

Poisson–Boltzmann Description of the Electrical Double Layer Including Ion Size Effects

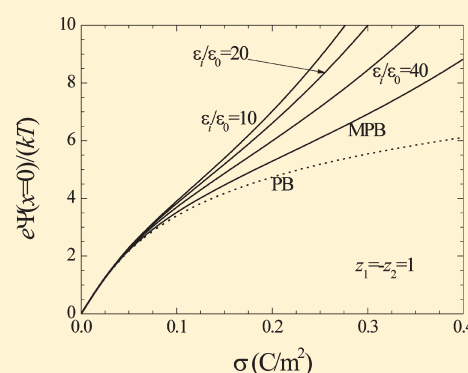
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ABSTRACT: The electrical double layer is examined using a generalized Poisson–Boltzmann equation that takes into account the finite ion size by modeling the aqueous electrolyte solution as a suspension of polarizable insulating spheres in water. We find that this model greatly amplifies the steric effects predicted by the usual modified Poisson–Boltzmann equation, which imposes only a restriction on the ability of ions to approach one another. This amplification should allow for an interpretation of the experimental results using reasonable effective ionic radii (close to their well-known hydrated values).



INTRODUCTION

When charged objects (colloidal particles, interfaces, membranes, proteins, etc.) are placed in contact with an ionic solution, spatial distributions of charge and electric potential, known as the electrical double layer, appear close to the interface. This structure plays a crucial role in colloid and polymer science, biophysics, medicine, and numerous separation technologies (e.g., water and wastewater filtration, membrane filtration, protein and cell separation, immobilization of enzymes, etc.).^{1–5} This is the reason for the great importance of and interest in theoretical models of the electrical double layer structure.

The most acknowledged and widely used theory of the electrical double layer is that of Gouy⁴ and Chapman.⁵ They described this system by means of a Poisson–Boltzmann (PB) equation for the charge distribution close to the interface. Considering plane geometry, the PB expression is

$$\epsilon_e \frac{d^2 \Psi}{dx^2} = -eN_A \sum_{i=1}^m z_i c_i^\infty \exp\left(-\frac{z_i e \Psi}{kT}\right) \quad (1)$$

where z_i and c_i^∞ are, respectively, the valence and the bulk concentration (in mol/m³) of ionic species $i \in \{1, 2, \dots, m\}$, Ψ is the electric potential, e is the elementary charge, N_A is Avogadro's number, k is the Boltzmann constant, T is the absolute temperature of the system, and ϵ_e is the macroscopic permittivity of the solution. Equation 1 follows from the Poisson equation

$$\nabla \cdot (\epsilon_e \nabla \Psi) = -eN_A \sum_{i=1}^m z_i c_i \quad (2)$$

where c_i is the local concentration (in mol/m³) of ionic species i , assuming that

- (i) the only macroscopic average forces acting over the ions are the thermal force \vec{F}_i^T

$$\vec{F}_i^T = -kT \nabla \ln(c_i) \quad (3)$$

and the electric force \vec{F}_i^E

$$\vec{F}_i^E = -z_i e \nabla \Psi \quad (4)$$

- (ii) at equilibrium, the total average force must be zero, so the ionic concentrations must satisfy the Boltzmann distribution

$$c_i = c_i^\infty \exp\left(-\frac{z_i e \Psi}{kT}\right) \quad (5)$$

- (iii) the permittivity of the solution has a constant value throughout the system.

