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NONPRIMITIVE ELECTROLYTE NEAR A CHARGED WALL: GENERALIZED MEAN --ETC(U)

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Nonprimitive Electrolyte Near a Charged Wall:  
Generalized Mean Spherical Approximation

by

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## INTRODUCTION

Much of the recent work on the statistical mechanics of the electrical double layer has focused on the application of theories based upon integral equations to models where the solvent is assumed to be structureless. These theories are an improvement of the classical Poisson-Boltzmann theory of Gouy [1] and Chapman [2], mainly because they give a better treatment of the short-ranged part of the ionic interactions. However, the influence of the solvent structure on the electrode-electrolyte interface is well recognized [3]. It is thus desirable to extend the integral equation approach to models where the solvent is another molecular species.

In this communication we consider a simplified model of an electrode-electrolyte interface which takes into account the discreteness of the solvent (Fig. 1). The electrode is represented as a hard infinite plane with a uniform surface charge density, while the electrolytic solution is modeled as a mixture of charged hard spheres (the ions) and dipolar (nonpolarizable) hard spheres (the solvent). In addition, we assume the electrode has a dielectric constant unit; thus we ignore the image effects. For this model we developed a treatment in which all the interactions (ion-ion, ion-solvent, solvent-solvent, electrode solution) are considered on the same (classical) statistical mechanical basis. In particular the solvent is taken as a fully orientable system and no special treatment of a hypothetical inner layer is made.

Blum and Henderson [4] and also Carnie and Chan [5] have studied this model within the mean spherical approximation (MSA), the simplest known integral equation. We have considered elsewhere [6] the application of another integral equation, related to the MSA, which may be referred as a generalized MSA (GMSA). In this approximation the Ornstein-Zernike (O-Z) equation for the particle-particle and electrode-particle correlations

is solved for closures which are generalizations of those of the MSA. The correlation functions thus obtained give information of the micro-structure of the system and also permit the evaluation of several thermodynamic and electrostatic properties of the interface. Here we present some further GMSA calculations of some of these properties which complement those of Reference [6].

## THEORY

### a. Electrode-Particle Correlation Functions

We divide the total ( $h$ ) and direct ( $c$ ) electrode-ion and electrode-dipole correlation functions into a nonelectrostatic and an electrostatic part

$$\begin{aligned} h_{\pm}(x) &= h_0(x) \pm h_1(x) \\ h_d(x, \theta) &= h_0(x) + \sqrt{3} h_d(x) \cos \theta \end{aligned} \quad (1a)$$

$$\begin{aligned} c_{\pm}(x) &= c_0(x) \pm c_1(x) \\ c_d(x, \theta) &= c_0(x) + \sqrt{3} c_d(x) \cos \theta, \end{aligned} \quad (1b)$$

$x$  and  $\theta$  being, respectively, the reduced distance ( $x/D$ ) from the electrode and the angle between the direction of the dipoles and the normal to the electrode.

The impenetrability of the hard wall implies that

$$\begin{aligned} h_0(x) &= -1 \\ h_1(x) = h_d(x) &= 0, \quad x < \frac{1}{2}. \end{aligned} \quad (2)$$



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and we assume

$$c_0(x) = A_0 e^{-z_0 x}$$

$$c_i(x) = E^* q^* x + A_i e^{-z_i x},$$

$$c_d(x) = \frac{E^* \mu^*}{\sqrt{3}} + A_d e^{-z_d x}, \quad x > \frac{1}{2}, \quad (3)$$

where  $A_\alpha$ ,  $z_\alpha$  ( $\alpha=s,i,d$ ) are parameters to be determined. When  $A_s=A_i=A_d=0$  we recover the MSA closures [4]. In Eq. (3) we use the dimensionless quantities  $q^{*2}=\beta q^2/D$ ;  $\mu^{*2}=\beta \mu^2/D^2$  and  $E^*=(\beta D^3)^{1/2}E$  ( $E=4\pi\sigma$ ),  $\beta$  being the Boltzmann thermal factor  $(k_B T)^{-1}$ .

If we consider row matrices  $\underline{M}=[M_i, M_d]$ , then the O-Z equation for the wall-particle correlation functions becomes [6,7]

$$h(x) = f(x) + \int_0^x dt h(x-t) \underline{Q}_B(t), \quad x > \frac{1}{2}, \quad (4)$$

where

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{-ikx} \tilde{\underline{C}}(k) \left[ \tilde{\underline{Q}}_B^\dagger(-k) \right]^{-1} \quad (5)$$

with

$$\tilde{\underline{C}}(k) = \int_{1/2}^{\infty} dx e^{ikx} \underline{C}(x) \quad (6)$$

and

$$\tilde{\underline{Q}}_B(k) = I - \int_0^{\infty} dr e^{ikr} \underline{Q}_B(r). \quad (7)$$

Here  $\underline{Q}_B(r)$  is the Baxter matrix of the electrolyte and is of the form

$$\underline{Q}_B(r) = \begin{bmatrix} Q_{ii}(r) & Q_{id}(r) \\ Q_{di}(r) & Q_{dd}(r) \end{bmatrix}. \quad (8)$$

Similar relations (involving scalars) are valid for the nonelectrostatic terms [8].

