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**MONTE CARLO SIMULATIONS OF SOLVENT EFFECTS ON
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by

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INTRODUCTION

Systems with electrolytes in contact with a charged or neutral surfaces are relevant to many areas of sciences: electrochemistry, biology, tribology, and colloid physics and chemistry. Among the models of the electrical double layer, the most widely used is the primitive model (PM), in which ions are represented as point charges that are embedded in hard spheres, the solvent is modeled as an isotropic dielectric continuum, and the surface is modeled as a hard wall with uniform surface charge density. For low surface charge and dilute electrolyte solutions, the classical theory of Gouy [1] and Chapman [2] (GC) gives predictions of the interfacial ion and potential distributions that are in excellent agreement with experiments and computer simulations. Vigorous investigation of the PM by computer simulations [3-9] during the last decade have revealed phenomena of the electrical double layer that are not captured by either the GC or other theories. For high surface charge densities or high electrolyte concentrations, the ion density profiles in the PM indicate a highly organized layering of ions at the charged surface. For both 1:1 and 2:2 electrolytes at high concentrations, there is charge inversion with coion densities exceeding the counterion density in the second layer. The obvious disadvantage of the PM is that the interfacial structure of the solvent is minimized, although it is well known that ion solvation and dipole orientation at the surface, both of which are critical in determin-

ing the potential and ion distributions, are correlated with the molecular structure of the solvent. The development of more realistic models of water and the attempt to refine the primitive model [10] allow the effects of the solvent structure on the double layer to be studied. The complexity of realistic models of water limits studies of these systems to computational simulations; however, very recent investigations [11-13] demonstrate the importance of solvent structure on the interface properties.

In this article, we present Monte Carlo simulations of a solvent primitive model (SPM) which is comprised of charged hard sphere ions and uncharged hard sphere solvent molecules. Ion density and potential profiles are compared for electrolytes in contact with charged and neutral walls for different electrolyte concentrations and sizes. It is found that the finite size of the solvent results in a highly ordered layering of ions at both charged and neutral walls. For electrolytes comprised of different sized anions and cations, the solvent-induced structure results in a space charged layer more than two molecules thick at a neutral wall.

MODEL SYSTEMS

The systems simulated in this work are mixtures of 1:1 primitive electrolytes and neutral hard sphere solvent molecules contained between two infinite planar surfaces. One of the surfaces (at $z = 0$) is uniformly charged and the other (at $z = H$) is neutral. In the computations, the systems are represented as a periodic array of closed rectangular boxes of height H and a square base of length L on a side. Let N_+ and N_- and q_+ and q_- denote the number and charge of cations and anions in the enclosed system, respectively. Electroneutrality requires

$$|N_- q_- - N_+ q_+| = \sigma A, \quad (1)$$

where σ is the surface charge density and $A = L^2$. The interaction potential between particles i and j is

$$U(r_{ij}) = \begin{cases} \infty, & r_{ij} < (d_i + d_j)/2 \\ \frac{q_i q_j}{\epsilon |r_i - r_j|}, & r_{ij} > (d_i + d_j)/2, \end{cases} \quad (2)$$

and between particle i and the wall is,

$$U(r_i) = \begin{cases} \infty, & z_i < d_i/2 \\ -2\pi\sigma q_i z_i / \epsilon, & z_i > d_i/2, \end{cases} \quad (3)$$

where z_i is the distance between the wall and particle i . In equations (2) and (3), d_i is the diameter of particle i , q_i equals the ion valence times the unit electronic charge e . ϵ is the dielectric constant and is assigned the value 78.5 in our calculations.

SIMULATION

The Coulomb interaction between ions in a confined system which is divided into many cells in the x and y directions is,

$$U(r) = \sum_{\mathbf{R}} \frac{1}{|\mathbf{R} + \mathbf{r}|}, \quad (4)$$

where

$$|\mathbf{R} + \mathbf{r}| = [(l + x)^2 + (m + y)^2 + z^2]^{1/2}. \quad (5)$$

Using the method initiated by van der Hoff and Benson [14] in the 50's, Lekner [15] obtained the following result,

$$U = 4 \sum_{lm} \cos(2\pi lx) K_0[2\pi l \sqrt{(m + y)^2 + z^2}] - \log[\cosh(2\pi z) - \cos(2\pi y)], \quad (6)$$

where $K_0(x)$ is the modified Bessel function. For large values of x , the function behaves as $e^{-x}/\sqrt{x}$. In the actual calculations, we only need to retain terms corresponding to $x \leq 8$, the contributions from long range tail will be of the order $\sim 10^{-4}$.