The PB equation is, therefore, a continuum mean-field approach assuming pointlike ions in thermodynamic equilibrium and neglecting statistical correlations; it has been successful in predicting ionic profiles close to planar and curved surfaces and

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the resulting forces. However, it is also known to strongly overestimate ionic concentrations close to highly charged surfaces and for multivalent ions: close to the surface, theoretical ion concentrations can easily exceed the maximal allowed coverage by several orders of magnitude. Stern was the first who tried to overcome this shortcoming of the PB theory by introducing the notion of what is now called the Stern layer.⁶ Since then, several attempts have been proposed to overcome these well-understood drawbacks and limitations of the PB equation. Roughly, two types of methods have been used: microscopic descriptions of the system with different approximation levels^{7–9} and phenomenological theories using macroscopic differential equations to describe the average behavior of the system (e.g., lattice-based models,^{10–14} different modifications of the standard Poisson–Boltzmann theory,^{15–20} hypernetted chain integral equations,²¹ exact contact value theorems,²² and density functional theory²³). Microscopy descriptions have the advantage of precisely representing the interactions responsible for the macroscopic behavior of the system, but only in equilibrium. On the contrary, phenomenological theories, less strict in the description of the interactions, make it possible to analyze the system behavior both in equilibrium and perturbed by an external signal.^{24,25}

In all phenomenological theories, a new average force acting over the ions and responsible for the interactions related to the finite ion size, F_i^S , is added to the theoretical model. Most of the work in this field, treating solely steric effects, use a Bikerman-type expression for this force:^{10,24}

$$\vec{F}_i^S = -kT\nabla \ln \left(\frac{1}{1 - \sum_{j=1}^m \frac{c_j}{c_j^{\max}}} \right) \quad (6)$$

where c_i^{\max} is the maximum local concentration that ionic species i can attain, which is related to the effective ionic radius, R_i , by means of the expression

$$c_i^{\max} = \frac{p}{\frac{4}{3}\pi R_i^3 N_A} \quad (7)$$

where p is the packing coefficient ($p = 1$ for perfect packing, $p = \pi/3(2)^{1/2} \approx 0.74$ for close packing, $p \approx 0.64$ for random close packing, and $p = \pi/6 \approx 0.52$ for simple cubic packing).

Using this additional force term, the equilibrium condition that the total average force acting over the ions must be zero leads to a Langmuir-type equation for the local ionic concentrations

$$c_i = \frac{c_i^\infty \exp\left(-\frac{z_i e \Psi}{kT}\right)}{1 + \sum_{j=1}^m \frac{c_j^\infty}{c_j^{\max}} \left[\exp\left(-\frac{z_j e \Psi}{kT}\right) - 1 \right]} \quad (8)$$

instead of eq 5. Combining this result with eq 2 gives a modified Poisson–Boltzmann (MPB) equation

$$\epsilon_e \frac{d^2 \Psi}{dx^2} = \frac{-eN_A \sum_{i=1}^m z_i c_i^\infty \exp\left(-\frac{z_i e \Psi}{kT}\right)}{1 + \sum_{i=1}^m \frac{c_i^\infty}{c_i^{\max}} \left[\exp\left(-\frac{z_i e \Psi}{kT}\right) - 1 \right]} \quad (9)$$

that takes into account steric effects due to the finite ion size. As noted above, in this modified theory the local ionic concentrations

cannot exceed c_i^{\max} in improving on the results predicted by the PB equation. Comparison with theories based on Monte Carlo (MC) simulations shows that this MPB equation works very well for a wide range of situations.⁹ However, it still presents two important shortcomings: the correction of the MPB over the PB equation appears only at high surface charges and small values of c_i^{\max} so that in order to fit the experimental data it is necessary to consider effective ionic radii that are much larger than the hydrated ionic radii, which is physically objectionable.^{25,26} It should be noted, moreover, that eq 8 does not necessarily imply that ions have a finite size: there is only a restriction on their ability to approach one another. On the contrary, a finite ion size implies that ions have a finite volume that can no longer be occupied by the suspending medium.

In this letter, we propose a simple way to include the finite size of the ions in the MPB equation by extending the hydrated ion model to that of an insulating sphere with effective radius R_i , charge $z_i e$, and permittivity ϵ_i . This modification implies that the presence of ions in the suspending medium should modify its macroscopic permittivity and that two new average forces acting over ions should be taken into account: a force, F_i^B , tending to move ions into regions of higher permittivity (a consequence of the so-called Born energy) and a dielectrophoretic force, F_i^D , acting on a dipole that appears wherever the local field is nonuniform. These considerations considerably amplify the deviations predicted by the MPB equation, leading to appreciable differences with respect to the PB equation even for relatively low surface charges and effective ionic radii close to their hydrated values.