We have obtained explicit expressions for  $Q_B(r)$  in the MSA [9,10] and GMSA [11] as simple sums involving powers of  $r$  and exponential functions of  $r$ . If we use the Eq. (3) with  $A_\alpha = 0$  ( $\alpha = s, i, d$ ) as the closure of the O-Z equation [Eq. (4)] we have a MSA/MSA or a MSA/GMSA calculation according to whether we use the bulk MSA or GMSA expressions for  $Q_B$ .

If we consider instead  $A_\alpha, z_\alpha$  ( $\alpha = s, i, d$ ) as adjustable parameters we have a GMSA/MSA calculation when  $Q_B$  (MSA) is used or a GMSA/GMSA calculation if  $Q_B$  (GMSA) is utilized. In both these last cases we can obtain the parameters demanding that the correlation function satisfy the linearized hypernetted chain (LHNC) [12] conditions

$$h_\alpha(x = \frac{1}{2}) = \exp[\eta_\alpha(x = \frac{1}{2})] - 1 \quad (\alpha = +, -) \quad (9a)$$

$$h_d(x = \frac{1}{2}) = [h_s(x = \frac{1}{2}) + 1] \eta_d(x = \frac{1}{2}) \quad (9b)$$

$$h'_\alpha(x = \frac{1}{2}) = \eta'_\alpha(x = \frac{1}{2}) \exp[\eta_\alpha(x = \frac{1}{2})] \quad (\alpha = +, -) \quad (9c)$$

$$h'_d(x = \frac{1}{2}) = h'_s(x = \frac{1}{2}) \eta_d(x = \frac{1}{2}) + [h_s(x = \frac{1}{2}) + 1] \eta'_d(x = \frac{1}{2}), \quad (9d)$$

where

$$\eta_\gamma(x) = h_\gamma(x) - c_\gamma(x) - \beta U_\gamma(x) \quad (\gamma = +, -, d) \quad (10)$$

with

$$\beta U_+(x) = -\beta U_-(x) = -E^* q^* x \quad (11a)$$

$$\beta U_d(x) = -\frac{E^* \mu^*}{\sqrt{3}} \quad (11b)$$

and

$$h(x = \frac{1}{2}) = f(x = \frac{1}{2}) \quad (12)$$

$$h'(x = \frac{1}{2}) = f'(x = \frac{1}{2}) + h(x = \frac{1}{2}) Q_B \quad (r = 0) \quad (13)$$

### b. Some Structural and Electrostatic Functions of the Interface

Once we obtain the total wall-particle correlation functions by numerical integration of Eq. (4) (adequate precision is obtained using the trapezoidal rule), we can evaluate

1 - The density profiles of the ions and the density-orientation profile of the dipoles

$$\begin{aligned}\rho_{\pm}(x) &= \rho_{\pm}[h_{\pm}(x) + 1] \\ \rho_d(x, \theta) &= \rho_d[h_d(x, \theta) + 1],\end{aligned}\quad (14)$$

2 - The charge density profile

$$\begin{aligned}q^*(x) &= \rho_i^* q^* h_i(x), \\ \text{where } \rho_i^* &= \rho_i D^3,\end{aligned}\quad (15)$$

3 - The polarization density profile

$$\begin{aligned}P^*(x) &= (\beta D)^{1/2} P(x) = \frac{\rho_d^* \mu^*}{\sqrt{3}} h_d(x), \\ \text{with } \rho_d^* &= \rho_d D^3, \text{ and}\end{aligned}\quad (16)$$

4 - The potential profile  $\phi^*(x) = (\beta D)^{1/2} \phi(x)$ , the solution of the Poisson equation,

$$\frac{d^2 \phi^*(x)}{dx^2} = -4\pi \left[ q^*(x) - \frac{dP^*(x)}{dx} \right], \quad (17)$$

which is given by

$$\begin{aligned}\phi^*(x) &= -4\pi \rho_i^* q^* \int_x^{\infty} dt (t-x) h_i(t) - \frac{4\pi}{\sqrt{3}} \rho_d^* \mu^* \int_x^{\infty} dt h_d(t) \\ &= \Delta \phi^* - E^* x + 4\pi \rho_i^* q^* \int_0^x dt (t-x) h_i(t) + \frac{4\pi}{\sqrt{3}} \rho_d^* \mu^* \int_0^x dt h_d(t),\end{aligned}\quad (18)$$

where  $\Delta \phi^* = \phi^*(x=0)$  is the total potential drop across the interface.