In a simulation, we choose ionic concentrations to mimick those of the PM electrolyte in equilibrium with the bulk salt at a given concentration. First, we run the grand canonical Monte Carlo (GCMC) simulations for the primitive electrolyte systems [3-4]. Then a canonical MC simulation is carried out for a solvent/electrolyte system at a total number density of [5],

$$(N_+ + N_- + N_0)d^3/HL^2 \sim 0.7, \quad (7)$$

where N_+ and N_- are the average number of free ions in the confined PM fluid. At such high particle densities, a grand canonical Monte Carlo simulation is very hard to perform due to the difficulties in inserting particles. This is why a canonical MC simulation is used in the second stage.

The parameters used in our simulations are listed in Table 1. The probability of accepting a move in the SPM simulation is 10 percent. During the run, the systems were equilibrated for 10^5 steps and then another $(2.5 - 4.0) \times 10^6$ steps were run to accumulate averages to calculate the density profiles $n(z)$ and the mean electrostatic potential $\psi(z)$. Very long runs are required compared to the primitive electrolytes simulations, in order to eliminate the noise in the density profiles. Taking the right wall as the reference point of the potential, $\psi(z)$ is obtained via the relation

$$\psi(z) = \frac{4\pi}{\epsilon} \sum_j \int_z^H dz_1 (z - z_1) q_j n_j(z_1). \quad (8)$$

Table 1: Parameters used in this paper, $\sigma^* = \sigma d^2/e$, side length L , surface separation H . Number of cations, anions, and neutral particles are N_+ , N_- , and N_0 , and $N_c = N_+ + N_-$, $\Delta N = N_- - N_+ = \sigma A$, $A = L \times L$. C is the bulk ion concentration for PM electrolytes in molar. The number of steps run in the simulations are given as N_{steps} in unit of 10^6 steps in the last column. In all the cases studied in this paper the neutral solvent particle and the anion have diameter of $d_0 = d_- = d = 4.25 \text{ \AA}$. For systems a , b , and c , $\ln \gamma_{\pm} = -0.127$, 0.271 , and -0.44 , respectively.

sys	H/d	L/d	d_+/d_-	σ^*	N_c	N_0	ΔN	$C(M)$	$N_{steps}/10^6$
a	12.0	4.36	1.0	0.42	26	134	8	1.0	4.0
b	12.0	4.47	1.0	0.70	32	136	14	1.0	2.5
c	12.0	4.36	0.5	0.42	26	134	8	1.0	2.5

RESULTS AND DISCUSSION

In the following we report our simulation results of the density profiles and mean electrostatic potentials for the different systems that are listed in table 1. The surface charge density, the ion and solvent density, and the mean electrostatic potential are reported in the dimensionless forms

$$\sigma^* = \frac{\sigma d^2}{e}, \quad n_i^* = \frac{n_i}{n_{i0}}, \quad \text{and} \quad \psi^* = \beta e \psi, \quad (9)$$

where n_{i0} is the bulk number density for species i and n_i is the number density in SPM.

To compare the results obtained here with those obtained for the primitive electrolytes, in figure 1, we show the SPM results as continuous, dotted or dashed curves and the PM results as open and filled circles for the case of $\sigma^* = 0.42$ and $C = 1M$.

As is well known, the Gouy-Chapman theory and simulations of the primitive electrolytes are in agreement for low surface charge density and electrolyte concentration. Under these conditions, both the density profile and the mean electrostatic potential are monotonic. In figure 1, we can see that the solvent size included in the SPM simulation has a dramatic effect on the electrolyte ion profiles. The presence of solvent molecules at the walls induces strong structure in the ion distributions at both charged and neutral walls. Near the left wall, the neutral particles and counterions have five layers, the coions show four layers and near the right wall there are four layers of each type of particles. A small residue of the coions near the left wall is seen in the SPM model simulation. These structural features are absent in the PM simulations. Figure 2 shows the mean electrostatic potential for the same system as in figure 1. The potential decreases rapidly near the charged wall and decays to zero.

As mentioned above, the noise in the density profiles prevents us from getting more accurate results to see a clear trend of the potential.

In figures 3 and 4, we change the ion concentration to $2M$ and use $\sigma^* \sim 0.4$. Again the layering of ions is very strong and similar to figures 1 and 2. Furthermore, a charge inversion occurred in the second and third layer with the coion density exceeding the counterion.

To examine the effects of ion diameters on the highly structured ion distributions of the SPM, we ran simulations for electrolyte comprised of dissimilar sized particles, namely, $d_+ = 0.5d_-$. The results are given in figures 5 and 6. These results show that the coion peaks shift due to the size effect but there is still significant layering structure in the ion and solvent density distributions. Ion-size induced charge separations are clearly seen near the neutral wall. Due to the noise in the density profiles, we cannot make an accurate estimate of the potentials resulting from these separations.

From the above analysis, the layered structures that appear in the SPM electrolytes are mainly due to the high total fluid density resulting from the presence of the solvent molecules. The small residue of coions near the charged surfaces is due to the layering of the solvent and counterions.

