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# Ion Distributions in a Cylindrical Capillary as Seen by the Modified Poisson–Boltzmann Theory and Monte Carlo Simulations

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The distributions of ions enclosed in a charged cylindrical capillary with impenetrable surfaces are studied by using (i) the Poisson–Boltzmann theory, (ii) the modified Poisson–Boltzmann theory, and (iii) the Monte Carlo method. The ions are treated in the primitive model approximation, while the inner surface of the capillary is taken to have a uniform charge density. The results for the wall-ion distributions are presented for the capillary containing mono- or divalent counterions and size symmetric 1:1 or 2:2 electrolytes. Some calculations for the mean activity coefficients of the added electrolytes are also reported. The Monte Carlo results for the concentration profiles and the electrolyte activities are used to assess the validity of the potential theories. The modified Poisson–Boltzmann theory is found to be in good agreement with the simulation results for both mono- and divalent ions present in the solution. As expected, the regular Poisson–Boltzmann theory provides reasonable descriptions of solutions containing monovalent ions but fares relatively poorly in describing systems where divalent ions are present.

## 1. Introduction

Partitioning of solute molecules between small liquid-filled pores and bulk solution plays an important role in several separation processes. For example, a material containing charged micropores surrounded by a bulk electrolyte often contains a different concentration of ions than the surrounding solution (see, for example, reviews).<sup>1–3</sup> The ability of a porous material to exclude electrolyte forms the basis of important technological processes for desalination of water: one process is known as reverse osmosis or hyperfiltration.<sup>4–6</sup> In analyzing experimental data it is useful to have a predictive theory to relate the measurable quantities to the molecular properties of electrolyte solution such as the size and valency of ions and solvent properties. For a quantitative description of the equilibrium properties, as well as the electrokinetic phenomena, a suitable model of the porous phase is needed. In several previous works<sup>7–15</sup> (see ref 2 for a more complete bibliography) the porous material was pictured as an array of noninteracting cylindrical micropores of infinite length and with the fixed charge distributed on the inner surface. The representative average micropore is assumed to be electroneutral, mimicking a macroscopic part of the porous material. The electrolyte in a representative micropore may be assumed to be in equilibrium with a bulk electrolyte of the same chemical composition. To obtain the thermodynamic and transport properties of the confined electrolyte, the spatial distributions of the small ions within the micropore must be calculated. Traditionally, these distributions were obtained via the Poisson–Boltzmann (PB) approximation, but in recent years other theoretical approaches have also been used.<sup>2,3,8–15</sup> Among theoretical techniques computer simulations certainly play an important role, since they are able to provide accurate data for a chosen model. Both the

Monte Carlo (MC)<sup>2,3,8–11</sup> and Molecular Dynamics (MD) methods<sup>12,13</sup> have been used to calculate the ionic profiles and some thermodynamic parameters for various model electrolytes in cylindrical micropores. In this context mention must be made of the hypernetted-chain/mean-spherical (HNC/MSA) theory adapted for these systems by Lozada-Cassou and co-workers.<sup>3,14,15</sup> The HNC/MSA approach and especially the three point extension of the HNC theory<sup>3</sup> are quite accurate in description of the electrical double layer in a planar or a nonplanar symmetry.

The computer simulations, as also the implementation of some of the sophisticated theories mentioned above, are often time-consuming and numerically involved. For this reason the traditional PB approximation is still the first choice for a quick and routine analysis of experimental data (see, for example, refs 4 and 5). By comparison with computer simulations it is known<sup>2,8–10</sup> that the PB theory yields accurate results only for monovalent ion systems and moderate charge densities on the inner capillary surface. It was demonstrated,<sup>2,3,8–10</sup> that this theory breaks down when divalent ions are present in the capillary. The demand is therefore for a numerically more tractable but accurate theory which could be used in a daily analysis of the experimental results.

