

Lattice Site Exclusion Effect on the Double Layer Interaction

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Received February 21, 2002. In Final Form: April 22, 2002

A lattice model for an electrolyte solution is proposed, which assumes that the hydrated ion occupies τ_i ($i = 1, 2$) sites on a water lattice. A lattice site is available to an ion “ i ” only if it is “free” (it is occupied by a water molecule, which does not hydrate an ion) and has also at least $(\tau_i - 1)$ first-neighbors free. The model accounts for the correlations between the probabilities of occupancy of adjacent sites and is used to calculate the “excluded volume” (lattice site exclusion) effect on the double layer interactions. It is shown that at high surface potentials the thickness of the double layer generated near a charged surface is increased, when compared to that predicted by the Poisson–Boltzmann treatment. However, at low surface potentials, the diffuse double layer can be slightly compressed, if the hydrated co-ions are larger than the hydrated counterions. The finite sizes of the ions can lead to either an increase or even a small decrease of the double layer repulsion. The effect can be strongly dependent on the hydration numbers of the two species of ions.

I. Introduction

The distribution of ions near a charged surface immersed in an electrolyte solution was first calculated on the basis of the Poisson–Boltzmann equation, assuming that the ions are point charges subjected to a mean electrostatic field. One of the first corrections of the theory was a result of the observation that, at high charges, the Poisson–Boltzmann equation predicts a too high density of counterions in the vicinity of the surface, whose volume exceeds the available volume. For this reason, Stern¹ suggested to consider in the vicinity of the surface a layer (the Stern layer) that contains bound counterions and is not available to the thermally moving counterions, and Bikerman^{2,3} proposed a modified Boltzmann expression which accounted for the finite volume of ions.

Ruckenstein and Schiby derived⁴ an expression for the electrochemical potential, which accounted for the hydration of ions and their finite volume. The modified Poisson–Boltzmann equation thus obtained was used to calculate the force between charged surfaces immersed in an electrolyte. It was shown that at low separation distances and high surface charges, the modified equation predicts an additional repulsion in excess to the traditional double layer theory of Derjaguin–Landau–Verwey–Overbeek.

The volume exclusion effect has received recently renewed attention.^{5–9} Paunov et al.⁵ argued that the excluded volume should be taken as eight times the real volume of the ions (this corresponds to the first-order correction in the virial expansion for a hard-sphere fluid)

and calculated on this basis the repulsive force. While this approximation is reasonable at very low concentrations, it breaks down when the volume of the spheres becomes about 10% of the total volume (since it predicts a maximum compaction of 12.5%). For hydrated ions with a large hydration radius, such as Na, this corresponds to a maximum electrolyte concentration of about 1 M.

In principle, the model can be improved by including in the “excluded volume”, in addition to the term proportional to the ion density, higher-order corrections proportional to powers of the ion density, which are related to the virial expansion for hard-sphere fluids. However, only the first eight virial coefficients have been calculated,¹⁰ and the power series converges slowly at high densities. To avoid this, one can account for the volume exclusion effect for hard-sphere fluids starting from an equation of state. The latter can be obtained with reasonable accuracy from the interpolation of the virial expansion, either using Padé approximants,¹¹ or other ad hoc analytical continuations of the series, a procedure first employed by Carnahan and Starling.¹² The method was employed by Lue et al.⁹ to calculate the counterions distribution starting from the corresponding modified Poisson–Boltzmann equation. The advantage of this method consists of its easy application to ions of different sizes, since good approximations of the equation of state (and hence of the excess chemical potential with respect to an ideal solution) are known for mixtures of hard spheres of different sizes.¹³

The main question is whether the hydrated ions behave as hard spheres; while this seems plausible for ions much larger than the water molecules, it is probably not entirely applicable to small ions, whose hydration shells continuously change. Marcelja calculated recently the double layer interaction⁸ using the anisotropic hypernetted chain method and potentials of mean force between pairs of ions in water, provided by Monte Carlo simulations. This

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method implicitly accounted for the excluded volume and also for other correlations between ions; however, it required accurate information about the interactions between pairs of ions in water. It was shown¹⁴ that the method is very sensitive to the details of the potential of the mean force between pairs of ions and that different models can lead to even qualitatively different results.

Another approach that accounted for the volume exclusion effect was based on lattice models.⁴ Recently, Kralj-Iglic and Iglic⁶ and, independently, Borukhov et al.⁷ derived an expression for the counterions distributions, starting from a modified Poisson–Boltzmann equation, for a lattice whose cell size was that of a hydrated ion (both kind of ions were considered of the same size). The lattice cell can be either occupied or not by a hydrated ion. This type of lattice allows for a maximum compaction of unity. For this reason, in this case the excess chemical potential (with respect to an ideal solution) is, in general, important either for very large ions at sufficiently large concentrations or for small ions at high ionic strengths and high surface potentials. It is not yet clear how this model^{6,7} can be extended to electrolytes with hydrated ions of different sizes.

A modality to overcome these difficulties was proposed earlier by Ruckenstein and Schiby,⁴ who considered that the ions of different kinds ($i = 1, 2$) occupy τ_i sites on a water lattice. Since the size of the cell of the water lattice is independent of the size of the ions, the model can be easily extended to any number of ions of different kinds. To compare the prediction of various models, let us first consider the case in which the ions of different kinds have the same volume ($\tau_1 = \tau_2 = \tau$).