We thus consider the electrolyte solution as a suspension made of insulating spheres with radius R_i and permittivity ϵ_i and water with permittivity ϵ_w . The resulting permittivity ϵ_e of this suspension can be determined using the Maxwell mixture formula,²⁷ which is quite accurate over the whole concentration range when the dispersions have a lower permittivity than the suspending medium:

$$\epsilon_e = \epsilon_w \frac{1 + 2p \sum_{i=1}^m \frac{c_i}{c_i^{\max}} \frac{\epsilon_i - \epsilon_w}{\epsilon_i + 2\epsilon_w}}{1 - p \sum_{i=1}^m \frac{c_i}{c_i^{\max}} \frac{\epsilon_i - \epsilon_w}{\epsilon_i + 2\epsilon_w}} \quad (10)$$

However, the electrostatic energy of an ion with radius R_i and charge $z_i e$ can be obtained by integrating the energy density corresponding to its electric field:

$$W = \frac{\epsilon_e}{2} \int_{R_i}^{\infty} E^2 dV = \frac{\epsilon_e}{2} \int_{R_i}^{\infty} \left(\frac{z_i e}{4\pi \epsilon_e r^2} \right)^2 4\pi r^2 dr = \frac{z_i^2 e^2}{8\pi \epsilon_e R_i} \quad (11)$$

This energy depends on the permittivity of the surrounding medium. Therefore, if the permittivity is position-dependent (eq 10), then the ion will tend to move to regions of higher permittivity in order to lower its energy. The resulting force, F_i^B , is

$$\vec{F}_i^B = -\nabla W = -\nabla \frac{z_i^2 e^2}{8\pi \epsilon_e R_i} = -\frac{z_i^2 e^2}{8\pi R_i} \nabla \left(\frac{1}{\epsilon_e} \right) \quad (12)$$

Finally, if hydrated ions behave as dielectric spheres, then they should be polarized by an external field. If this field is nonuniform, then the dielectrophoretic force will attract an ion toward regions of a stronger (weaker) field if its equivalent permittivity is

higher (lower) than that of the surrounding medium. Generally, the ion permittivity is lower than that of the electrolyte solution so that the dielectrophoretic force tends to diminish the concentration both of counterions and coions close to charged surfaces. The magnitude of the dielectrophoretic force is²⁸

$$\begin{aligned} \vec{F}_i^D &= (\vec{m}_i \cdot \nabla) \vec{E} \\ &= \left(4\pi\epsilon_e R_i^3 \frac{\epsilon_i - \epsilon_e}{\epsilon_i + 2\epsilon_e} \vec{E} \cdot \nabla \right) \vec{E} = 2\pi\epsilon_e R_i^3 \frac{\epsilon_i - \epsilon_e}{\epsilon_i + 2\epsilon_e} \nabla(E^2) \end{aligned} \quad (13)$$

where \vec{m}_i is the induced dipole moment of an ion.

In equilibrium, the total force acting over the ions must be zero

$$\vec{F}_i^T + \vec{F}_i^E + \vec{F}_i^S + \vec{F}_i^B + \vec{F}_i^D = 0 \quad (14)$$

so that the equilibrium concentrations become

$$c_i = \frac{c_i^\infty \exp\left(\frac{W_i}{kT}\right) \exp\left(-\frac{z_i e \Psi}{kT}\right)}{1 + \sum_{j=1}^m \frac{c_j^\infty \exp\left(\frac{W_j}{kT}\right)}{c_j^{\max}} \left[\exp\left(-\frac{z_j e \Psi}{kT}\right) - 1 \right]} \quad (15)$$

where

$$W_i = \frac{z_i^2 e^2}{8\pi R_i} \left(\frac{1}{\epsilon_e^\infty} - \frac{1}{\epsilon_e} \right) - 2\pi R_i^3 \int_x^\infty \frac{\epsilon_e(\epsilon_i - \epsilon_e)}{\epsilon_i + 2\epsilon_e} \frac{d}{dx} \left(\frac{d\Psi}{dx} \right)^2 dx \quad (16)$$

for plane geometry. The two addends in this expression represent ion energy changes when the ion is moved from far away from the particle to its final position. The first corresponds to the change in the Born energy, and the second represents the work required to move the ion against the dielectrophoretic force.