Previous studies have indicated<sup>16–21</sup> that the modified Poisson–Boltzmann (MPB) theory leads to a good description of the electrical double layer in various geometries. In particular, the MPB was found to be accurate vis-à-vis the MC simulations and/or the HNC/MSA theory for the planar,<sup>16</sup> spherical,<sup>17,18</sup> and cylindrical<sup>19–21</sup> double layers. We therefore thought it of interest to apply the MPB formalism to the capillary problem. In this paper we have employed the MPB for some exploratory calculations to predict the ionic profiles and some thermodynamic properties of a primitive model electrolyte enclosed within a hard cylindrical micropore with a uniform distribution of charge on the inner surface. Two situations were considered: (i) a charged micropore with an equivalent number of

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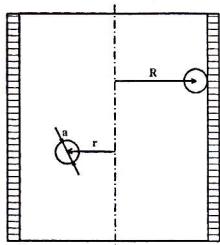


Figure 1. Cross section through the model capillary.

mono- or divalent counterions (no co-ions present) and (ii) a charged micropore enclosing a 1:1 or a 2:2 model electrolyte. In the latter case the electrolyte was assumed to be in equilibrium with an external (bulk) electrolyte of the same chemical composition. In both cases the charge on the inner surface is canceled exactly by the extra ions in the capillary. Parallel canonical MC simulations were performed for the same system with the ionic profiles being evaluated using Widom's method<sup>22</sup> in addition to the usual histogram method. Widom's particle insertion technique is subject to smaller uncertainties than the histogram method where the distributions are obtained from bins having a finite width. Furthermore, Widom's method allows calculations of the ion concentrations at the capillary surface (contact values) and in the middle of the micropore (where the electrostatic field is zero), thus avoiding an uncertain extrapolation procedure. The excess chemical potential (logarithm of the mean activity coefficient) of the electrolyte inside the micropore can be calculated using the same method.<sup>22,23</sup> These new MC data are used here to provide a critical evaluation of the MPB and PB predictions for the ionic profiles and the mean activity coefficient of the enclosed electrolyte.

## 2. Theory

**2.1. Model.** The Hamiltonian involves the interaction potential between two ions of species *s* and *t* and is given by

$$\phi_{st}(r_{st}) = \begin{cases} \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{Z_s Z_t e^2}{r_{st}} & \text{if } r_{st} \geq a_{st} \\ \infty & \text{if } r_{st} < a_{st} \end{cases} \quad (1)$$

Here  $r_{st}$  is the distance between the particles and we are assuming additive diameters  $a_{st} = (a_s + a_t)/2$ ,  $a_s$  being the diameter of particle of type *s*. In this paper we treat only symmetric electrolytes so  $a_s = a_t = a$ . Also,  $\epsilon_0$  is the vacuum permittivity,  $\epsilon_r$  is the relative permittivity of the system,  $Z_s$  is the valency of ion type *s*, and  $e_0$  is the proton charge. The fixed charge  $q$ , which is assumed to be negative here, is smeared uniformly over the inner surface of the capillary with the charge density

$$\sigma = \frac{q}{2\pi R_c h} \quad (2)$$

where  $R_c (=R + a/2)$  and  $h$  are the radius and the length, respectively, of the capillary (cf. Figure 1). In this model the wall is assumed to be impenetrable: the centers of the ions can approach up to the distance  $a/2$  (radius of an ion) to the surface. The ions (positive counterions and negative co-ions) are distributed within the volume  $V = \pi(R_c - a/2)^2 h$ .

The electrostatic part of the ion-wall potential,  $\phi_{wt}$ , is independent of the position in the cell. In ref 13 (see eq 8) the approximate expression of  $\phi_{wt} = \text{constant}$ , valid for long capillaries ( $h \gg R_c$ ), is given. The condition  $h \gg R_c$  appears to be satisfied to a sufficient degree of accuracy for  $h/R_c = 10$ :<sup>13</sup>

in our calculation  $h/R_c$  is about 44. While the actual value of  $\phi_{wt}$  is not important for the Monte Carlo sampling, it is needed for the calculation of the single ion activities from Widom's method.<sup>13,22,23</sup> In all the calculations reported in this work it is ensured that the electroneutrality condition within the micropore is satisfied; in this respect our model differs from some other studies, where different boundary conditions were explored.<sup>13,15</sup>

**2.2. Monte Carlo Simulations.** The above interparticle potential was utilized for the canonical MC simulations following the standard Metropolis algorithm. The number of ions in a micropore varied from 2400 to 4900 and its length was  $h = 1700 \times 10^{-10}$  m. The use of periodic boundary conditions for this length seems valid from earlier experience.<sup>8–10</sup> In this simulation we use, in addition to the conventional histogram method, also Widom's particle insertion method<sup>22</sup> to obtain ionic distributions. Widom's method has been also used to obtain the activity coefficients of ionic species present in the micropore; some details of the procedure are given in ref 23. In doing the statistics, care was exercised with generally 5–10 million configurations used to reach the equilibrium, while the following 50–70 million configurations were utilized in the sampling process, depending on the number of particles involved.