For n hard spherical particles of radius R and volume τv (v being the volume of a cell of the lattice) and for large values of τ (the continuum limit), the volume V available to the particles can be calculated as follows.¹⁵ The center of a new particle cannot be located within a distance $2R$ from an existing particle; hence each existing particle can be thought of as carrying a “forbidden region” of radius $2R$ (volume $8\tau v$), where a new particle cannot be placed. However, by subtracting $8\pi v$ from the total volume V of the system, one obtains an underestimate of the available volume, since the “forbidden regions” of the existing particles overlap (and hence the overlapping regions are subtracted twice). Assuming that the particles are uniformly distributed in the available space, the overlapping volume per particle is¹⁵ $34\tau v \pi v / V \approx 34(\tau v) \times (\tau \eta)$ (where $\eta = n v / V = n / N$ is the ratio between the total volume occupied by the ions and the total volume of the system, $\tau \eta$ is the ratio between the total volume of the hydrated ions and the total volume of the systems, and N is the total number of sites (n ions + $(\tau - 1)n$ water molecules hydrating the ions + free water molecules). Since the second correction should be counted only once per each pair of particles, the available volume is¹⁵

$$V = V(1 - 8\tau\eta + 17(\tau\eta)^2 - \dots) \quad (1)$$

The first three terms of the series are overestimating the available volume, since they do not account for the overlapping of the “forbidden regions” for triplets, and a new correction (proportional to the third power of density) should be included, and so on. The calculation of the remaining terms of the (slowly) converging series is however increasingly difficult. The first two terms of the

series (1) constitute the result proposed recently for the volume available to a hard sphere fluid by Paunov et al.⁵

On the other hand, if the hydrated ions are totally deformable (hence, they can occupy a site if the site is free and other $(\tau - 1)$ sites are free, regardless of their positions), the available volume is given by¹⁵

$$V = V(1 - \tau\eta) \quad (2)$$

which is the result of Kralj-Iglic and Iglic⁶ or Borukhov et al.⁷ However, the hydrated ions are probably not totally rigid (since the hydration shell changes its shape and its water molecules, which are bound to the ion in a transient manner only. To account for this, Ruckenstein and Schiby⁴ considered that the ion of volume τv can occupy a site of the water lattice only if the site and its $(\tau - 1)$ neighbors are free (i.e., free of ions and hydration molecules). The probability for a randomly chosen site to be free is $(1 - \tau\eta)$. Considering that the probabilities of occupancy of neighboring sites are independent, the available volume is⁴

$$V = V(1 - \tau\eta)^\tau \quad (3a)$$

The result can be extended to ions of different sizes τ_i

$$V_i' = (1 - \tau_1\eta_1 - \tau_2\eta_2)^{\tau_i} \quad (i = 1, 2) \quad (3b)$$

where $\eta_i = n_i / N$, n_i being the number of ions of kind “ i ”. In this model, the “available volume” is different for each kind of ion.

For $\tau = 1$, eq 3a becomes identical to eq 2 and for not too large values of τ ($\tau < 8$) predicts an available volume between those of eqs 1 and 2 and, hence, can be interpreted as corresponding to a partially deformable hydrated ion. However, for large values of τ , the probability of occupation of one site becomes strongly affected by the occupation of their adjacent sites.

The purpose of this paper is to calculate the electrochemical potential and the double layer repulsion using a lattice model, applicable to hydrated ions of different sizes, that accounts for the correlation between the probabilities of occupancy of adjacent sites. As the other lattice models,^{4–7} this model accounts only for the steric, excluded volume effects due to ionic hydration. In fact, short-ranged electrostatic interactions between the ions and the dipoles of the water molecules, as well as the van der Waals interactions between the ions and the water molecules, are responsible for the formation of the hydrated ions. The long-ranged interactions between charges are taken into account through an electrostatic (mean field) potential. The correlation between ions is expected to be negligible for sufficiently low ionic concentrations.

II. The Lattice Model

In the model of Ruckenstein and Schiby, the ion can replace a water molecule on the lattice of water only if the site and $(\tau - 1)$ of its first neighbor sites are “free” (i.e., occupied by water molecules which do not hydrate other ions); the probability of occupation of any of the τ sites was taken to be the same.⁴ Here we will account to some extent for the correlation between the probabilities of occupancy of adjacent sites, assuming a coordination number w in the water lattice.

The number of sites available to an ion is (in the large N limit) the total number of sites, N , times the probability that a randomly chosen site can be occupied by an ion. This implies that the site and at least $(\tau - 1)$ of its first

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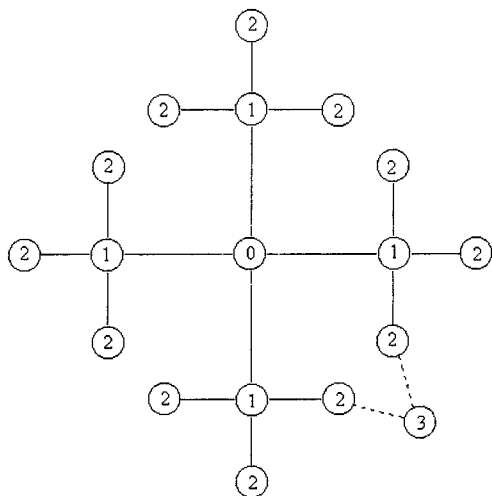