Combining eqs 2 and 15 leads to the new modification of the Poisson–Boltzmann (NMPB) equation proposed in this letter

$$\epsilon_e \frac{d^2 \Psi}{dx^2} + \frac{d\epsilon_e}{dx} \frac{d\Psi}{dx} = \frac{-eN_A \sum_{i=1}^m z_i c_i^\infty \exp\left(\frac{W_i}{kT}\right) \exp\left(-\frac{z_i e \Psi}{kT}\right)}{1 + \sum_{i=1}^m \frac{c_i^\infty \exp\left(\frac{W_i}{kT}\right)}{c_i^{\max}} \left[\exp\left(-\frac{z_i e \Psi}{kT}\right) - 1 \right]} \quad (17)$$

which can be solved numerically to yield the electrostatic potential, ion concentration, and permittivity of the solution as functions of the distance to the surface.²⁹ Note that for $\epsilon_i = \epsilon_w$ eq 17 reduces to the MPB equation used in previous work by taking into account only steric effects because then $\epsilon_e = \epsilon_w$ in eq 10 so that $W_i = 0$ in eq 16. Moreover, if it is also considered that $c_i^{\max} \rightarrow \infty \forall i \in \{1, 2, \dots, m\}$, then eq 17 simplifies to the classic PB equation.

Note also that although a verification of the NMPB equation by means of MC simulations would be highly desirable this is not possible in practice because the inclusion of the polarization properties of ions into the MC procedure can only be done at great computational cost because of the fact that interaction forces between polarized dielectric spheres of hydrated ions are not pairwise additive.

Table 1. Parameter Values Used in the Simulation except When Indicated Otherwise

$e = 1.602 \times 10^{-19}$ C	$N_A = 6.022 \times 10^{23}$ mol ⁻¹	$k = 1.381 \times 10^{-23}$ J/K
$T = 298$ K	$\epsilon_w = 80\epsilon_0$	$\sigma = 0.75$ C/m ²
$z_1 = 2$	$c_1^\infty = 100$ mol/m ³	$R_1 = 3\text{Å}$
$z_2 = -2$	$c_2^\infty = 100$ mol/m ³	$R_2 = 3\text{Å}$

RESULTS AND DISCUSSION

To illustrate the quantitative impact of the present theory, we consider a single plane surface with charge density $\sigma > 0$ in contact with a binary aqueous electrolyte solution and use hydrated ion relative permittivity values of 40, 20, and 10 (typical values for monovalent and divalent ions are 25 and 8, respectively³²) and close packing ($p = 0.74$). The remaining system parameters are given in Table 1. Note that for the sake of simplicity we did not take into account the existence of a minimum approach distance of ions to the charged surface. In the considered case when all the ionic species have the same effective size, this would add only a constant to the surface potential value.³⁰

Figure 1 represents the counterion concentration (Figure 1a), the permittivity of the solution (Figure 1b), and the electric potential (Figure 1c) profiles. The numerical solutions of the MPB and PB equations are included for comparison. As can be observed, in all cases both the NMPB and MPB equations predict that the concentration of counterions attains its maximum concentration, c_i^{\max} , in the vicinity of the surface where a saturation layer appears (which contrasts with the standard PB equation where the ion concentration can be arbitrarily high). Because of this, the dielectric permittivity of the electrolyte solution changes from values close to ϵ_w far away from the surface to

$$\epsilon_e^{\text{sat}} = \frac{(1 + 2p)\epsilon_i + (1 - p)2\epsilon_w}{(1 - p)\epsilon_i + (2 + p)\epsilon_w} \epsilon_w \quad (18)$$

