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# The planar electric double layer capacitance for the solvent primitive model electrolyte

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## Abstract

The planar electric double layer capacitance of the solvent primitive model electrolyte is studied using simulation and two versions of the modified Poisson-Boltzmann theory. At small values of the surface charge and varying electrolyte concentration, the capacitance has a behaviour analogous to that of the restricted primitive model electrolyte. As the electrolyte concentration is increased at a fixed total packing fraction, the minimum at zero surface charge changes to a maximum. This qualitative change is predicted by both simulation and the modified Poisson-Boltzmann theories. The transition envelope, separating the change in the capacitance from a minimum to a maximum at zero surface charge, is shifted from the restricted primitive model value to higher ion densities at fixed total packing fractions.

## Introduction

The solvent plays a critical role in the formation of the aqueous electric double layer. There are at least two aspects which are crucial, (i) the interaction of the solvent molecules with the electrode and (ii) the influence on the properties of the electrolyte solution. The traditional approach based on the Gouy, Chapman, Stern theory[1-3], concentrates on the first aspect. Immediately adjacent to the electrode is a region, called the inner layer, whose properties are essentially determined by the solvent molecules. The electrolyte in the diffuse layer is modelled by point ions moving in a medium of constant permittivity so the solvent only enters through the Coulomb potential. An insight into the influence of the solvent was first seen in a mean spherical approximation analysis of an ion-dipole mixture against a plain hard wall[4,5], the ions and dipoles being modelled by hard spheres with a point charge or dipole at their respective centres. The dipoles modify the structure of the electrolyte for several molecular layers into the solution, reduce the capacitance relative to that of the dielectric continuum result and provide a first principle derivation of the Stern inner layer. We consider here the much simpler solvent primitive model (SPM) which is a mixture of charged and uncharged hard spheres moving in medium of constant permittivity[6,7]. The main feature of the SPM is to judge the effect of solvent size, via the uncharged hard spheres, on both the thermodynamic and structural properties. This is a very simple model as multiple moments and the complex structure of solvent molecules is ignored. No inner region is explicitly treated, although any electrolyte model treating both solute and solvent molecules will give rise to an equivalent region next to the electrode.

The SPM electrolyte with ions and solvent of equal or different size has been studied using both simulation[8-13], density functional theory[6,7,11,14-19], Poisson-Boltzmann (PB) theory with an exclusion volume term[20] and the modified Poisson-Boltzmann (MPB) theory[13,21,22]. In reference 22, denoted by I, emphasis was placed on the structural properties of the planar electric double layer rather than the thermodynamic properties. Here we consider in greater detail the capacitance prediction of the model, with Monte Carlo simulations and two formulations of the MPB theory.

## Model and Methods

The planar electric double layer is modelled by a SPM electrolyte in the neighbourhood of a plane, uniformly charged, hard electrode of constant permittivity $\varepsilon_r$. The ions and uncharged hard spheres have the same diameter $d$ and are immersed in a uniform continuous dielectric having the same permittivity as that of the electrode, so there is no imaging. At any point in the solution a perpendicular distance $x$ from the electrode, the mean electrostatic potential $\psi(x)$ satisfies Poisson's equation

$$d^2\psi(x)/dx^2 = -(e/\varepsilon_0\varepsilon_r)\sum_k z_k n_k^0 g_k(x) \tag{1}$$

where $e$ is the elementary charge, $z_k$ the valence, $n_k^0$ the mean number density of molecules of type $k$ and $g_k(x)$ the singlet distribution function. The sum in $k$ is over all the species with $z_k$ = 0 for the solvent. Eqn (1) reduces to Laplace's equation in the region $0 < x < d/2$ with solution

$$\psi(x) = \psi(0) - \sigma x/\varepsilon_0\varepsilon_r \tag{2}$$

where $\sigma$ is the constant uniform charge on the electrode.