**2.3. Modified Poisson–Boltzmann Theory.** In the potential approach to the theory, the fundamental equation is the Poisson equation, which in the cylindrical geometry reads

$$\frac{1}{r} \frac{d}{dr} \left( r \frac{d\psi(r)}{dr} \right) = - \frac{e_0}{\epsilon_0 \epsilon_r} \sum_s Z_s n_s g_s(r) \quad (3)$$

where  $n_s (=c_s N_A)$  is the mean number density of ionic species *s*,  $c_s$  being the mean concentration and  $N_A$  the Avogadro number,  $\psi(r)$  is the mean electrostatic potential, and  $g_s(r)$  is the wall-ion distribution function. In the PB theory the  $g_s(r)$  is

$$g_s(r) = H(R_c - \frac{a}{2} - r) g_s(0) \exp[-Z_s e_0 \psi(r)/k_B T] \quad (4)$$

$H(x)$  is the Heaviside function,  $g_s(0)$  is the distribution at  $r = 0$ ,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature. The principal approximations inherent in the classical theory are the neglect of interionic correlations and the neglect of the ion size. The MPB theory stems from efforts to take these effects into account in a potential formulation (see, for example, refs 16, 17, and 19–21). In the MPB analysis, we have

$$g_s(r) = \left( \frac{\xi(r)}{\xi(0)} \right) g_s(0) \exp \left[ - \frac{\beta Z_s^2 e_0^2 (F - F_0)}{8\pi\epsilon_0\epsilon_r a} - \beta Z_s e_0 [L[u(r)] - L[u(0)]] \right] \quad (5)$$

$$L[u] = \frac{F}{2r^{1/2}} [u(r + a) + u|r - a|] - \frac{F - 1}{2ar^{1/2}} \int_{|r-a|}^{r+a} u(y) dy \quad (6)$$

$$F = \begin{cases} 1/(1 + \kappa a), & 0 \leq r \leq (R_c - 3a/2) \\ 1/\left\{ (1 + \kappa a) - \frac{\kappa a}{4\pi a^2} S \right\}, & R_c - 3a/2 \leq r \leq R_c - a/2 \end{cases} \quad (7)$$

$$F_0 = F(0) \quad (8)$$

also,

$$S = 4a^2 \int_{\theta_0}^{\pi/2} \sin \theta \left[ \pi - \cos^{-1} \left\{ \frac{c - \cos^2 \theta}{(2r/a) \sin \theta} \right\} \right] d\theta$$

$$\theta_0 = \sin^{-1} \left[ \frac{R_c - a/2 - r}{a} \right]$$

$$c = 1 - \left( \frac{R_c - a/2}{a} \right)^2 + \left( \frac{r}{a} \right)^2 \quad (9)$$

The quantity  $u(r) = r^{1/2}\psi(r)$ , while  $\beta = 1/(k_B T)$ ,  $\xi(0)$  is the exclusion volume term at  $r = 0$ , and  $\kappa$  is the local Debye-Hückel parameter, viz.,

$$\kappa^2 = \frac{\beta e_0^2}{\epsilon_0 \epsilon_r} \sum_s Z_s^2 n_s g_s(r) \quad (10)$$

The exclusion volume term is calculated from the first member of the Bogoliubov-Born-Green-Yvon hierarchy

$$\xi(r_1) = g_s(r_1 | Z_s = 0)$$

$$= H(r_1) \exp[- \int_0^{r_1} \sum_t n_t \int_{S_{12}} \hat{x} \cdot \hat{r}_{12} g_t(2) \times \exp(-\beta Z_t e_0 \phi) dS dr] \quad (11)$$

$$\phi = \frac{F}{4\pi a} \int_{V_d} \nabla^2 \psi dV \quad (12)$$

The inner integral in eq 11 is over the exclusion surface about the discharged ion at  $r_1$ , while  $\phi$  is the fluctuation potential on the same exclusion surface, which encloses the exclusion volume  $V_d$ . The unit vectors  $\hat{x}$  and  $\hat{r}_{12}$  are to a field point 2 on this exclusion surface from the capillary axis and  $r_1$ , respectively. For convenience, the zero of the PB mean electrostatic potential is at  $r = 0$ , but such a choice cannot be made for the MPB theory.