We obtain [6] analytical expressions for  $\Delta\phi^*$  and also for  $P^*$  the total polarization

$$\begin{aligned} P^* &= (\beta D)^{1/2} P = \frac{\rho_d^* \mu^*}{\sqrt{3}} \int_0^\infty dt h_d(t) \\ &= \frac{\rho_d^* \mu^*}{\sqrt{3}} \lim_{s \rightarrow 0} \hat{h}_d(s), \end{aligned} \quad (19)$$

$$\begin{aligned} \Delta\phi^* &= -4\pi \rho_i^* q^* \int_0^\infty dt th_i(t) - \frac{4\pi}{\sqrt{3}} \rho_d^* \mu^* \int_0^\infty dt h_d(t) \\ &= 4\pi \lim_{s \rightarrow 0} \left[ \rho_i^* q^* \frac{\partial \hat{h}_i(x)}{\partial s} - \frac{\rho_d^* \mu^*}{\sqrt{3}} \hat{h}_d(s) \right], \end{aligned} \quad (20)$$

where

$$\begin{aligned} \lim_{s \rightarrow 0} \hat{h}_d(s) &= -\frac{E^* \mu^*}{\sqrt{3} d_0 d_2} \frac{[a_1 T_{id} + a_2 (1 - T_{ii})]}{d_0 (1 - T_{dd;1})} \\ &+ \sum_{\alpha=i,d} \frac{A_\alpha}{z_\alpha d_0 (1 - T_{dd;1})} \left\{ \left[ \tilde{Q}_B^+(jz_\alpha) \right]_{ad}^{-1} a_1 - \left[ \tilde{Q}_B^+(jz_\alpha) \right]_{ai}^{-1} a_2 \right\}, \end{aligned} \quad (21)$$

$$\begin{aligned} \lim_{s \rightarrow 0} \frac{\partial \hat{h}_i(s)}{\partial s} &= \frac{E^* q^*}{d_0^2} \left\{ \frac{1}{2} + \frac{[(1 - T_{ii})(1 - T_{dd}) - T_{id} T_{di}]}{d_0 (1 - T_{dd;1})} \right\} \\ &+ \sum_{\alpha=i,d} \frac{A_\alpha}{z_\alpha d_0 (1 - T_{dd;1})} \left\{ \left[ \tilde{Q}_B^+(jz_\alpha) \right]_{ai}^{-1} (1 - T_{dd}) + \left[ \tilde{Q}_B^+(iz_\alpha) \right]_{ad}^{-1} T_{di} \right\}, \end{aligned} \quad (22)$$

and  $j = \sqrt{-1}$  and  $a_1$  and  $a_2$  are the non-null elements of the matrix

$$\Delta \equiv \begin{bmatrix} a_1 & a_2 \\ 0 & 0 \end{bmatrix} = - \lim_{r \rightarrow \infty} Q_B(r), \quad (23)$$

and  $T_{ii}$ ,  $T_{dd}$ , etc., are the elements of the matrix

$$I = \int_0^\infty dr [Q_B(r) + \Delta]. \quad (24)$$

The bulk strength parameters  $d_0$  and  $d_2$  are defined by

$$d_0^2 = 4\pi\rho_i^*q^{*2}; \quad d_2^2 = \frac{4\pi}{3}\rho_d^*\mu^{*2}. \quad (25)$$

Finally

$$(1 - T_{dd;1}) = [(1 - T_{dd})^2 + (T_{di})^2 - d_2^2]^{1/2}. \quad (26)$$

From Eq. (20) we can evaluate the differential capacity from

$$C_d^* = D C_d = \frac{1}{4\pi} \frac{\partial E^*}{\partial \Delta\phi^*} = \frac{1}{4\pi} \left( \frac{\partial \Delta\phi^*}{\partial E^*} \right)^{-1}. \quad (27)$$

## RESULTS

In Figs. 2 and 3 we show the charge and polarization density profiles calculated by using the *GMSA/GMSA*, *GMSA/MSA* and *MSA/MSA* approximations. The oscillations observed are consequence of the discrete character of the solvent. This follows from a simple observation of the corresponding curves resulting from models where the solvent is treated as a continuum [13,14].

In Fig. 4 we compare the potential profile for the three integral equations considered. Here again the oscillations are notable. The change in slope of the potential at the Helmholtz plane ( $x=1/2$ ), which implies a change of the direction of the electric field, is due to the large polarization at this plane. This is more clearly seen if we write

$$-\left. \frac{d\phi^*(x)}{dx} \right|_{x=1/2} = E^* - 4\pi P^* \left( x = \frac{1}{2} \right). \quad (28)$$

If we attempted to define a local dielectric constant in the impenetrable region or Stern layer [ $0 \leq x \leq 1/2$ ] by requiring that the electric displacement be continuous at  $x=1/2$  we

would arrive at a negative local dielectric constant in this region. This illustrates the difficulties and ambiguities associated with attempts to define a local dielectric constant. The point is that the dielectric constant is a macroscopic quantity, computed using an infinitely large volume, and any attempts to define a local dielectric constant will lead to inconsistencies.