Figure 1. A schematic planar projection of the direct bonding of a water molecule in an ice lattice. A central site (0) has four first-neighbors (1), which are adjacent to the central site and to three other molecules (2). Each of the 12 second neighbors (2) of the central site (0) is adjacent to only one first-neighbor (1) of the central site. Some of the third-order neighbors (3) of the central site (molecules separated through three successive bondings by the central site) are, however, adjacent to two second neighbors. Only one of the third neighbors is drawn.

neighbors are “free” water molecules. It will be assumed that the probability of occupation of any first neighbor (of a central site) is independent of each other. This is obviously not valid for a normal liquid, which has a large number of nearest neighbors. Indeed, at close compaction, each of the 12 first neighbors of a selected site has as first neighbors (is adjacent to) other 3 first neighbors of the same selected site, and hence their occupation probabilities are not independent, because the ions that may occupy the first neighbors compete for hydration molecules. However, for sparse lattices, it is a reasonable approximation. Indeed, for ice (with a coordination number of 4), all the first and second neighbors of the central site are distinct (i.e., none of the first neighbors is adjacent to other first neighbors of the same central site and each of the second neighbors of the central site is adjacent to only one of the first neighbors of the same site; see Figure 1). Each of the third neighbors of the central site is, however, adjacent to two second neighbors of the central site; this leads to a small correlation between the occupancy of the second neighbors, which will be, however, neglected. A molecule of liquid water has between 4.4 and 4.9 first neighbors,¹⁶ which is much closer to the coordination in ice (4) than to that in a normal liquid (~ 12). We will therefore assume that for a water lattice the probability of occupation of one of the w sites first-neighboring a central site is independent of the occupation of the other $(w - 1)$ sites.

In what follows an expression will be established for the probability for a random site to be available to a hydrated ion, by assuming first that a single kind of ion is present. The chance for a site, chosen randomly (which will be called central site), to be occupied by an ion is η , and the probability for the site to be “free” is

$$p_{f,0} = 1 - \tau\eta \quad (4a)$$

Let us now obtain an expression for the probability for an ion to occupy one site adjacent to a free central one.

An ion surrounded by w water molecules can be hydrated by $(\tau - 1)$ molecules in $C_w^{\tau-1}$ distinct configurations, where $C_w^{\tau-1} = w! / [(w - \tau + 1)!(\tau - 1)!]$ is the number of combinations in which $(\tau - 1)$ objects (water molecules hydrating the ion) can be selected out of w objects (available water molecules). However, because one of the adjacent molecules (the central site) is “free”, there are only $C_{w-1}^{\tau-1}$ configurations possible for the hydrated ion to sit on the lattice (the number of combinations in which $(\tau - 1)$ hydrating water molecules can be chosen out of the remaining $(w - 1)$ available water molecules).

It will be assumed that all the possible configurations of the ion hydrated by the $(\tau - 1)$ water molecules are equally probable and that the number of hydrated configurations of an ion is not affected by its concentration. The last approximation is valid only for small ion concentrations and is reasonable because the density of ions is in general much smaller than unity; only the density of hydrated ions ($\tau\eta$) can become comparable to unity.

The probability for an ion to occupy a site adjacent to a free central one ($p_{oi,1}$) is therefore

$$p_{oi,1} = \eta \frac{C_{w-1}^{\tau-1}}{C_w^{\tau-1}} = \eta \frac{w - \tau + 1}{w} \quad (4b)$$

and consequently, the probability for the site to be not occupied by an ion ($p_{fi,1}$) is given by

$$p_{fi,1} = 1 - \eta \frac{w - \tau + 1}{w} \quad (4c)$$

We will now calculate the probability for a water molecule, first-neighboring a free central site, not to participate in the hydration of an ion. Since one of its neighbors (the central site) is a free water molecule, it can hydrate only an ion occupying one of the remaining $(w - 1)$ adjacent sites (which are second-neighbors of the central site). Even if an ion occupies one of these sites, it can be hydrated by $(\tau - 1)$ out of the other $(w - 1)$ of its first-neighbors, which are third-order-neighbors of the central site (the third-order-neighbors are connected to the central site through three successive bonds, regardless of their mutual angles). Since there are $C_{w-1}^{\tau-1}$ configurations in which the ion can be hydrated by the water molecules located in the third-neighboring sites of the central site, out of a total of $C_w^{\tau-1}$ configurations of possible hydration of an ion, the probability for an ion to occupy a site second neighbor to a central site, and not to be hydrated by the molecule occupying the first-neighboring site, is

$$p_{oi,2} = \eta \frac{C_{w-1}^{\tau-1}}{C_w^{\tau-1}} = \eta \frac{w - \tau + 1}{w} \quad (4d)$$

Therefore, a water molecule first-neighboring a free central site does not hydrate an adjacent ion, located on a second-neighboring site of the central site, in the following two circumstances: (1) there are no ions occupying any of the $(w - 1)$ sites, and (2) there is one or more ions occupying some or all of the $(w - 1)$ positions, ions which are hydrated by water molecules located on the third-order-neighboring sites of the central site. Since the probabilities of occupation of the first neighbors of each site are assumed independent of each other, the probability for none of the $(w - 1)$ sites to be occupied by ions is $(1 - \eta)^{(w-1)}$ and the probability for an ion to occupy one site and the other $(w - 2)$ sites to be free of ions is $\eta(1 - \eta)^{(w-2)}$. Because there are $(w - 1)$ modes in which an ion can occupy one of the $(w - 1)$ sites, the probability for an