Equations 3 and 4 constitute the PB theory, while eqs 3 and 5–12 will be collectively known as the MPB equation. The relevant boundary conditions for both the PB and the MPB theories are

$$\left. \frac{d\psi(r)}{dr} \right|_{r=0} = 0 \quad (13)$$

and

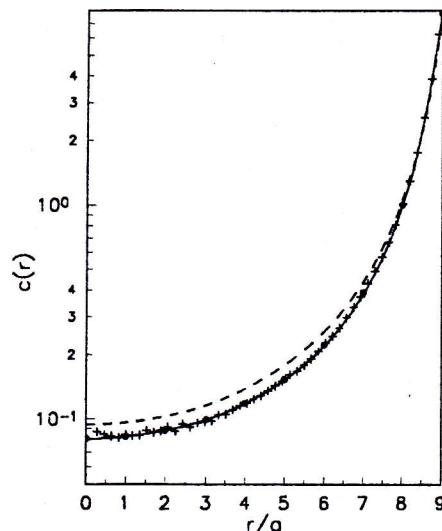
$$\left. \frac{d\psi(r)}{dr} \right|_{r=R_c} = -\frac{\sigma}{\epsilon_0 \epsilon_r} \quad (14)$$

In the ion-free region,  $R_c - a/2 < r < R_c$ , the Laplace equation for the mean electrostatic potential

$$\frac{1}{r} \frac{d}{dr} \left( r \frac{d\psi(r)}{dr} \right) = 0 \quad (15)$$

has the analytic solution

$$\psi(r) = \psi(R_c) + R_c \left\{ \frac{d\psi(r)}{dr} \right\}_{r=R_c} \log_e \left( \frac{r}{R_c} \right) \quad (16)$$



**Figure 2.** Local concentrations of the monovalent counterions inside a capillary as obtained by the Monte Carlo simulation (+, histogram method; circles, Widom's method), the PB equation (dashed line), and the MPB theory (full line). The mean concentrations of co-ions  $c_- = 0$  and counterions  $c_+ = 0.850\ 08\text{ M}$ .

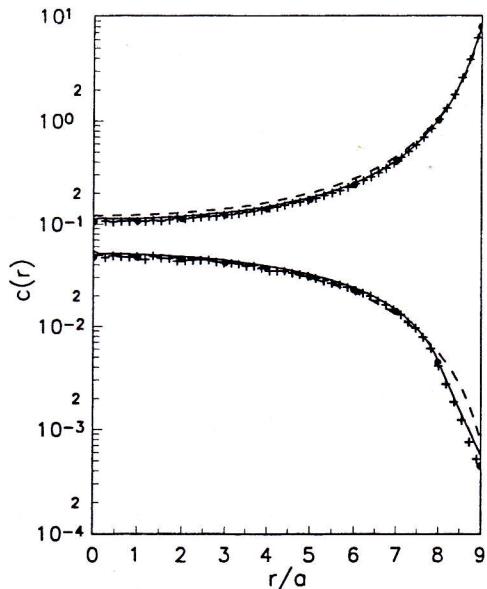
This equation is used in the numerical solution of the PB and MPB equations.

### 3. Results

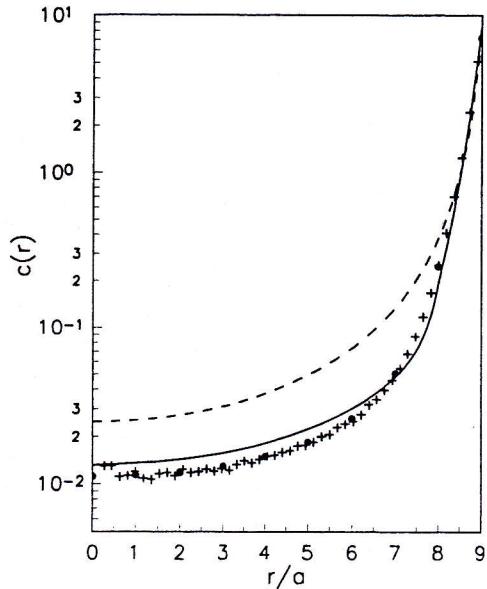
The PB and the MPB equations were solved numerically using a quasi-linearization iteration procedure.<sup>24</sup> The procedure has earlier proved successful in solutions of these equations in the electric double layer theory involving different geometries (see, for example, refs 16, 17, and 19–21). The PB equation, in particular, was solved independently using a fourth-order Runge-Kutta procedure<sup>2,8–10</sup> and gave the same results as that from the iteration procedure. This provided a useful check on the numerics.