Figures 5 and 6 show the differential capacity as a function of the total potential drop across the complete double layer. The MSA/MSA curve is independent of  $\Delta\phi$  and so is unphysical except near  $\Delta\phi=0$ . The other two curves are more reasonable and, in particular, show the differential capacitance increasing with the magnitude of the potential. Ultimately, we expect GMSA differential capacitance curves to flatten.

## CONCLUSIONS

The MSA gives considerable insight into the structure and properties of the double layer. However, it has the drawback that the MSA results are linear in the charge density on the electrode. The GMSA results presented here overcome this difficulty. These results represent our first attempt to apply the GMSA and have some difficulties. For example, the density profiles do not satisfy the contact value conditions of Blum and Henderson [4]. We expect to develop other and better schemes for choosing the GMSA parameters in the near future.

In contrast to the featureless curves of the Gouy-Chapman theory, the MSA and GMSA ionic profiles, potential profile and polarization density show oscillations which imply a layering of sheets of alternating charge near the electrode. These oscillations are even more pronounced in the GMSA than in the MSA. In contrast the differential capacitance curves are rather featureless. In view of the simplicity of our model which ignores the

interaction of the metal with the double layer and which is based on a oversimplified picture of the solvent, the differential capacitance curves are reasonable, especially considering that we have not attempted to adjust any parameters to fit any experimental data.

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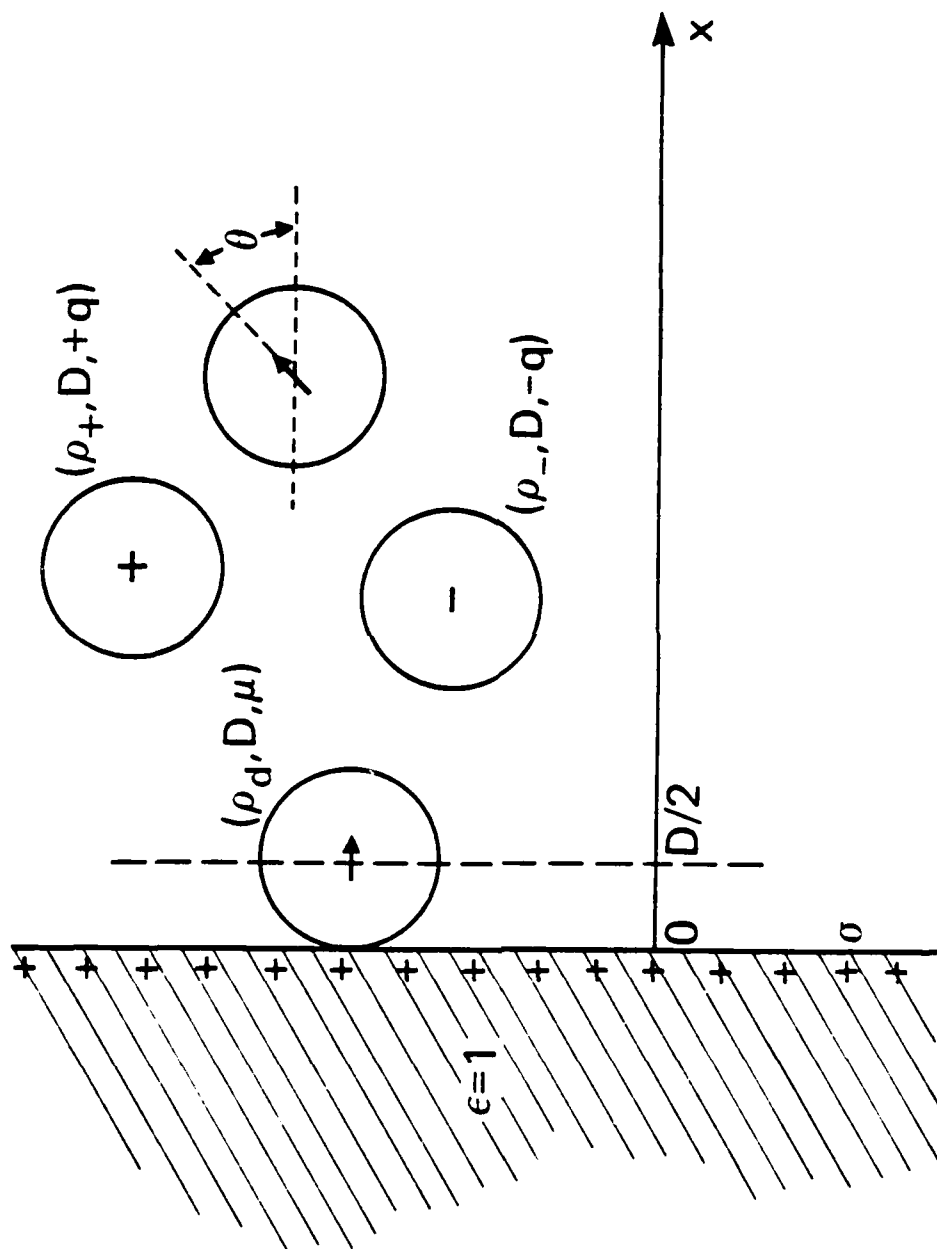


