilon_0\epsilon_r d}{|Z_+ Z_-|\beta e^2}. \tag{4}$$

In the above equations, Z_s is the valency of species s, e is the magnitude of the electronic charge, ϵ_0 is the vacuum permittivity, and $\beta = 1/(k_B T)$ with k_B the Boltzmann constant. The total reduced density is given by $\rho^* = \sum_s \rho_s^*$ with the summation extending over all the species. Also, $T^* = 1/\Gamma$, where Γ is the plasma coupling parameter, which is a measure of the strength of the electrostatic interactions.

In Figs. 1 and 2 we show the electrode-ion singlet distribution profiles $g_s(x/d)$ (lower panels) and the reduced mean electrostatic potential $\psi^*(x/d)$ (upper panels) for the 2:2 electrolyte near a planar electrode with a negative surface charge. The corresponding

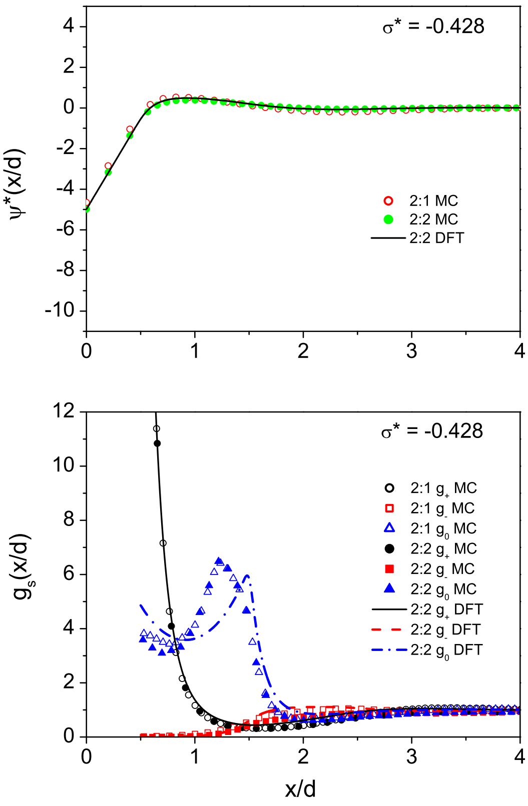

Fig. 1. Reduced mean electrostatic potential ψ^* (upper panel), electrode – ion singlet distributions g_s (lower panel) for a 2:2 valency dimer electrolyte model of the planar electric double layer at concentration $c = 1$ mol/dm^3 (reduced density $\rho^* = 0.139$) and reduced surface charge density $\sigma^* = -0.428$. 2:1 MC results at the same 1 mol/dm^3 (reduced density $\rho^* = 0.185$) from Ref. [34] have been added for comparison purposes. The notations g_+, g_0, and g_- denote the singlet distributions for the positively charged ends of the dimers, the neutral ends of the dimers, and the negatively charged spheres, respectively. The rest of the legend is given within the figure.

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