To obtain a closed system of equations for $\psi(x)$ in $x > 0$, we need to express $g_k(x)$ in $x > d/2$, in terms of the mean electrostatic potential. The simplest is the mean field closure which gives the PB equation of the classical theory. Here we use the MPB approach to cater for the approximations inherent in the PB equation. Using the bulk electrolyte result of Kirkwood[23], the ion singlet distribution function is

$$g_k(x) = \xi_k(x)\exp[-\beta e z_k \psi(x) + \chi_k(x)] \tag{3}$$

where $\xi_k(x) = g_k(x; z_k = 0)$ is the exclusion volume term, $\chi_k(x)$ is the fluctuation term and $\beta = 1/k_BT$, $k_B$ Boltzmann's constant and $T$ the absolute temperature. The PB theory is given by putting $\chi_k = 0$ and $\xi_k(x) = 1$ for $x > d/2$, $\xi_k(x) = 0$ for $x < d/2$. A calculation of $\chi_k(x)$, based on Loeb's[24] closure for the fluctuation potential, forms the basis of the MPB theory, see the review by Carnie and Torrie[25]. We use here the expression in the exponential given by Outhwaite and Bhuiyan[26], also see Eqn (5) of I. Two approaches have been used to calculate the exclusion volume term. One is based on the Bogoliubov-Born-Green-Yvon[27] hierarchy of integral equations and is the MPB5 theory, the 5 denoting the most accurate version of $\xi_k(x)$[28]. The extension for the SPM is given in reference 21.The other approach is based on the work of Carnie et al.[29] and involves the direct correlation function. This theory is denoted by MPB+EVT with the notation coming from reference 20. The appropriate SPM formulation is given in I. The MPB5 and MPB+EVT theories were solved numerically[21,22] using the previously developed quasi-linearisation procedure.

The simulations were performed using the grand canonical Monte Carlo (GCMC) technique previously used in I. The GCMC approach is based on that of Torrie and Valleau[30] with some modifications. In the original approach the activity of the electrolyte solution must be set so that a specific concentration cannot be given at the onset. This inconvenience is overcome by using the inverse GCMC[31] to find the activity coefficient for a given concentration. Also for the SPM the linked-list method[32] was used for the short range ion-solvent, solvent-solvent interactions which improves the efficiency and speed of the simulations.

## Results and Discussion

The simulations and theoretical calculations were performed for 1:1 electrolytes at $T$ = 298.15K, $d$ = 400pm and relative permittivity $\varepsilon_r = 78.5$ with the total packing fraction $\eta_{\text{tot}} = (\pi/6)\sum_k n_k^0 d^3$ being 0.32. These parameters were chosen to coincide with the equal diameter results of I. For the electrolyte concentration $c$ = 1M, a total packing fraction of 0.32 means that the solvent concentration $c_s$ = 13.86M. The surface charge was taken to have values between 0 C/m$^2$ and 0.5 C/m$^2$, the corresponding results for negative values following by symmetry.

For the symmetric valence restricted primitive model (RPM) electrolyte, simulations have delineated how the capacitance changes shape as the electrolyte concentration increases[33-35]. Figure 1 illustrates the typical behaviour, in the neighbourhood of low surface charge, using the MPB+EVT theory. At low surface charge and electrolyte concentration, the capacitance is similar to the classical result. However, as the concentration increases the minimum at $\sigma = 0$ gradually rises and eventually turns into a maximum. The MPB5 theory has been found to give a good picture of the capacitance of the RPM model for low surface charge[33,34], but only a limited study has been made for the SPM. In Figures 2 and 3 the MPB5 and MBP+EVT integral capacitances are compared with those from simulation. To calculate the integral capacitance at zero surface charge a least squares even degree polynomial is fitted to the integral capacitance for small positive and negative surface charge. The polynomial value at zero surface charge then gives the required integral capacitance[36]. For the symmetrical SPM electrolyte considered here, the integral and differential capacitances are equal at zero surface charge, but this is not the case for asymmetrical electrolytes as then the integral capacitance → ±∞ at zero electrode potential. At the lower concentration $c$ = 1M, figure 2, the MPB+EVT is slightly higher than the simulation but has the correct qualitative behaviour for the considered range of $\sigma$. In contrast, the MPB5 is only qualitatively correct for $|\sigma| \leq 0.2\text{C/m}^2$, is larger than MPB+EVT in this region, and predicts a maximum at larger $|\sigma|$. Increasing the electrolyte concentration to 2.5M leads to the MPB+EVT capacitance being much higher than the simulation, but still qualitatively correct. In contrast the MPB5 is incorrect, having a single maximum at zero surface charge.