In the present work we have considered four different ionic systems in the capillary, namely, (i) monovalent counterions only, (ii) monovalent counterions with added 1:1 electrolyte, (iii) divalent counterions only, and (iv) divalent counterions with added 2:2 electrolyte. For the calculations reported in this paper the capillary radius  $R_c = 40.375 \times 10^{-10}\text{ m}$ , the common ionic diameter  $a = 4.25 \times 10^{-10}\text{ m}$ , and the pore surface charge density  $\sigma = -0.1484\text{ C/m}^2$ . Also, these calculations apply to waterlike solvent at room temperature  $T = 298\text{ K}$  with  $\epsilon_r = 78.54$ . These physical parameters together with the chosen concentrations are representative of earlier works on similar systems in the literature.<sup>2,8–10</sup>

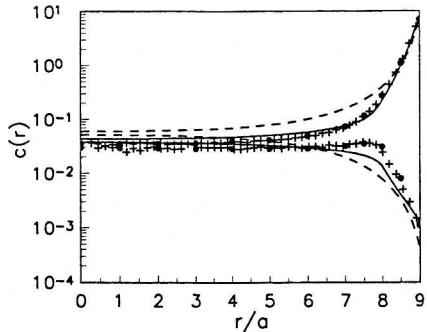
**3.1. Ionic Profiles.** We begin by considering the structural features of the ion atmosphere inside the capillary. The machine simulated concentration profiles alongside the theoretically predicted ones corresponding to the above four cases are displayed in Figures 2–5, respectively. The MC distribution functions from both the standard histogram method and Widom's particle insertion method are also shown for comparison. The points obtained by the histogram method show relatively more scatter, especially near the center of the pore, than their Widom counterparts. This scattering is also more for the co-ion distribution in Figure 3, which in part arises from the fewer number of particles being sampled. A clear advantage of Widom's test particle formalism evidenced in the figures is the fact one can reach right up to the edges of the MC box without any extrapolation being necessary.



**Figure 3.** Local concentrations of the monovalent counterions and monovalent co-ions inside a capillary;  $c_- = 0.020\ 65\text{ M}$ ,  $c_+ = 0.870\ 73\text{ M}$ . Legend as for Figure 2.



**Figure 4.** Local concentrations of the divalent counterions inside a capillary;  $c_- = 0$ ,  $c_+ = 0.425\ 04\text{ M}$ . Legend as for Figure 2.



**Figure 5.** Local concentrations of the divalent counterions and divalent co-ions inside a capillary;  $c_- = 0.026\ 21\text{ M}$ ,  $c_+ = 0.451\ 25\text{ M}$ . Legend as in Figure 2.

For monovalent simple ion systems, viz., Figures 2–3, there is, in general, little difference between the simulations and the theoretical results. The PB profiles are displaced slightly from

the MC ones, while the MPB profiles lie almost on top of the MC ones. This PB behavior is expected and consistent with the well-known characteristics of monovalent ions in the double layer and polyelectrolyte literature.

In higher valency ion systems, the interionic correlation effects can be substantial and such systems constitute essentially a more stringent test of theoretical approximations. We note immediately from Figures 4 and 5 that the deviations of the PB are more than seen for monovalent ions. In Figure 5 the MC co-ion profile shows a mild peak or a plateau-like region near the cylinder wall. This arises from divalent co-ions trying to pack themselves near the layer of divalent counterions next to the wall. Obviously this is a feature that owes its origin to the strong correlations among divalent ions and, in contrast, no such layering was observed in the corresponding monovalent profile in Figure 3. Although compared to the PB the MPB coion profile lies closer to that from the simulations near the wall, it tends to fall below unity further away from the wall than does the MC. In this respect the MPB behavior is reminiscent of the corresponding distribution of divalent ions in the cylindrical cell model.<sup>25,26</sup> However, at larger distances from the wall the MPB profile follows the MC profile closely.