in the saturated layer whereas in the PB and MPB equations the dielectric permittivity value is a constant equal to ϵ_w throughout the system (Figure 1b). However, the Born and dielectrophoretic forces contribute to increase the double layer thickness because they are both repulsive for a hydrated ion permittivity lower than that of water (Figure 1a). The increment of the electrical double layer thickness together with the decrement of the solution permittivity strongly increases the potential drop across the electrical double layer, as can be observed in Figure 1c. Note that in the considered example the surface potential increases by roughly a factor of 2 solely because of steric effects (MPB) and by an additional factor of 2 due to a local change in the solution permittivity (NMPB). This behavior is qualitatively similar to that of the Ben-Yaakov et al. model.²⁰

Figure 2 represents the surface potential as a function of the surface charge density for $z_1 = -z_2 = 1$ (Figure 2a) and $z_1 = -z_2 = 2$ (Figure 2b) and the remaining parameter values indicated in the figure. This relationship is crucial to the interpretation of the double layer capacity as well as the impedance, dielectric properties, and electrokinetic phenomena in colloidal systems. Results predicted by the PB equation (point lines) and the MPB equation (dashed lines) are included for comparison. (A comparison with existing simulation data is not included because it would mainly show the ability of the Bikerman model to represent the excluded volume effect.) As can be observed and

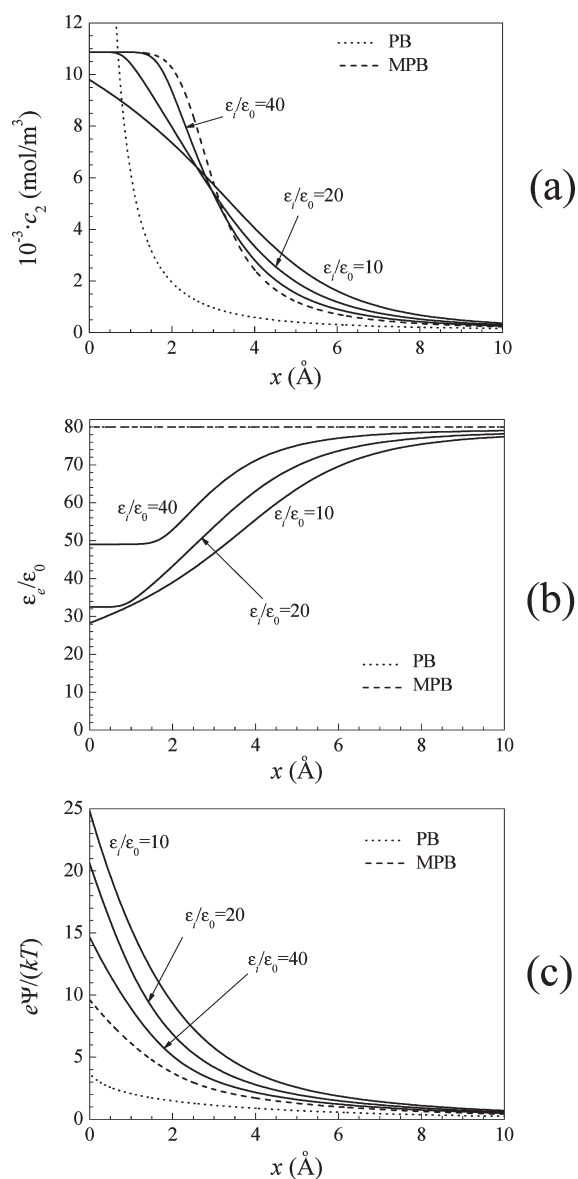


Figure 1. Ionic concentration (a), permittivity of the solution (b), and the electric potential (c) profiles for the indicated values of the hydrated ion permittivity. The remaining parameters are given in Table 1. The numerical solutions of the PB and the MPB equations are included for comparison.

as already noted in previous work dealing with this subject, steric effects included in the MPB equation only increase the potential drop across the electric double layer for medium and high surface charge densities. However, this increase is greatly amplified when the variation of the solution permittivity is taken into account and important differences appear even for relatively weak values of the surface charge density, most notably in Figure 2b. Note that in this figure, for example, for a surface charge of 0.4 C/m² the PB equation predicts a surface potential of 75 mV ($e\Psi/kT = 3$), a value that increases to roughly 100 mV and to nearly 200 mV according to the MPB and NMPB equations, respectively.