Figure 4 illustrates with the MPB+EVT theory how the SPM differential capacitance can change with increasing electrolyte concentration from a minimum at $\sigma = 0$ with a maximum at either side, to a single maximum at $\sigma = 0$. This capacitance behaviour is analogous to that of the RPM. The transition in Figure 4 at $\eta_{\text{tot}} = 0.32$ is at approximately $c$ = 3.01M. The reduced values corresponding to the approximate transition at c = 3.01M in Figure 4 are $\eta_{\text{ion}} = 0.12$, $T^* = (4\pi\varepsilon_0\varepsilon_r k_B T d)/(|z_+z_-|e^2) = 0.56$ and $\eta_{\text{ion}}$ does not include the solvent contribution. The overall transition envelope for $\eta_{\text{tot}} = 0.32$ in the reduced temperature $T^*$ and ion packing fraction $\eta_{\text{ion}}$ plane is shown in Figure 5. The transition envelope separates the region into two parts, a minimum from a maximum at $\sigma = 0$. Both the simulation and theoretical results indicate that the inclusion of the solvent shifts the envelope from the RPM envelope to higher ion densities. The simulation predicts a greater shift than that given by MPB+EVT. The theory also predicts that for $T^*$ approximately greater than 0.5 the SPM envelope is nearly independent of $T^*$.

The single maximum in the RPM capacitance occurs at relatively high electrolyte concentrations. The ions adjacent to the electrode form a densely packed layer which leads to counterions occupying second or higher order layers. Increasing the surface charge increases the thickness of the double layer, giving rise to the capacitance maximum. With the SPM the solvent molecules drive the structure of the electric double layer leading to density oscillations with layering and charge inversion. The neutral hard spheres give rise to a structured and more compact double layer than the RPM. At low surface charge coions can be found near the electrode while the counterions are located closer to the electrode surface. Thus the capacitance increases relative to the RPM and hence the electrolyte concentration of the transition increases. The simulation SPM envelope at fixed $\eta_{\text{tot}}$ is a nearly linear relation in the $T^*$ - $\eta_{\text{ion}}$ plane. Reducing the temperature $T^*$ increases the effect of the electrode electric field on the ions and the ionic correlations. Since $\eta_{\text{tot}}$ is fixed, the increase of $\eta_{\text{ion}}$ reduces the solvent density and so at low $T^*$ the envelope tends to the RPM behaviour.

## Conclusion

The SPM provides a first order treatment of the steric effects of the solvent in the electrolyte solution. Although the change in shape of the planar electric double layer capacitance has been well studied for the RPM, no exhaustive study has been made for the SPM. Progress in simulation techniques now provide accurate information for the SPM, including spherical[37] and cylindrical[38] geometries. Direct comparison with experimental results is difficult. In real aqueous electric double layers the dielectric constant changes from about 6 in the vicinity of the electrode to about 78 in the bulk. This means that there is some flexibility in the choice of $\varepsilon_r$. We have used 78.5 which is relevant for the diffuse part of the electric double layer, but overestimates the capacitance values. A small $\varepsilon_r$ should give better capacitance results but the important electrostatic correlation effects will be overestimated. A more appropriate model would explicitly treat an inner layer with a low permittivity[3,39,40]. The molar concentration of pure water ~ 55.5M so assuming its diameter is 300pm, then its packing fraction is 0.47. Unfortunately this value of 0.47 cannot be obtained by either the MPB theory or simulation. Due to the molecules being of equal size in the model, the solvent has the larger size of 400pm. Since the important fixed parameter is the total packing fraction $\eta_{\mathrm{tot}}$, which depends on the solvent diameter, the solvent concentration is lower than that of water. We expect that the present results signal the correct qualitative behaviour in the thermodynamic properties due to the solvent size.

In I the influence of size of the solvent molecules on the electric double layer properties was considered using simulation and the MPB+EVT theory. Here the MPB5 theory is also considered, but only for the equisized ion and solvent case. The MPB5 is an accurate theory for the RPM, but is failing for the SPM. Although the capacitance is qualitatively correct at the lower electrolyte concentration and lower surface charges, the MPB5 has a maximum at $\sigma = 0$ for the higher electrolyte concentration $c = 2.5$M. A maximum does occur in the SPM capacitance, but at a higher electrolyte concentration for a given $\eta_{\mathrm{tot}}$. The simulation results indicate that the transition envelope at fixed $\eta_{\mathrm{tot}}$ is at higher ion densities than the RPM envelope, with an approximate linear behaviour in the $T^*$ - $\eta_{\mathrm{ion}}$ plane. The MPB+EVT also predicts a shift to higher ion densities than that of the RPM, but the shift is less and for values of $T^*$ approximately greater than 0.5, the envelope is nearly independent of $T^*$. One possible cause of the relative failure of the MPB+EVT theory stems from the use of the Percus-Yevick[41] distribution function for uncharged hard spheres in the exclusion volume term, see I. The inclusion of solvent molecules leads to a structured electric double layer, in contrast to the RPM case, giving rise to the shift in the SPM envelope to higher electrolyte concentrations. A decrease in temperature means an increase in the effect of the electric field of the electrode and of the ionic correlations, leading at low $T^*$ to the SPM and RPM envelopes having a similar behaviour.