**3.2. Mean Activity Coefficient.** One of the more interesting quantities among thermodynamic properties of an electrolyte in the capillary is the mean activity coefficient. This has relevance in determining the equilibrium of the electrolyte in the pore to that in the bulk. The mean activity of electrolyte in the pore has been studied previously using the grand canonical Monte Carlo (GCMC) techniques.<sup>2,8–10</sup> Lo et al.<sup>12</sup> utilized the canonical MC procedure to calculate single ionic coefficients for ionic species in a charged micropore. They found that the chemical potential of the counterion differs from that of the co-ion due to the effects of the charged capillary.<sup>12,13</sup> The two chemical potentials can be brought into contact by assuming the existence of the so-called Donnan potential between the electrolyte in capillary and an equilibrium bulk solution. Of course, the mean activity coefficient as a thermodynamic property can be determined unambiguously. For comparison purposes, and also for testing the numerical procedure, we have repeated the calculation of Lo and co-workers<sup>13</sup> for the chemical potential of ions (cf. Figure 4 of ref 13) using Widom's particle insertion techniques. Good agreement with the results for the chemical potential published in ref 13 was obtained.

The calculation of the mean activity coefficient of an electrolyte in a charged capillary follows straightforwardly from thermodynamic considerations,<sup>27</sup> viz.,

$$\frac{\gamma_{\pm}}{\gamma_{\pm}(0)} = \frac{\sqrt{c_-(0)c_+(0)}}{\sqrt{c_-c_+}} \quad (17)$$

where  $\gamma_{\pm}$  is the mean activity coefficient of electrolyte in the micropore and  $\gamma_{\pm}(0)$  is the value of the mean activity coefficient at the pore axis ( $r = 0$ ), where the electrostatic field vanishes. Further,  $c_-$  and  $c_+$  are the concentrations of co-ions and counterions in a micropore, while  $c_-(0)$  and  $c_+(0)$  are the corresponding concentrations at  $r = 0$ .

The ratio  $\gamma_{\pm}/\gamma_{\pm}(0)$  was calculated for four different concentrations of the size symmetric 1:1 and 2:2 electrolytes in the capillary. These results are presented in Table 1. The ratio of the mean activity coefficients, given by eq 17, increases with increasing electrolyte concentration for the range of parameters studied here. Note also that the agreement between the MPB and MC results is quite good; the PB theory is, as expected, not accurate for solutions with divalent counterions. The

**TABLE 1:**  $\gamma_{\pm}/\gamma_{\pm}(0)$  Ratios for 1:1 and 2:2 Electrolytes in a Micropore<sup>a</sup>

$c_-/\text{M}$	$\gamma_{\pm}/\gamma_{\pm}(0)(\text{MC})$	$\gamma_{\pm}/\gamma_{\pm}(0)(\text{PB})$	$\gamma_{\pm}/\gamma_{\pm}(0)(\text{MPB})$
1:1 Electrolyte			
0.01	$0.513 \pm 0.005$	0.550	0.520
0.020 65	$0.528 \pm 0.002$	0.565	0.534
0.035 40	$0.550 \pm 0.002$	0.584	0.554
0.100 00	$0.630 \pm 0.003$	0.650	0.633
2:2 Electrolyte			
0.005	$0.21 \pm 0.01$	0.424	0.219
0.01	$0.23 \pm 0.01$	0.445	0.247
0.026 21	$0.29 \pm 0.01$	0.501	0.320
0.043 30	$0.33 \pm 0.01$	0.546	0.381
0.1	$0.47 \pm 0.01$	0.645	0.572

<sup>a</sup> The concentrations of the bare mono- and divalent counterions are 0.850 08 and 0.425 04 M, respectively.

**TABLE 2:** Mean Activity Coefficient,  $\gamma_{\pm}$ , for 1:1 and 2:2 Electrolytes in a Micropore<sup>a</sup>

$c_-/\text{M}$	$\gamma_{\pm}(\text{MC})$	$\gamma_{\pm}(\text{MPB})(\text{approx 1})$	$\gamma_{\pm}(\text{MPB})(\text{approx 2})$
1:1 Electrolyte			
0.01	$0.419 \pm 0.003$	0.432	0.433
0.020 65	$0.426 \pm 0.002$	0.434	0.434
0.035 40	$0.438 \pm 0.001$	0.442	0.442
0.100 00	$0.486 \pm 0.003$	0.488	0.488
2:2 Electrolyte			
0.005	$0.082 \pm 0.004$	0.0878	0.0886
0.01	$0.079 \pm 0.002$	0.0849	0.0851
0.026 21	$0.080 \pm 0.002$	0.0824	0.0825
0.043 30	$0.080 \pm 0.002$	0.0816	0.0816
0.1	$0.081 \pm 0.002$	0.0834	0.0834

<sup>a</sup> The concentrations of the bare mono- and divalent counterions are 0.850 08 and 0.425 04 M, respectively.

dependencies of the excess chemical potential on other model parameters, such as the pore radius  $R_c$  and the pore charge density  $\sigma$ , have not been explored in this first study. We have postponed these calculations for a future work.