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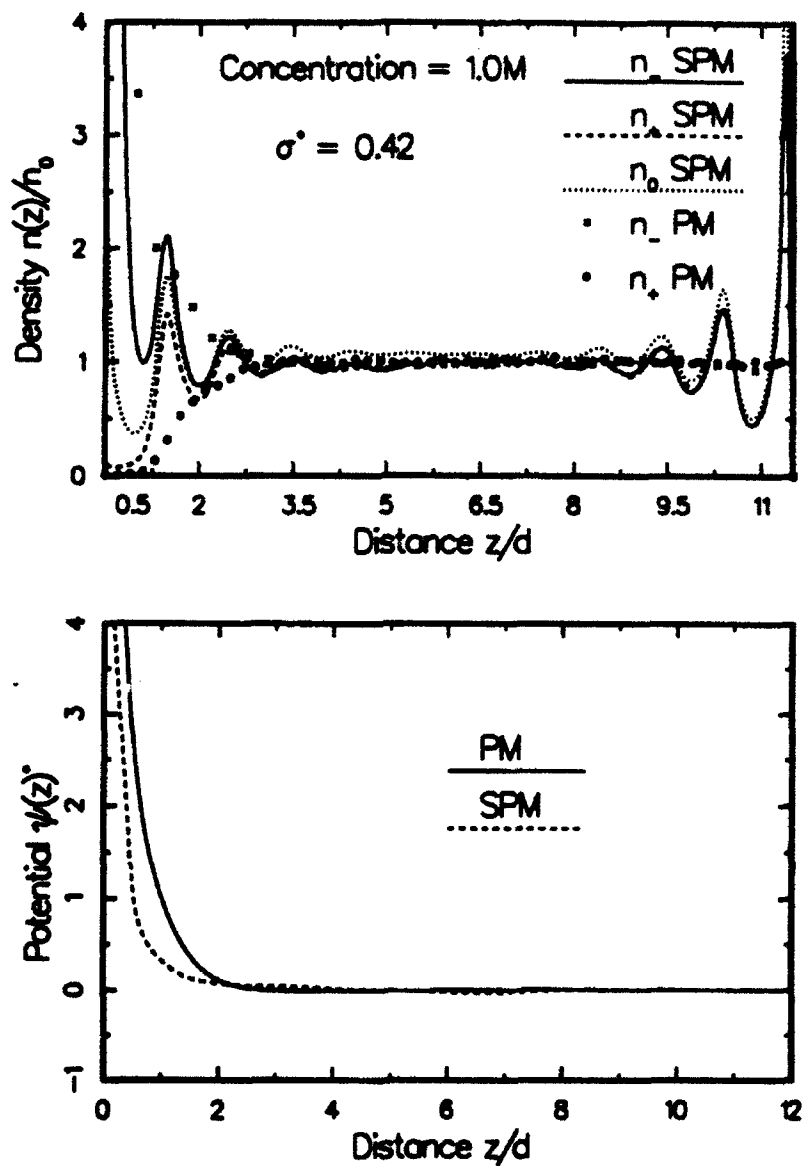


Figure 1. (Upper) Density profiles $n^*(z) = n(z)/n_0$
 Figure 2. (Lower) Mean electrostatic potential $\psi^*(z)$.