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## Figure captions

Fig. 1 The dependence of the MPB+EVT RPM differential capacitance on the electrode charge density for the electrolyte concentration *c* varying from 0.5 to 5.0 M with steps of 0.5 M.

Fig. 2 Dependence of the SPM integral capacitance on the electrode charge density for the packing fraction $\eta_{\mathrm{tot}} = 0.32$ at the electrolyte concentration $c = 1.00$ M (symbols– GCMC, dashed line – MPB+EVT, solid line – MPB5).

Fig. 3 Dependence of the SPM integral capacitance on the electrode charge density for packing fraction $\eta_{\mathrm{tot}} = 0.32$ at the electrolyte concentration $c = 2.50$ M (symbols– GCMC, dashed line – MPB+EVT, solid line – MPB5).

Fig. 4 The dependence of the MPB+EVT SPM differential capacitance on the electrode charge density at packing fraction $\eta_{\mathrm{tot}} = 0.32$ for the electrolyte concentration c = 2.50 M (dotted line), 3.010 M (solid line) and 3.50 M (dashed line).

Fig. 5 The transition envelope of the MPB+EVT theory for the RPM electrolyte (dashed line), SPM electrolyte $\eta_{\mathrm{tot}} = 0.32$ (solid line) and of the GCMC simulations for the RPM electrolyte[34] (circles) and for SPM electrolyte (squares).