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ion to occupy one of the $(w-1)$ sites and to be not hydrated by the water molecules first neighboring the central site is $(w-1)\eta(1-\eta)^{w-2}[(w-\tau+1)/w]$. Adding the probabilities for ions to occupy two, three, ..., $(w-1)$ sites, none of them being hydrated by the water molecules adjacent to the central free site, one obtains the following expression for the probability for a water molecule, first neighboring the central free site, not to hydrate any ion

$$p_{\text{fh},1} = (1-\eta)^{w-1} + (w-1)\eta(1-\eta)^{w-2}\left(\frac{w-\tau+1}{w}\right) + \dots + \eta^{w-1}\left(\frac{w-\tau+1}{w}\right)^{w-1} = \sum_{k=0}^{w-1} C_{w-1}^k \eta^k (1-\eta)^{w-1-k} \left(\frac{w-\tau+1}{w}\right)^k \quad (4e)$$

Consequently, the probability for one neighbor of the central site neither to be occupied by an ion nor to participate in the hydration of another ion is given by

$$p_{\text{f},1} = p_{\text{f},1} p_{\text{fh},1} \quad (4f)$$

Hence, the probability for all w first neighbors of the central site to be free is $(p_{\text{f},1})^w$ and the probability for $(w-1)$ to be free and one not free (i.e., either occupied by an ion or hydrating another ion) is $w(p_{\text{f},1})^{w-1}(1-p_{\text{f},1})$ (there are w places that can be occupied by a nonfree water molecule). The last term of the sum is the probability for $(\tau-1)$ water molecules to be free and $(w-\tau+1)$ to be occupied, which is $C_w^{\tau-1} p_{\text{f},1}^{\tau-1} (1-p_{\text{f},1})^{w-\tau+1}$. Therefore, the probability for a central site (chosen randomly) and at least $(\tau-1)$ of its first neighbors to be "free" is given by

$$P = p_{\text{f},0} (p_{\text{f},1})^w + w p_{\text{f},1}^{w-1} (1-p_{\text{f},1}) + \dots + C_w^{\tau-1} p_{\text{f},1}^{\tau-1} (1-p_{\text{f},1})^{w-\tau+1} \quad (4g)$$

When two ionic species, of hydrated sizes τ_1 and τ_2 are present, the probabilities for a randomly chosen central site to be free is given by

$$p_{\text{f},0} = 1 - \tau_1 \eta_1 - \tau_2 \eta_2 \quad (5a)$$

the probability for a first-neighboring site not to be occupied by an ion by

$$p_{\text{fh},1} = 1 - \eta_1 \frac{w-\tau_1+1}{w} - \eta_2 \frac{w-\tau_2+1}{w} \quad (5b)$$

and the probability for a water molecule from a first-neighboring site of a central free one not to participate in the hydration of an ion by

$$p_{\text{fh},1} = (1-\eta_1-\eta_2)^{w-1} + (w-1)(1-\eta_1-\eta_2)^{w-2} \times \left[\eta_1 \left(\frac{w-\tau_1+1}{w} \right) + \eta_2 \left(\frac{w-\tau_2+1}{w} \right) \right] + \dots \quad (5c)$$

With $p_{\text{f},1} = p_{\text{fh},1} p_{\text{fh},1}$, the probability for a random central site to be available to an ion is

$$P_i = p_{\text{f},0} (p_{\text{f},1})^w + w p_{\text{f},1}^{w-1} (1-p_{\text{f},1}) + \dots + C_w^{\tau_i-1} p_{\text{f},1}^{\tau_i-1} (1-p_{\text{f},1})^{w-\tau_i+1} \quad (5d)$$

$(i = 1, 2)$

where the volumes available to each species, $V_i' = P_i V$, are different ($\tau_1 \neq \tau_2$).

III. The Excess Chemical Potential

The chemical potential for a fluid of n identical particles interacting with a hard-core potential (which is zero at separations larger than the distance of closest approach and infinity for smaller separations) can be calculated using the equation

$$\mu = -kT \left(\frac{\partial \ln Z}{\partial n} \right)_{V,T} \quad (6a)$$

where k is the Boltzmann constant, T the absolute temperature, and Z the partition function

$$Z = \langle z \rangle^n / n! \quad (6b)$$

In eq 6b, $\langle z \rangle$ represents the individual partition function, averaged over all possible configurations

$$\langle z \rangle = \frac{1}{h^3} z \int \int \int \exp\left(-\frac{p^2}{2mkT}\right) d^3p \times \left\langle \int \int \int \exp\left(-\frac{U}{kT}\right) d^3x \right\rangle = \frac{zV}{\Lambda^3} \quad (6c)$$

where z accounts for the internal degree of freedom of the particle, h is the Planck constant, and Λ is the thermal de Broglie wavelength. The individual partition function is proportional to the available volume V , which is the volume available to a particle, out of the total volume V , when the other $(n-1)$ particles occupy nonoverlapping positions. Using eqs 6a–c, one obtains for the chemical potential the expression