Figure 1. The model of the electrode-electrolyte interface  $\rho_+ = \rho_- = \rho_i/2$  (ionic number density),  $\rho_d$  (solvent number density),  $D$  (diameter of all the hard spheres in the mixture),  $\mu$  (dipolar moment of the solvent molecules),  $\sigma$  (surface charge density),  $\epsilon$  (dielectric constant of the electrode).

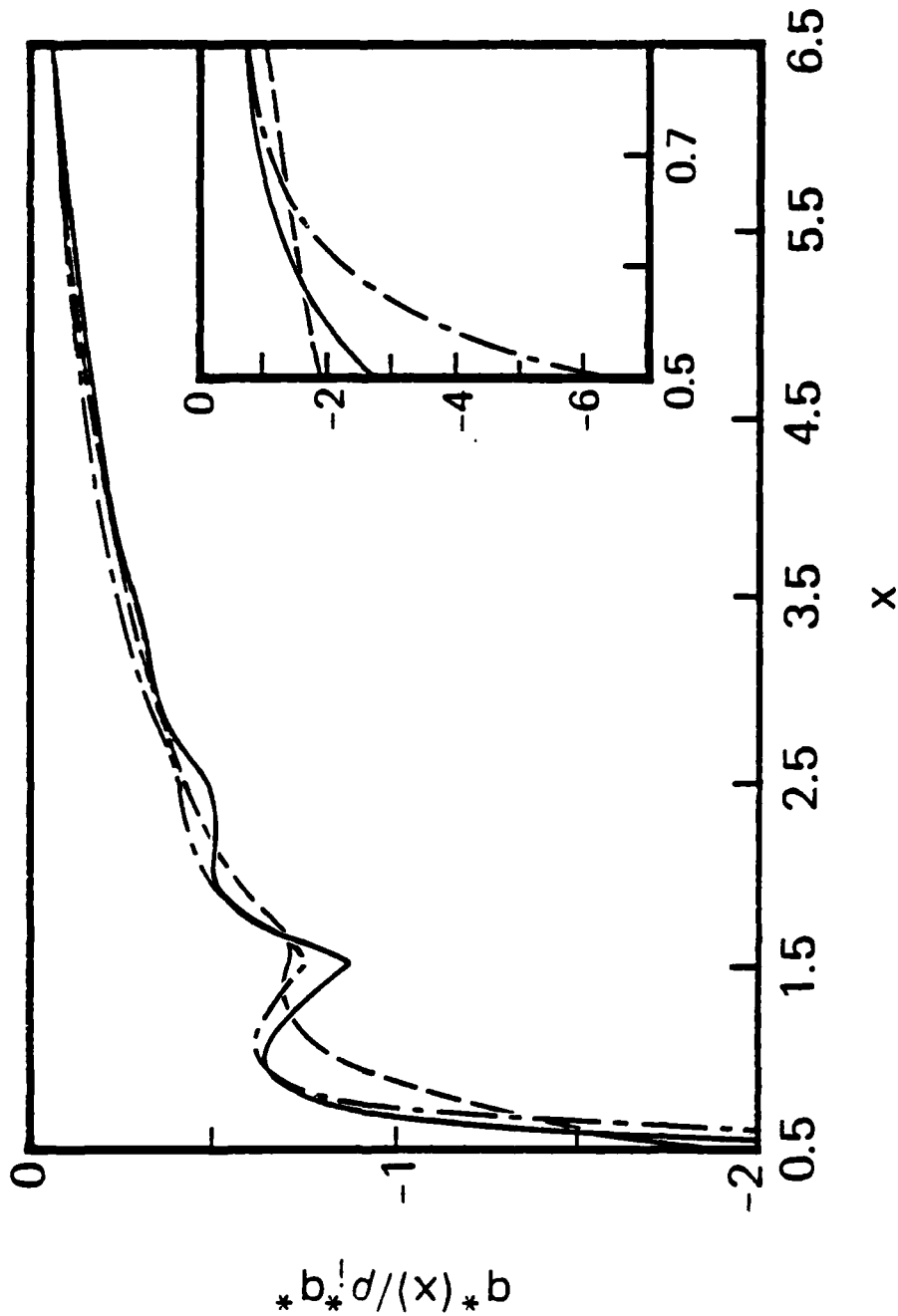


