

THE STRUCTURE OF SIZE-ASYMMETRIC ELECTROLYTES AT CHARGED SURFACES: THE UNRESTRICTED PRIMITIVE MODEL IN THE HNC/MSA APPROXIMATION

U. MARINI BETTOLO MARCONI, J. WIECHEN and F. FORSTMANN

*Institut für Theoretische Physik, Freie Universität Berlin
Arnimallee 14, D-1000 Berlin 33, Federal Republic of Germany*

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Results are presented of ion density distribution functions, potential of zero charge and differential capacitance calculated for a primitive model electrolyte with hard core ions of unequal size near an electrode surface. The hypernetted chain/mean spherical approximation (HNC/MSA) is used. Comparing with the modified Gouy–Chapman (MGC) theory we emphasize the effects of size asymmetry.

1. Introduction

A starting point for the understanding of the properties of the metal–electrolyte interface is the well-known modified Gouy–Chapman (MGC) theory [1–3]. An important drawback of this theory is the neglect of short-range correlations between the ions in the electrical double layer. Within the framework of the modified Poisson–Boltzmann (MPB) theory [4,5], modern integral equation theories [6–11] and Monte Carlo calculations [12] there have been extensive investigations of the structure of the restricted primitive model (RPM) electrolyte, in which the ion sizes and valences are equal for the two species and the solvent is replaced by a homogeneous background of dielectric constant ϵ , in front of a charged hard wall, thereby assessing the most important particle size effects.

The assumption of equal size ions is a good approximation only for a limited number of solutions. Therefore Valleau and Torrie [13] and Bhuiyan et al. [14] have solved the MGC model for the asymmetric electrolyte. This model exhibits a concentration dependent potential of zero charge (pzc), i.e. a dipolar charge distribution with a potential step in front of the uncharged electrode. While in their calculation the size difference is only accounted for by postulating two different planes of closest approach for the two spe-

cies, it is now interesting to examine the size difference effects in a theory, which also includes the short-range correlations between the ions. Such an investigation would allow to describe the concurring electrostatic and short-range effects in the double layer, which is very important in explaining the behaviour of the differential capacity. In this paper we present the results of solutions of the integral equations in the hypernetted chain/mean spherical approximation (HNC/MSA).

2. HNC/MSA equations

The density profile of species λ of valence z_λ , ion diameter σ_λ and bulk density ρ_λ^B in front of the wall (at $x = 0$) is given by

$$\begin{aligned} \rho_\lambda(x) &= \rho_\lambda^B \exp[-\beta z_\lambda e\psi(x) - \beta\mu_\lambda(x)] , \\ & \quad x \geq \sigma_\lambda/2 ; \\ & = 0 , \quad x \leq \sigma_\lambda/2 , \end{aligned} \quad (1)$$

where $\beta = 1/kT$ is the inverse temperature. $\psi(x)$ is the electrostatic potential, which satisfies the one-dimensional Poisson equation

$$d^2\psi(x)/dx^2 = -(4\pi/\epsilon) \sum_\lambda z_\lambda e\rho_\lambda(x) \quad (2)$$

subjected to the boundary conditions

$$d\psi/dx|_{x=0} = -(4\pi/\epsilon)\omega, \quad (3)$$

$$\psi(x) \rightarrow 0, \quad \text{as } x \rightarrow \infty, \quad (4)$$

where ω is the surface charge.

$\mu_\lambda(x)$ is that part of the potential of mean force of species λ , which is due to the finite size of the ions and not included in $\psi(x)$. It is neglected in a MGC calculation. In the HNC it has the form [7-10]

$$\begin{aligned} \mu_\lambda(x) = 2\pi kT \sum_\nu \int_{-\infty}^{\infty} dy [\rho_\nu^B - \rho_\nu(y)] \\ \times \int_{|x-y|}^{\infty} ds s c_{\lambda\nu}^{SR}(s), \end{aligned} \quad (5)$$

where $c_{\lambda\nu}^{SR}(s)$ is the short-range part of the bulk direct correlation function $c_{\lambda\nu}(s)$ given by

$$c_{\lambda\nu}^{SR}(s) = c_{\lambda\nu}(s) + \beta z_\lambda z_\nu c^2 / \epsilon s. \quad (6)$$

In our calculations we use the direct correlation functions in the MSA and take their values from the analytic solution given by Blum and Höye [15].