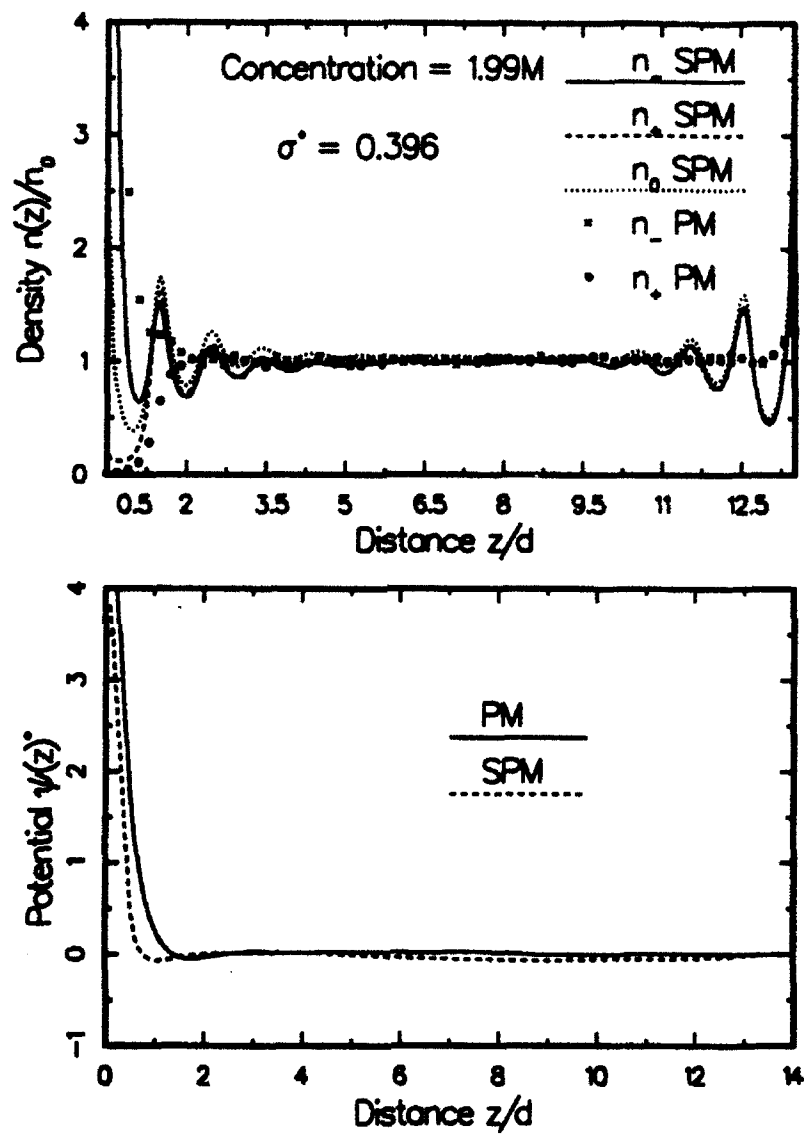


Figure 3. (Upper) Density profiles $n^*(z) = n(z)/n_0$
 Figure 4. (Lower) Mean electrostatic potential $\psi^*(z)$.

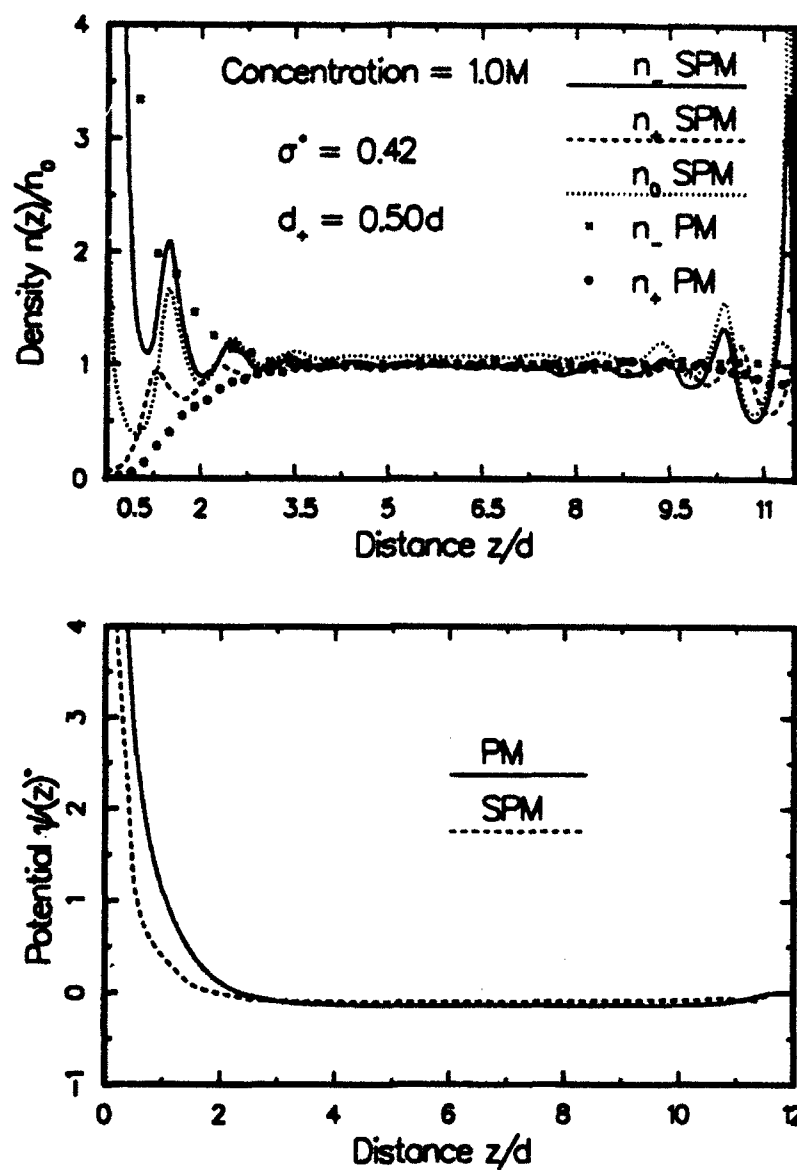


Figure 5. (Upper) Density profiles $n^*(z) = n(z)/n_0$
 Figure 6. (Lower) Mean electrostatic potential $\psi^*(z)$.