Widom's test particle method allows us to calculate the absolute value of the mean activity coefficient in the micropore,  $\gamma_{\pm}$ , and not merely a ratio given by eq 17.<sup>22,23</sup> Our MC results for  $\gamma_{\pm}$  are presented in Table 2. The MPB result for this quantity can be obtained from eq 17, providing that we know  $\gamma_{\pm}(0)$ . The MPB bulk individual activity coefficients and hence the mean activity coefficient were calculated using the formalism developed earlier.<sup>28,29</sup> Note that the concentrations of cations  $c_+(0)$  and anions  $c_-(0)$  are not equal; i.e., the electrolyte solution is not electroneutral (locally) at position  $r = 0$ . To calculate  $\gamma_{\pm}(0)$ , two different approximations were used. In the first one (approximation 1) the individual activity coefficient  $\gamma_+(0)$  was approximated by the MPB value of the individual activities of the species in a symmetric Z:Z valency isotropic (electroneutral) electrolyte with the concentration of cations and anions equal to  $c_+(0)$ . The individual activity coefficient for anions was evaluated in an analogous manner, but at concentration of electrolyte equal to  $c_-(0)$ . The mean activity  $\gamma_{\pm}(0)$  was now evaluated in the usual manner. In the second approximation (approximation 2) we assumed that  $\gamma_{\pm}(0) = \gamma_{\pm,\text{bulk}}$ , where  $\gamma_{\pm,\text{bulk}}$  is the mean activity coefficient of the equilibrium bulk electrolyte at concentration  $c_b$  defined by  $c_b^2 = c_+(0)c_-(0)$ . The latter approximation is exact within the PB formalism and has been used before.<sup>30</sup> The results presented in Table 2 indicate that the approximations are consistent with each other and yield reasonably good agreement with the simulation results for  $\gamma_{\pm}$ .

As a partial check of the canonical MC results we also performed two new GCMC simulations. These simulations apply to electrolyte solutions with the parameters as described in

section 3: the mean co-ion concentration in micropore was  $c_- = 0.020\ 65\ \text{M}$  in the case of 1:1 and  $c_- = 0.043\ 30\ \text{M}$  for the 2:2 electrolyte, while the corresponding mean counterion concentrations ( $c_+$ ) were 0.870 73 and 0.468 34 M, respectively. The canonical MC result for the mean activity coefficient of 1:1 electrolyte was  $0.426 \pm 0.002$ , while the GCMC result was  $0.424 \pm 0.002$ . Similarly, the canonical MC result for the 2:2 electrolyte is  $0.080 \pm 0.002$ , and the GCMC result for the same quantity is  $0.0805 \pm 0.002$ .

## Discussion

We have presented here numerical results for the structure and thermodynamics of a model electrolyte in a charged capillary using the PB and MPB theories, and MC simulations. The accuracy of the theoretical predictions have been tested against the new computer simulations.

The shortcomings of the PB approximation are clearly seen in the predicted ionic profiles of divalent counterions and co-ions as displayed in Figures 4 and 5. An important achievement of the paper is the physical insight that one gains from interpreting the discrepancies between the PB and the simulations—the result of neglecting interionic and steric effects in the classical theory and their relationship with the so-called *anomalous* experimental results<sup>5,6,31</sup> for systems containing multivalent ions. For example, as seen from Figure 5, strong correlations between divalent ions cause the concentration of co-ions to be higher near the wall than that due to the PB theory. This means that the model micropore rejects considerably less electrolyte than that predicted by the PB theory, as has been noted earlier.<sup>2,8</sup> This is further confirmed by the rather high value of the PB  $\gamma_{\pm}$  as judged by the MC data. A negative rejection, implying a higher concentration of the co-ions in the micropore than in the equilibrium bulk solution, has been observed in some experiments where divalent or trivalent counterions were present in the system.<sup>5,6,31</sup> The behavior of the parallel MPB distribution and mean activity coefficient on the other hand, would appear to be qualitatively consistent with the experiments. Another relevant point here is the fact that the fixed charge has a strong effect on the mean activity coefficient of the electrolyte in a micropore;  $\gamma_{\pm}$  is very low in comparison with the values for a bulk electrolyte at the same concentration. This is consistent with earlier works (cf. Figure 5 of ref 8). The MPB theory describes the simulation results much better than does the classical PB approximation, with the MPB theory retaining its utility for electrolytes with divalent counterions.