Eqs. (1)-(5) have been solved numerically. Details of the procedure will be given elsewhere [16].

3. Results

We consider a monovalent solution at room temperature ($T = 298$ K) with the dielectric constant of water ($\epsilon = 78.5$) and choose the ion diameters like Valleau and Torrie [13] in the following way: $\sigma_- = 4$ Å, $\sigma_+ = 9.2$ Å, $\sigma_+/\sigma_- = 2.3$.

As in the MGC theory we find that the absolute value of the pzc increases practically linearly with the square root of the concentration c , always being only a few percent larger than the corresponding MGC values (fig. 1). This behaviour can easily be interpreted in terms of the density profiles at pzc, which are given in fig. 2 for a concentration of 0.1 M. Due to hard-sphere repulsions among the ions they pile up near the wall. The electrolyte appears more concentrated in this region. Therefore the HNC/MSA results have the tendency to behave like MGC results for higher concentration. The partial densities of both species are enhanced (fig. 2), leading to a larger dipole mo-

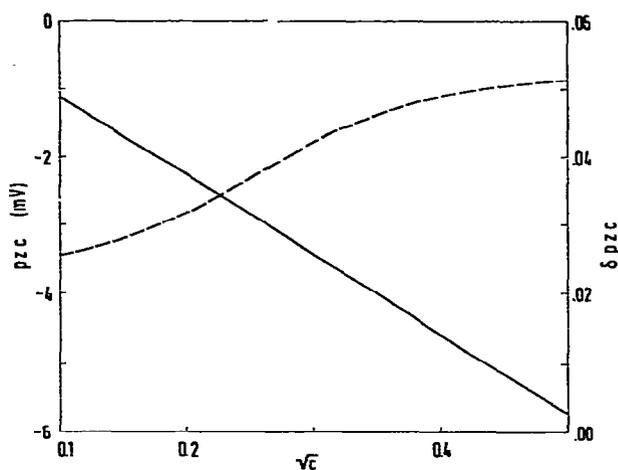


Fig. 1. Dependence of the potential of zero charge (pzc) on concentration according to the HNC/MSA theory (full curve) and its relative deviation from the MGC curve $\delta pzc = |pzc(\text{HNC/MSA})/pzc(\text{MGC}) - 1|$ (dashed curve).

ment of the charge distribution and a larger pzc. Since with increasing concentration hard-sphere repulsions become more important, the relative deviation from the MGC result grows (fig. 1).

Fig. 3 shows a comparison between the HNC/MSA and MGC differential capacities given by

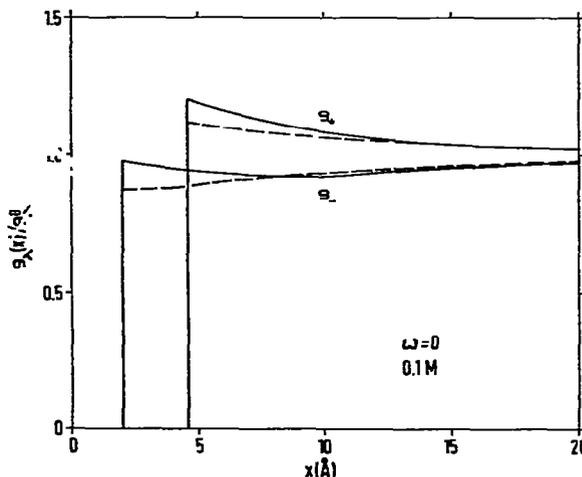


Fig. 2. Reduced density profiles for a 0.1 M monovalent primitive model electrolyte with different ion diameters ($T = 298$ K, $\epsilon = 78.5$, $|z_\lambda| = 1$, $\sigma_+ = 9.2$ Å, $\sigma_- = 4$ Å) at zero surface charge. The full and dashed curves give the HNC/MSA and MGC results, respectively.