Figure 2. The normalized charge density profile  $q^*(x)/\rho_i^*q^* = h_i(x)$  for a nonprimitive electrolyte ( $q^*=40$ ,  $\mu^{*2}=2.5$ ,  $\rho_i^* = 0.007$ ,  $\rho_d^* = 0.6$ ) near a charged hard wall ( $E^*=1.5$ ).  
 — GMSA/GMSA, - - - - GMSA/MSA, - · - · - MSA/MSA.

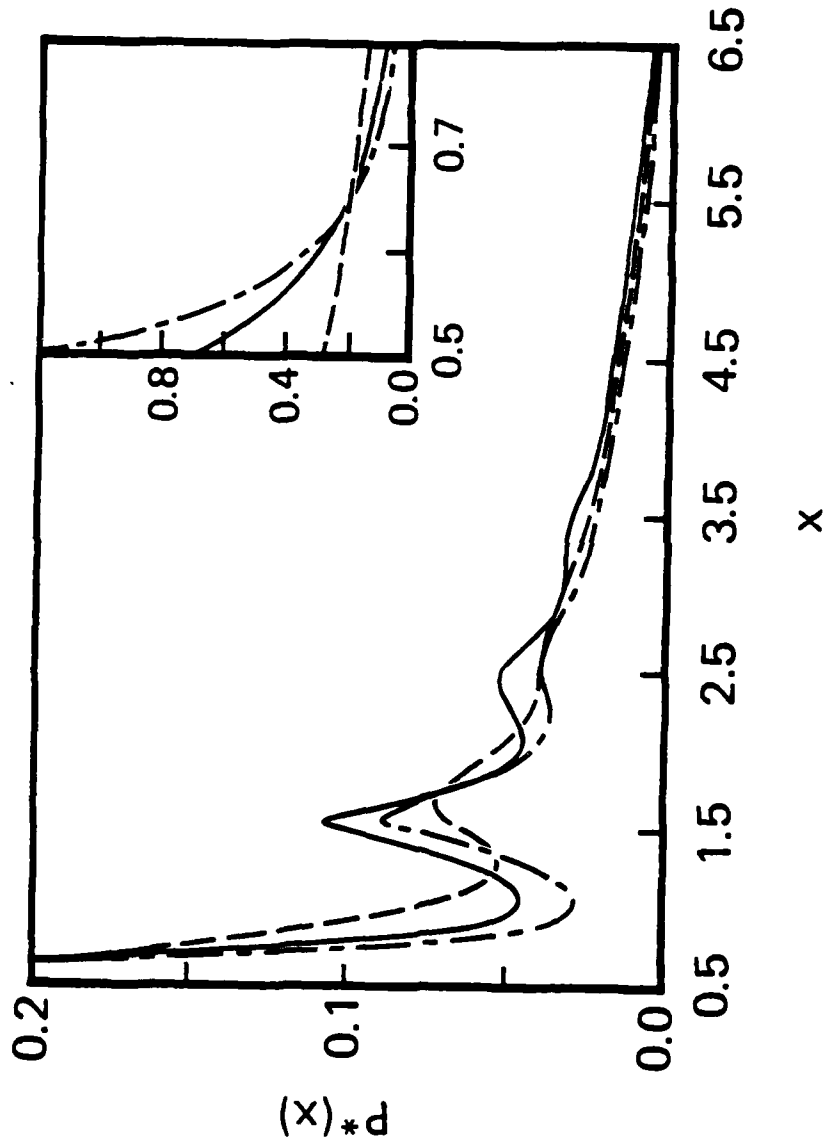


Figure 3. The reduced polarization density profile  $P^*(x)$ . The system and notation are the same as in Fig. 2.