It was shown in ref 31 that the relationship between the surface charge density and the surface potential can be analytically deduced in the framework of the MPB equation (eq 9), provided that all of the ionic species have the same maximum concentration

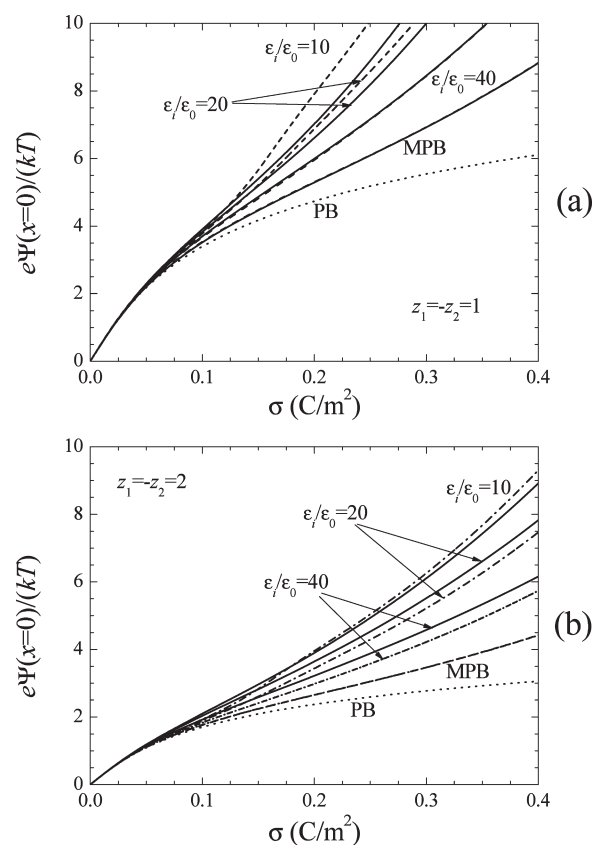


Figure 2. Surface potential as a function of the surface charge density for the indicated values of the hydrated ion permittivity and for $z_1 = -z_2 = 1$ (a) and $z_1 = -z_2 = 2$ (b). The remaining parameters are given in Table 1. Results predicted by the NMPB, MPB, and PB equations are represented by solid, dashed, and dotted lines, respectively, and dashed-dotted lines represent the approximate analytical expression (eq 19).

values. This is no longer true in the considered NMPB case because of the variation of the electrolyte solution permittivity with the distance to the interface. However, an approximate result can still be obtained by assuming that the solution permittivity value is everywhere equal to $\epsilon_e(x=0)$ and neglecting the dielectrophoretic contribution in eq 16:

$$\sigma^2 = 2N_A kT c^{\max} \epsilon_e(x=0) \ln \left\{ 1 + \sum_{i=1}^m \frac{c_i^{\infty}}{c^{\max}} \left[\exp \left(-\frac{z_i e \Psi(x=0)}{kT} \right) - 1 \right] \right\} \quad (19)$$

In this expression, $\epsilon_e(x=0)$ is determined by eq 10 with $c_i(x=0)$ expressed as a function of the surface potential by means of eq 15 considering that $W_i = 0$ (in view of the considered approximation). As can be seen in Figure 2, this expression reproduces the numerical results fairly well, therefore providing a rough estimate of the magnitude of the deviations between the predictions of the NMPB and the MPB equations.