$$\mu = -kT \ln\left(\frac{z}{\Lambda^3}\right) + kT \ln \frac{n}{V} = \mu_0 + kT \ln\left(\frac{n}{V}\right) = \mu_{\text{id}} + \mu_{\text{excess}} \quad (6d)$$

where

$$\mu_{\text{id}} = -kT \ln\left(\frac{z}{\Lambda^3}\right) + kT \ln \frac{n}{V} \quad (6e)$$

is the chemical potential in an ideal mixture and

$$\mu_{\text{excess}} = kT \ln(VV) \quad (6f)$$

is the excess chemical potential, due to the hard-core interactions. Since for a lattice the available volume is $V = PV$, where P is the probability for a randomly chosen site to be occupied by an ion, eq 6f becomes

$$\mu_{\text{excess}} = -kT \ln P \quad (6g)$$

The excess chemical potential for a dilute hard-sphere fluid in the Paunov et al. approximation (eqs 1 and 6f) is given by⁵

$$\mu_{\text{excess}}^{\text{P}} = -kT \ln(1 - 8\tau\eta) \quad (7a)$$

for a lattice model in which each ion occupies one site (Iglic–Iglic model) (eqs 2 and 6f) by^{6,7}

$$\mu_{\text{excess}}^{\text{II}} = -kT \ln(1 - \tau\eta) \quad (7b)$$

for the Ruckenstein and Schiby lattice model (eqs 3 and 6f) by⁴

$$\mu_{\text{excess}}^{\text{RS}} = -\tau kT \ln(1 - \tau\eta) \quad (7c)$$

and for the present lattice model (eqs 4e and 6f) by

$$\mu_{\text{excess}}^{\text{MR}} = -kT \ln[p_{f,0}(p_{f,1}^w + wp_{f,1}^{w-1}(1 - p_{f,1}) + \dots + C_w^{\tau-1} p_{f,1}^{\tau-1}(1 - p_{f,1})^{w-\tau+1})] \quad (7d)$$

The excess chemical potential of a hard-sphere fluid can be calculated on the basis of an equation of state using the expressions¹⁷

$$A_{\text{excess}} = nkT \int_0^{\tau\eta} \left(\frac{pV}{nkT} - 1 \right) d(\tau\eta) \quad (8)$$

$$\mu_{\text{excess}} = \frac{1}{n} \left(A_{\text{excess}} + kT\tau\eta \frac{\partial A_{\text{excess}}}{\partial \tau\eta} \right)$$

where p is the pressure, A_{excess} represents the excess Helmholtz free energy, and $\tau\eta$ is the fraction of the volume occupied by the hydrated ions. Using the Carnahan–Starling equation of state¹²

$$\frac{pV}{nkT} = \frac{1 + \tau\eta + (\tau\eta)^2 - (\tau\eta)^3}{(1 - \tau\eta)^3} \quad (9)$$

the excess chemical potential becomes

$$\mu_{\text{excess}}^{\text{CS}} = kT \frac{\tau\eta(8 - 9\tau\eta + 3(\tau\eta)^2)}{(1 - \tau\eta)^3} \quad (7e)$$

In Figure 2 the excess chemical potentials provided by the models listed above (eqs 7a–e) are compared. We used $w = 5$, which is the closest integer to the estimate of the number of first neighbors in water (4.4–4.9),¹⁶ and (a) $\tau = 6$, (b) $\tau = 5$, and (c) $\tau = 4$. A more realistic model (but more tedious to calculate) could have been obtained by the statistical averaging of systems with different values of w and τ .

When the ion is hydrated by all the adjacent molecules ($w = \tau - 1$), there is a strong lattice-site exclusion effect at high ionic concentrations, since the central site can be available to an ion only when both its first and second neighbors are free of ions (a total of $1 + w + w(w - 1) = w^2 + 1$ sites). On the other hand, when the hydration number ($\tau - 1$) is low, almost any “free” site can be occupied by an ion, since in this case there is a high chance to find at least $(\tau - 1)$ free water molecules around a selected site. In the next section it will be shown that there is a strong dependence of the site-exclusion effect on the hydration number and, hence, that specific ion effects can be important in the double layer interactions.

IV. Excluded-Site Effect on the Double Layer Repulsion

IV.1. General Equations. At thermodynamic equilibrium, the electrochemical potential, (eq 6d) is con-