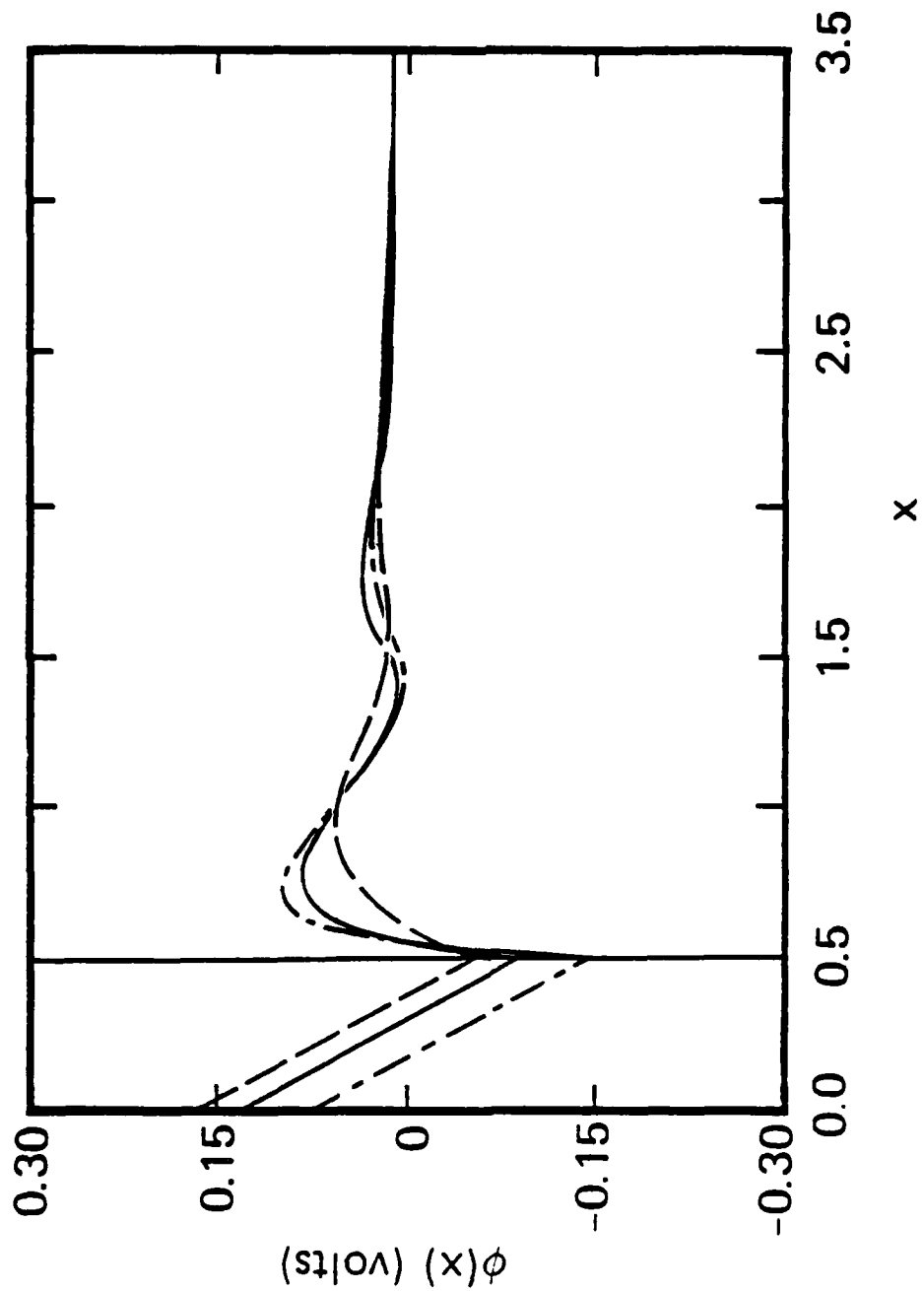


Figure 4. The potential profile for the same system of Fig. 2. ( $D=0.4\text{nm}$ ,  $T=298.15\text{K}$ ,  $C=0.1\text{ mol/P}$ ). — GMSA/GMSA, - - - GMSA/MSA, - · - · - MSA/MSA.