In summary, we derived a new modified Poisson–Boltzmann (NMPB) equation that includes ion size effects by modeling the aqueous electrolyte solution as a suspension of polarizable insulating spheres in water. This model should allow for the interpretation of experimental data in electrochemical systems with relatively weak values of the surface charge density using reasonable effective ionic radii (similar to their hydrated values).

This improves over previous theoretical models that include steric effects, which can be used only for experiments involving large multivalent ions and high surface charges and requires, even then, excessively large effective ionic radii. An approximate equation for the surface charge density—surface electric potential relationship, valid for a wide range of system parameter values, is also reported.

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REFERENCES

- (1) Andelman, D. Electrostatic Properties of Membranes: The Poisson-Boltzmann Theory. In *Handbook of Biological Physics*; Lipowsky, R., Sackmann, E., Eds.; Elsevier Science: Amsterdam, 1995; Vol. 1, Chapter 12.
- (2) Evans, D. F. Wennerström, H. *The Colloidal Domain*; VCH Publishers: New York, 1994.
- (3) Hunter, R. J. *Zeta Potential in Colloid Science: Principles and Applications*; Academic Press: London, 1981.
- (4) Gouy, G. Sur la constitution de la charge électrique à la surface d'un électrolyte. *J. Phys. Theor. Appl* **1910**, *9*, 457.
- (5) Chapman, D. L. A contribution to the theory of electrocapillarity. *Philos. Mag.* **1913**, *25*, 475.
- (6) Stern, O. Zur theorie der electrolytischen Doppelschicht. *Z. Electrochem.* **1924**, *30*, 508.
- (7) Torrie, G. M.; Valleau, J. P. Electrical double layers. I. Monte Carlo study of a uniformly charged surface. *J. Chem. Phys.* **1980**, *73*, 5807.
- (8) Lozada-Cassou, M.; Saavedra-Barrera, R.; Henderson, D. The application of the hypernetted chain approximation to the electrical double layer: comparison with Monte Carlo results for symmetric salts. *J. Chem. Phys.* **1982**, *77*, 5150.
- (9) Ibarra-Armenta, J. G.; Martín-Molina, A.; Quesada-Pérez, M. Testing a modified model of the Poisson-Boltzmann theory that includes ion size effects through Monte Carlo simulations. *Phys. Chem. Chem. Phys.* **2009**, *11*, 309.
- (10) Bikerman, J. J. Structure and capacity of electrical double layer. *Philos. Mag.* **1942**, *33*, 384.
- (11) Eigen, M.; Wicke, E. The thermodynamics of electrolytes at higher concentration. *J. Phys. Chem.* **1954**, *58*, 702.
- (12) Borukhov, I.; Andelman, D.; Orland, H. Steric effects in electrolytes: a modified Poisson-Boltzmann equation. *Phys. Rev. Lett.* **1997**, *79*, 435.
- (13) Woelki, S.; Kohler, H. H. A modified Poisson-Boltzmann equation. I- Basic relations. *Chem. Phys.* **2000**, *261*, 411.
- (14) Bohinc, K.; Kralj-Iglic, V.; Iglic, A. Thickness of electrical double layer. Effect of ion size. *Electrochim. Acta* **2001**, *46*, 3033.
- (15) Levine, S.; Bell, G. M. Theory of a modified Poisson-Boltzmann equation. I. The volume effect of hydrated ions. *J. Phys. Chem.* **1960**, *64*, 1188.
- (16) Outhwaite, C. W.; Bhuiyan, L. B. An improved modified Poisson-Boltzmann equation in electric-double-layer theory. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 707.
- (17) Biesheuvel, P. M. Volume exclusion effects in the ground-state dominance approximation for polyelectrolyte adsorption on charged interfaces. *Eur. Phys. J. E* **2005**, *16*, 353.
- (18) Bhuiyan, L. B.; Outhwaite, C. W. Comparison of exclusion volume corrections to the Poisson-Boltzmann equation for inhomogeneous electrolytes. *J. Colloid Interface Sci.* **2009**, *331*, 543.