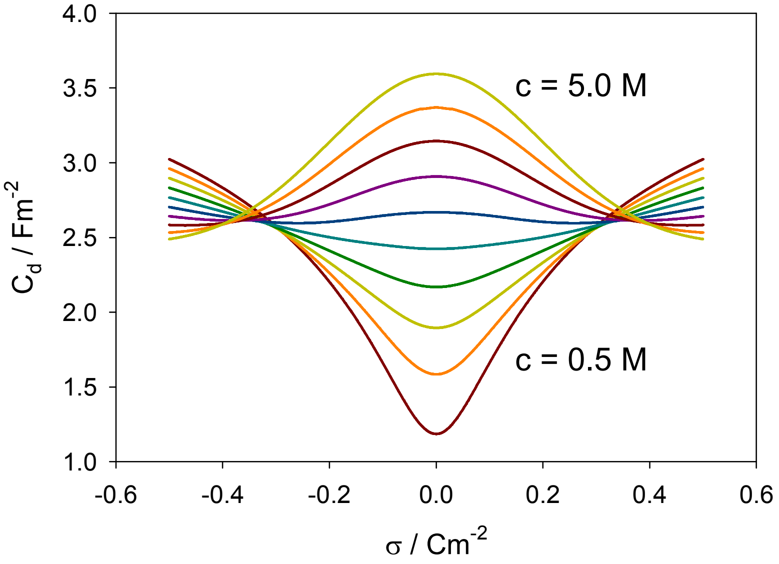

Fig. 1

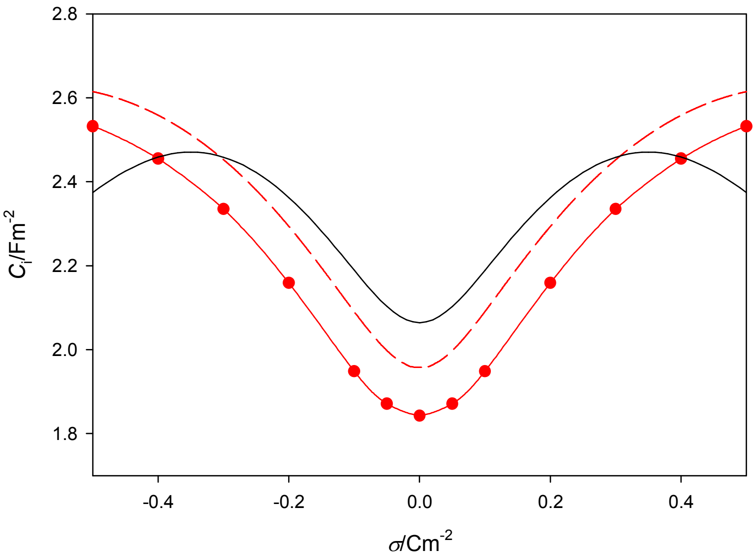

Fig. 2

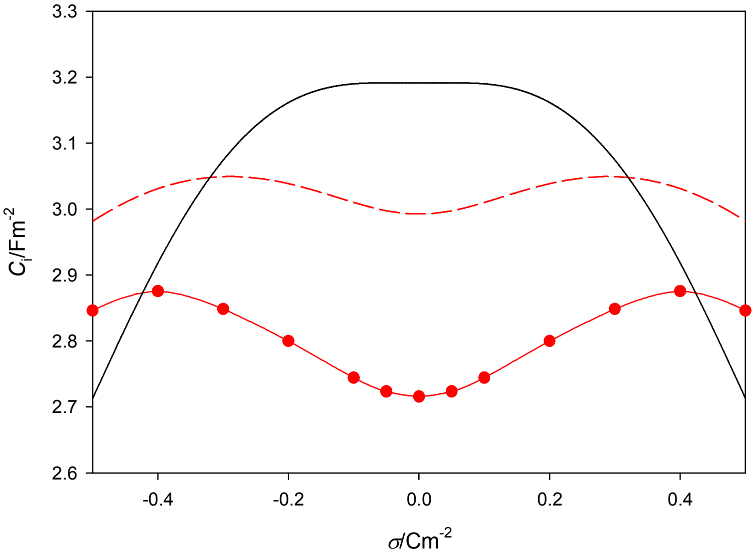

Fig. 3

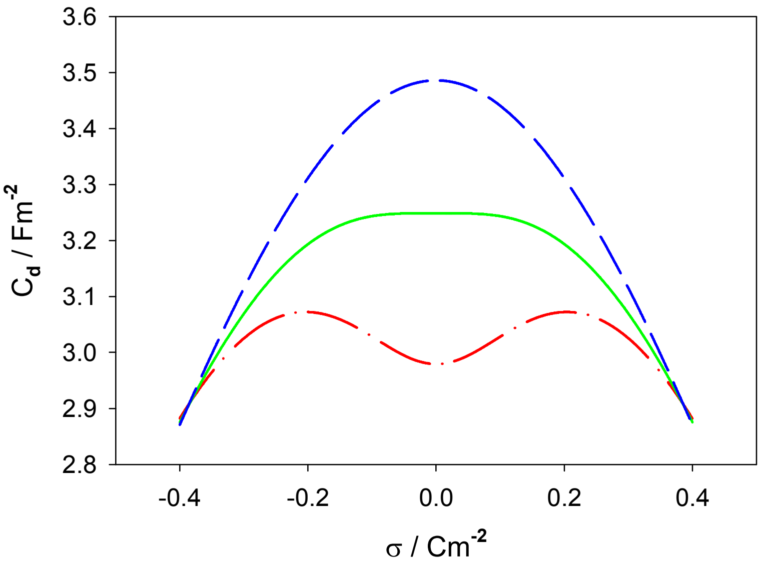

Fig. 4

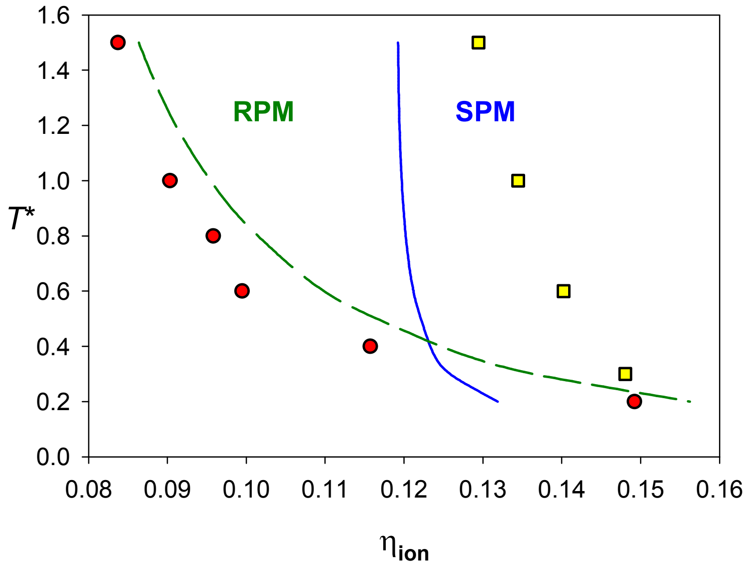
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Fig. 5