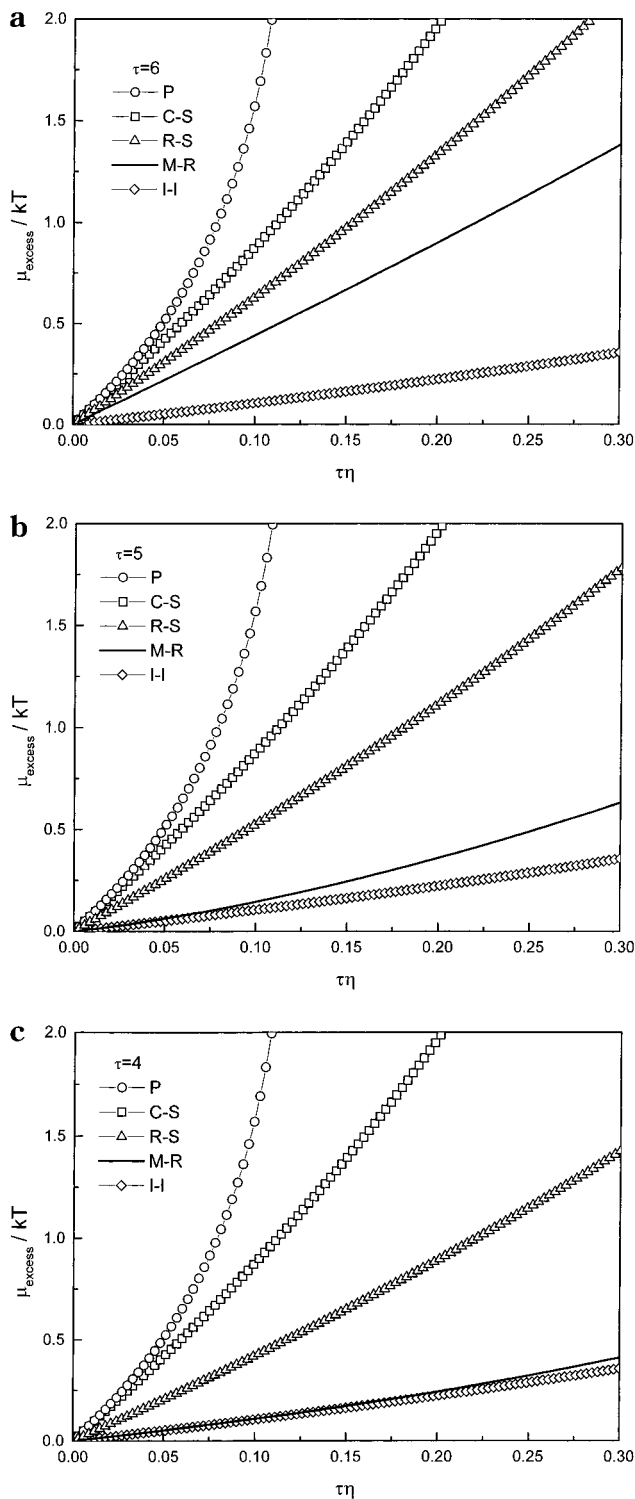


Figure 2. The excess chemical potential relative to that of an ideal solution, for the models discussed in the text (eqs 7a–e) and (a) $\tau = 6$, (b) $\tau = 5$, and (c) $\tau = 4$.

stant in the system

$$\mu_i^0 + kT \ln(n_i(x)/V) - kT \ln P_i(n_1(x), n_2(x), \psi(x)) + q_i \psi(x) = \text{constant} \quad (10)$$

($i = 1, 2$)

where μ_i^0 is the standard chemical potential of species i , q_i is the charge of an ion of species i ($q_i = (-1)^{i+1}e$, with e the protonic charge), ψ is the mean potential, and x

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denotes the distance from one of the two charged, planar surfaces separated by a distance l . It will be assumed that the surface charge and potential are negative; hence the subscript 1 denotes the counterions and the subscript 2 is for co-ions. Consequently, the concentration of each species of ions for a 1:1 electrolyte is given by

$$n_i(x) = n \frac{P_i(x)}{P_i(x=\infty)} \exp\left(-\frac{q_i \psi(x)}{kT}\right) \quad (11a)$$

($i = 1, 2$)

where $n_1 = n_2 = n$ for $x = \infty$.

A modified Poisson–Boltzmann equation is obtained by replacing in the Poisson equation for parallel plates

$$\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{e(n_1(x) - n_2(x))}{\epsilon \epsilon_0 V} \quad (11b)$$

n_1 and n_2 by their expressions (11a), $\epsilon \epsilon_0$ being the dielectric constant of water. The above equation has to satisfy the boundary conditions $\partial \psi(x)/\partial x|_{x=l/2} = 0$ at the middle distance between the plates, and either $\psi_S = \psi(x=0) = \text{const}$ (for constant surface potential) or $\partial \psi(x)/\partial x|_{x=0} = \text{const}$ (for constant surface charge density), where ψ_S represents the surface potential.

Caution should be taken when calculating the double-layer force between two parallel plates. It is clear that the force is not proportional to the excess concentration of ions at the middle distance (with respect to the concentration of ions at infinity), since this Langmuir equation involved the assumption of ions of negligible sizes. We will use instead the procedure introduced by Verwey and Overbeek,¹⁸ which is based on general thermodynamic principles, and does not imply the Boltzmann distribution of ions.¹⁹ The force, per unit area, between two parallel plates separated by a distance l is given by

$$p_\psi(l) = 2 \frac{\partial}{\partial l} \int_0^{\psi_S} \sigma(\psi) d\psi \quad (12a)$$

at constant surface potential ψ_S and

$$p_\sigma(l) = -2 \frac{\partial}{\partial l} \int_0^{\sigma_S} \psi(\sigma) d\sigma \quad (12b)$$

at constant surface charge density σ_S , where the surface charge density is related to the surface potential through the expression

$$\frac{\partial \psi(x)}{\partial x} \Big|_{x=0} = -\frac{\sigma}{\epsilon \epsilon_0} \quad (13)$$

The relation between the surface charge density and surface potential, as a function of the distance l , is obtained using the additional boundary condition required by symmetry $\partial \psi(x)/\partial x|_{x=l/2} = 0$. Consequently, eqs 12 can be integrated numerically to provide the value of the double layer force.