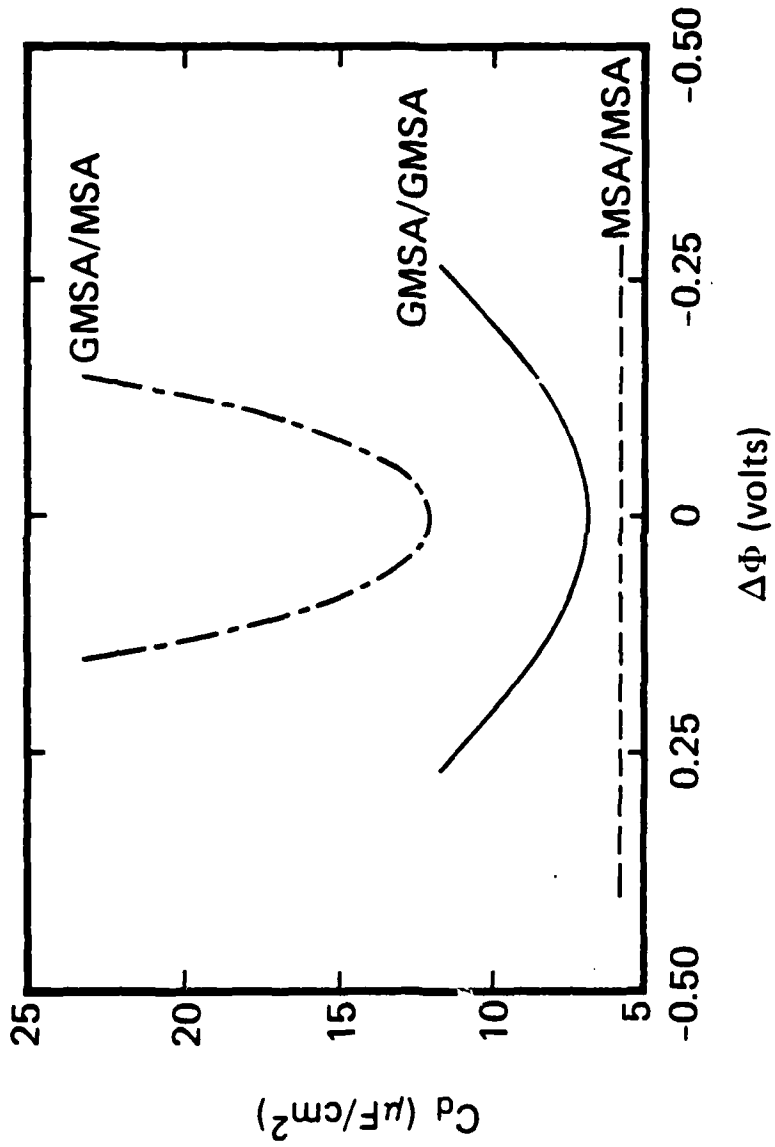


Figure 5. The differential capacity vs. the potential drop across the interface. The system is the same as in Fig. 4.

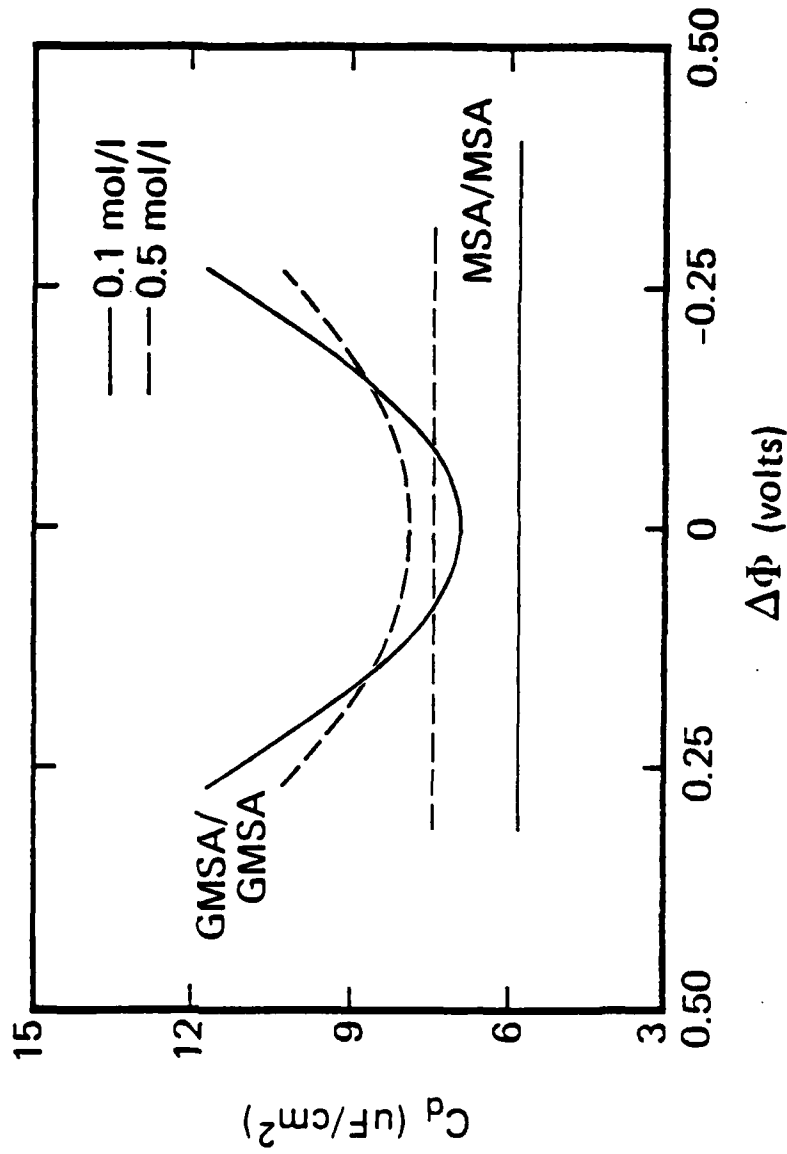


Figure 6. The differential capacity vs. the potential drop across the interface for two different concentrations of electrolyte. The remaining parameters are the same as in Fig. 4.