The experimental results for multivalent counterions mentioned above cannot be explained by a mean field theory, and there is a suggestion<sup>31</sup> that there must be other interactions involved which overshadow the Coulomb interactions. In our opinion, as demonstrated by the current simulations, strong correlations between the divalent counterions and co-ions significantly contribute toward the destroying of normal rejection behavior of charged microporous material. In the literature, experimental data are usually analyzed in terms of the PB theory,<sup>5,6,31</sup> and as often is the case when monovalent counterions are present, agreement between theory and experiment is satisfactory. However, such agreement becomes considerably less for solutions with multivalent counterions. For such systems the PB theory can preclude *normal rejection* of an electrolyte from the pore and can lead to a wrong sign for the streaming (electrokinetic) potential. These *anomalous* results have not been satisfactorily explained so far and we suggest that the effect is primarily due to interionic correlations (see also ref 2). This conjecture appears to be confirmed by the present calculations,

where it is also noted that the MPB theory is able to account for these correlations to an appreciable degree. New and more diverse experiments, especially for solutions containing multivalent and/or mixed valency ions, would be very welcome and useful.

Some additional comments on the MPB might be in order. As mentioned in the Introduction, the MPB has been a successful theory of the electrical double layer phenomenon in planar, spherical, and cylindrical symmetries<sup>16–21</sup> (see also reviews, refs 16, 32, and 33). The present work represents the first instance where the theory has been applied to an inverted, concave interfacial geometry. It is well-known that of the three aforesaid symmetries, the cylindrical symmetry (especially the inverted case) is perhaps the most complex one to treat, as the substantial averaging associated with the planar and spherical geometries is now missing. In this context, the preliminary results presented in this paper, in particular the reasonable agreement between the MC and the MPB, are encouraging. The MPB has been equally successful in describing a wide variety of bulk electrolytes and electrolyte mixtures, with the MPB results being, in general, on a par with those from the liquid structure integral equations. Admittedly, there are shortcomings also. For instance, both in the bulk and interfacial double layer, the MPB theory is not applicable at very high concentrations, viz., *molten salt regime*. This is primarily because of the approximations introduced in solving the related fluctuation potential problem. A full numerical solution of the fluctuation potential would potentially greatly enhance the range of applicability of the theory. Such a project is contemplated for the future. Nonetheless, this aspect notwithstanding, in the *electrolyte solution regime* under most practical and laboratory conditions, viz., surface charge density of magnitude  $\sim 0.3 \text{ C/m}^2$  for planar electrodes, the MPB studies to date clearly indicate the theory to be a viable statistical mechanical approach.

The density functional theory (DFT) and the second-order inhomogeneous integral equation theory are other formalisms, which could be used for the capillary problem. Patra and Yethiraj<sup>34,35</sup> have applied the DFT to study the ion atmosphere around a cylindrical polyion. The DFT and MPB results in this situation are comparable, both being improvements to the classical PB theory. More recently, Goulding et al.<sup>36</sup> have used the DFT in a study of the pore, but the focus was mainly on steric effects of neutral hard spheres in a neutral cylindrical pore. The inhomogeneous integral equation technique has been successful in treating the hard wall/hard sphere problem.<sup>37</sup> Plischke and Henderson solved the HNC2 and MSA2 equations for the primitive model electrolyte next to a planar layer<sup>38,39</sup> (for a review, see ref 40). It is expected that these theories will also provide useful insights into pore problems.

The results presented in this paper are based on the primitive model, i.e., the solvent is treated as a dielectric continuum. In a recent paper Lee et al.<sup>41</sup> have investigated the effect of adding neutral particles mimicking solvent to electrolyte in the capillary. The conclusion of their new study is that addition of a neutral component yields concentration profiles which are more structured than in absence of the extra species. On the other hand, the electroneutrality of the micropore (in their study the Donnan potential is compensated by extra ions in the capillary (see also ref 13)) is much less model dependent. This gives some confidence in the thermodynamic results obtained for the primitive model electrolyte in a cylindrical capillary.

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