IV.2. Distribution of Ions near a Charged Surface. The distribution of counterions in the vicinity of a single charged surface, at a high surface potential ($\psi_S = 0.1$, Figure 3a) is represented as a function of the distance x

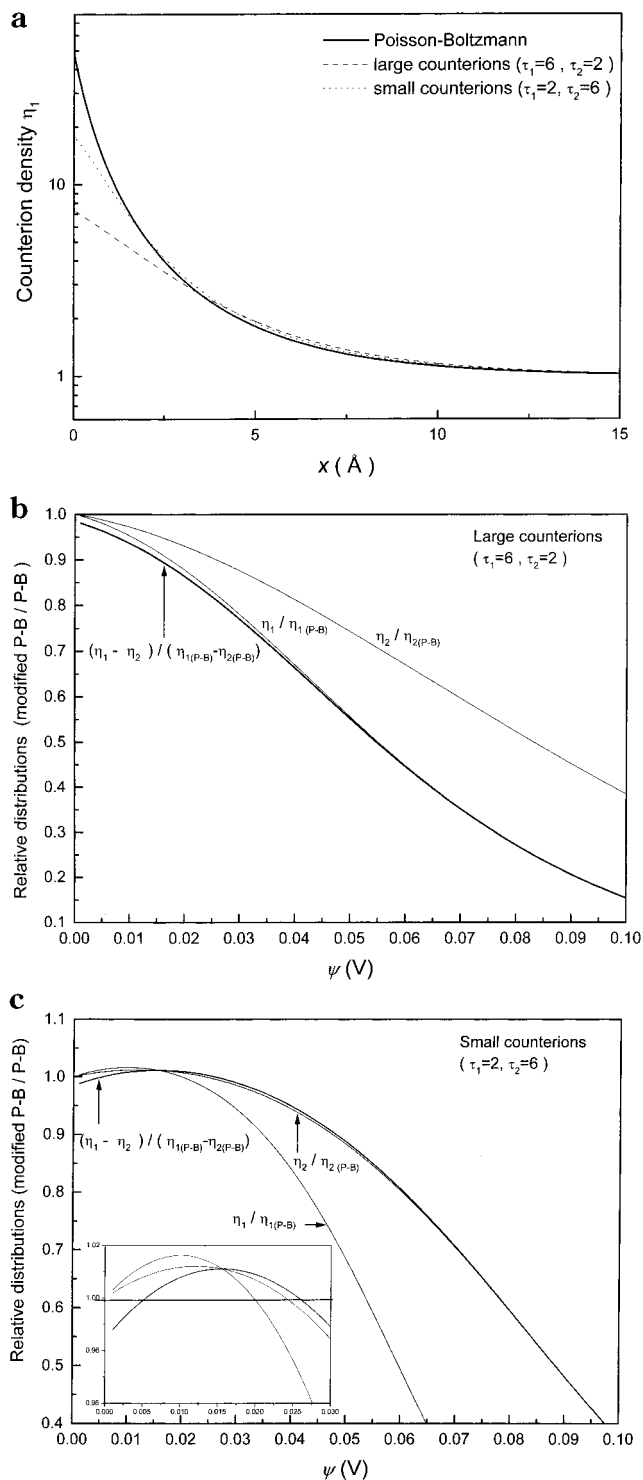


Figure 3. (a) Ion distributions in the vicinity of a single charged surface at high potentials ($\psi_S = 0.1$ V), for large ($\tau_1 = 6$, $\tau_2 = 2$) and small ($\tau_1 = 2$, $\tau_2 = 6$) counterions: $n/V = 1.0$ M and $T = 300$ K. (b) Ion and charge distributions (relative to those predicted by the Boltzmann distribution) as functions of the mean potential. Large counterions ($\tau_1 = 6$, $\tau_2 = 2$): $n/V = 1.0$ M and $T = 300$ K. (c) Ion and charge distributions (relative to those predicted by the Boltzmann distribution) as functions of the mean potential. Small counterions ($\tau_1 = 2$, $\tau_2 = 6$): $n/V = 1.0$ M and $T = 300$ K.

from the surface for $w = 5$, $\tau_1 = 6$, and $\tau_2 = 2$ (large counterions) and for $\tau_1 = 2$, $\tau_2 = 6$ (small counterions). In both cases, the densities of counterions and co-ions in the vicinity of the surface are smaller than those predicted by the Poisson–Boltzmann equation, since the agglomeration

(18) Verwey, E. J. W.; Overbeek, J. Th. G. *Theory of stability of lyophobic colloids*; Elsevier: Amsterdam, 1948.

(19) For a detailed discussion, see: Ruckenstein, E. *Adv. Colloid Interface Sci.* **1998**, *75*, 169.

of the finite-size counterions near the surface reduces the available volume.

Let us examine now the effect of the excluded volume at low surface potentials. In the linear approximation of the Poisson–Boltzmann expression, the increase in the number of counterions in the vicinity of the interface equals the decrease in the number of co-ions. If the co-ions have a larger size, one expects the available volume near the surface to be larger than that in the bulk. As a result, a concentration of ions in excess to that predicted by the Poisson–Boltzmann equation is expected to occur in the vicinity of the surface, when the volume exclusion is taken into account.