- (19) Iglič, A.; Gongadze, E.; Bohinc, K. Excluded volume effect and orientational ordering near charged surface in solution of ions and Langevin dipoles. *Bioelectrochemistry* **2010**, *79*, 223.
- (20) Ben-Yaakov, D.; Andelman, D.; Podgornik, R. Dielectric decrement as a source of ion-specific effects. *J. Chem. Phys.* **2011**, *134*, 074705.
- (21) Gonzales-Tovar, E.; Lozada-Cassou, M.; Henderson, D. Hypernetted chain approximation for the distribution of ions around a cylindrical electrode. 2.- Numerical solution for a model cylindrical polyelectrolyte. *J. Chem. Phys.* **1985**, *83*, 361.
- (22) Henderson, D.; Blum, L.; Lebowitz, J. L. An exact formula for the contact value of the density profile of a system of charged hard spheres near a charged wall. *J. Electroanal. Chem.* **1979**, *102*, 315.
- (23) Boda, D.; Fawcett, W. R.; Henderson, D.; Sokolowski, S. Monte Carlo, density functional theory, and Poisson-Boltzmann theory study of the structure of an electrolyte near an electrode. *J. Chem. Phys.* **2002**, *116*, 7170.
- (24) Aranda-Rascón, M. J.; Grosse, C.; López-García, J. J.; Horno, J. Electrokinetics of suspended charged particles taking into account the excluded volume effect. *J. Colloid Interface Sci.* **2009**, *335*, 250.
- (25) Bazant, M. Z.; Kilic, M. S.; Storey, B. D.; Ajdari, A. Towards an understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions. *Adv. Colloid Interface Sci.* **2009**, *152*, 48.
- (26) Biesheuvel, P. M.; van Soestbergen, M. Counterion volume effects in mixed electrical double layers. *J. Colloid Interface Sci.* **2007**, *316*, 490.
- (27) Maxwell, J. C. *A Treatise on Electricity and Magnetism*; Vol. 1, Oxford: The Clarendon Press, 1893.
- (28) Pohl, H. A. Some effects of nonuniform fields on dielectrics. *J. Appl. Phys.* **1958**, *29*, 1182.
- (29) A numerical solution of equation 17 can be obtained using a finite differences scheme (i.e., discretizing the space), for which a change in the spatial variable is made in order to obtain a finite region of study. Then the following algorithm is used:
 1. The starting point is the solution of eq 17 for an uncharged surface: $\Psi(x) = 0$, $W_i(x) = 0$, $c_i(x) = c_i^\infty$, and $\epsilon_e(x) = \epsilon_e^\infty$, where ϵ_e^∞ is calculated using eq 10.
 2. The surface density is slightly increased:
 - 2.1. Equation 17 is linearized and solved using the previous values for $W_i(x)$, $c_i(x)$, and $\epsilon_e(x)$;
 - 2.2. Equation 15 is used to calculate $\sum_{i=1}^m (c_i(x)/c_i^{\max})$;
 - 2.3. These values are used to calculate new values of $\epsilon_e(x)$ using eq 10;
 - 2.4. These values are used to calculate new values of $W_i(x)$ using eq 16; and
 - 2.5. Points 2.1–2.4 are repeated until convergence is attained.
 3. Point 2 is repeated until the desired surface density is attained.
- (30) López-García, J. J.; Aranda-Rascón, M. J.; Grosse, C.; Horno, J. Equilibrium electric double layer of charged spherical colloidal particles: effect of different distances of minimum ion approach to the particle surface. *J. Phys. Chem. B* **2010**, *114*, 7548.
- (31) López-García, J. J.; Aranda-Rascón, M. J.; Horno, J. Electrical double layer around a spherical colloid particle: the excluded volume effect. *J. Colloid Interface Sci.* **2007**, *316*, 196.
- (32) Gavryushov, S. Electrostatics of B-DNA in NaCl and CaCl₂ solutions: ion size, interionic correlation, and solvent dielectric saturation effects. *J. Phys. Chem. B* **2008**, *112*, 8955.