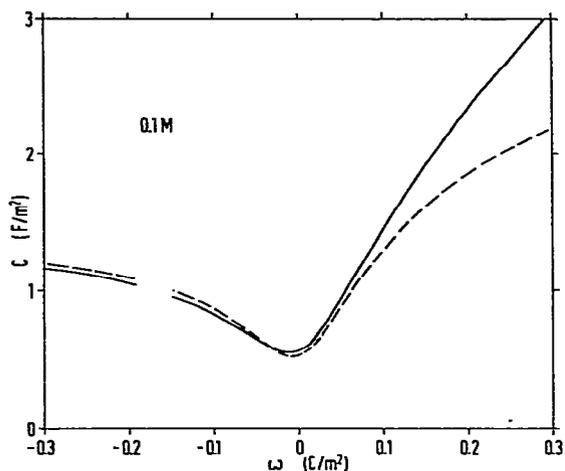


Fig. 3. Surface charge dependence of the differential capacity. Parameters and meaning of curves as for fig. 2.

$$C = \partial\omega/\partial\psi(0) \quad (7)$$

as a function of surface charge for 0.1 M. The asymmetry already present in the MGC calculation [13] is increased by the hard-sphere correlations. In order to understand this, one can look at the density profiles for two relatively high surface charges of same magnitude and opposite sign ($\omega = \pm 0.3 \text{ C/m}^2$).

For positive electrode charge (fig. 4a) HNC/MSA predicts for the counterion density a magnification near the electrode and a reduction further away compared to MGC, while for the co-ion density it does the opposite, which is a sign of a better screening. Therefore $\psi(0)$ is decreased and the differential capacity increased. The same effect has been seen in calculations for equal size ions [4–12] and it is clear that for high surface charges, when one species dominates, the unequal size results must parallel those of the equal size ones.

For negative surface charges the very large positive ions ($\sigma_+ = 9.2 \text{ \AA}$) are attracted towards the surface. Their screening capability is hampered by packing problems. The density profile (fig. 4b) shows a second peak near $x = 13.8 \text{ \AA} = 1.5 \sigma_+$, which is the location of a second layer of countercharge further away from the surface. This spreading of the screening charge increases the surface potential and decreases the differential capacity even below the MGC value (fig. 3).

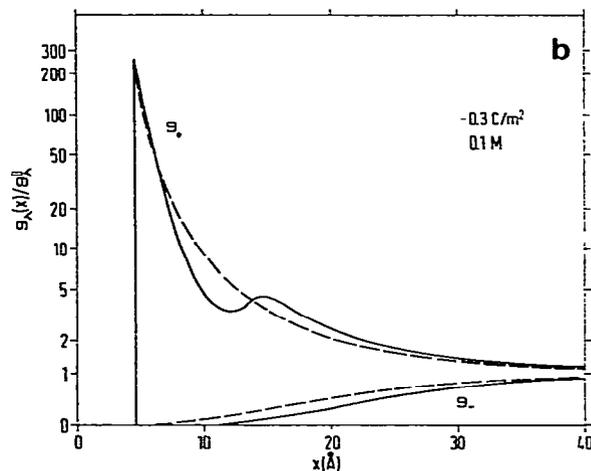
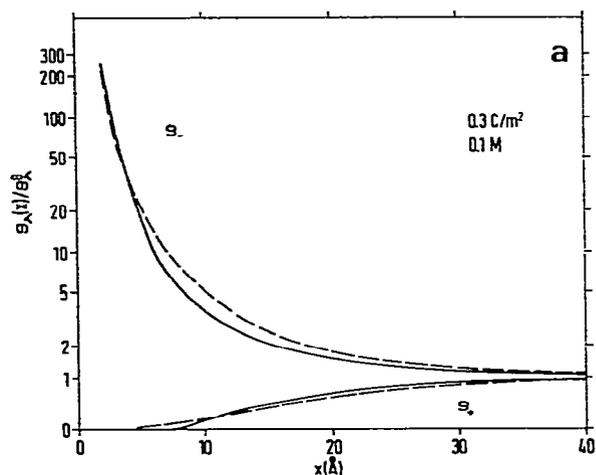


Fig. 4. (a) As for fig. 2, but with surface charge. $\omega = 0.3 \text{ C/m}^2$. An arsh vertical scale is used. (b) As for fig. 2, but with surface charge. $\omega = -0.3 \text{ C/m}^2$. An arsh vertical scale is used.

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