Of course, when the potential of the surface becomes sufficiently large, the linear approximation fails, and the (exponential) increase in the counterions density in the vicinity of the surface predicted by the Poisson–Boltzmann equation largely exceeds the depletion of co-ions and the available volume is expected to become smaller than that in the bulk.

To illustrate this, let us use the simple approximation suggested by Bikerman²

$$n_i(\psi) = n \frac{\left(1 - \frac{n_1(\psi)v_1 + n_2(\psi)v_2}{V}\right)}{\left(1 - n \frac{v_1 + v_2}{V}\right)} \exp\left(-\frac{q_i\psi}{kT}\right) \quad (14)$$

(where v_i is the volume of the hydrated ions), which combined with Poisson equation becomes, in the linear approximation

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{2ne^2}{\epsilon\epsilon_0 kT} \psi \left(\frac{1}{1 + \frac{n(v_1 - v_2)}{V} \frac{e\psi}{kT}} \right) = \frac{1}{\lambda'^2} \left(\frac{1}{1 + \frac{n(v_1 - v_2)}{V} \frac{e\psi}{kT}} \right) \psi = \frac{1}{\lambda'^2} \psi \quad (15)$$

When $v_1 > v_2$, the effective Debye–Hückel length λ' (which now depends on $\psi(x)$) is larger than that obtained for the Poisson–Boltzmann equation. Consequently, the diffuse double layer is larger in the vicinity of a charged surface, as predicted earlier.^{4–7,9} However, when $v_2 > v_1$ (small counterions), $\lambda' < \lambda$ and the diffuse double layer is compressed. The effect is proportional to the ionic strength and is, in general, small for typical electrolyte concentrations, since $|n(v_1 - v_2)/V| \ll 1$ and $|e\psi/kT| < 1$.

Let us now calculate the dependence of the ions and charge densities on the mean potential in the present lattice model. For large counterions (Figure 3b) the ratios between counterion and co-ion densities and those calculated with the Poisson–Boltzmann equation are monotonic decreasing functions of the mean potential ψ . For small counterions, however, at low potentials (Figure 3c), the two ratios slightly exceed unity, because the available volume (as compared to V at $\psi = 0$) increases. The ratio between the local charge density (which is proportional to $\eta_1 - \eta_2$) and that calculated from the Poisson–Boltzmann equation also exceeds slightly unity in a range of potentials. The subunit ratios at very low potentials occur because the available volumes are different for the two types of ions and depend differently on the potential ψ ; one of them grows initially slowly and decreases later slowly, while the other grows initially quicker but decreases later also quicker.

IV.3. Modification of the Double Layer Repulsion Due to the Finite Volume of Ions. In the linear approximation of the Poisson–Boltzmann equation, the potential between two surfaces, separated by the distance l is given by

$$\psi(x) = \psi_s \frac{\cosh\left(\frac{x}{\lambda} - \frac{l}{2\lambda}\right)}{\cosh\left(\frac{l}{2\lambda}\right)} \quad (16)$$

and eq 13 yields

$$\sigma_s = \frac{\epsilon\epsilon_0 \psi_s}{\lambda} \tanh\left(\frac{l}{2\lambda}\right) \quad (17)$$

The double layer forces obtained from eqs 12, 16, and 17 are

$$p_\psi(l) = \frac{\epsilon\epsilon_0 \psi_s^2}{2\lambda^2 \cosh^2\left(\frac{l}{2\lambda}\right)} \quad (18a)$$

at constant surface potential and

$$p_\sigma(l) = \frac{\sigma_s^2}{2\epsilon\epsilon_0 \sinh^2\left(\frac{l}{2\lambda}\right)} \quad (18b)$$

at constant surface charge.

At constant surface charge, an increase in the Debye length implies an increase in the repulsion at any distance. However, this is not true for constant surface potential, since the function $(l/2\lambda)^2 \cosh^{-2}(l/2\lambda)$ (for fixed l) has a maximum at $l/2\lambda \approx 1.2$. Consequently, an increase in the effective Debye length corresponds to an increase in repulsion only at large separations ($l > 2.4\lambda$) but to a decrease in repulsion at smaller separations.

At sufficiently high surface charges or potentials, the thickness of the double layer (the effective Debye length) increases when the finite volumes of the ions are taken into account. The replacement of λ by a larger value in eq 18b leads to a higher repulsion at any separation distance. This suggests that the accounting of the ion sizes will lead to a higher repulsion at a high constant surface charge. Figure 4a ($n/V = 0.01$ M, $\sigma_s = \text{constant} = 0.32$ C/m²) confirms this expectation. The replacement of λ with a larger value in eq 18a suggests that, at high constant surface potentials, the double layer interaction will be decreased at short separation distances by the finite sizes of the ions. This expectation is confirmed by Figure 4b ($n/V = 0.01$ M, $\psi_s = \text{constant} = 0.1$ V). The modification of the double layer repulsion due to the sizes of the ions is, however, much smaller when the counterions are smaller and is strongly dependent on the hydration number, when the latter has a value near to w .

At low surface charges, the effective Debye length can either increase or decrease, depending on the relative sizes of the two species of ions. Consequently, the double layer repulsion might become smaller than that predicted by the Poisson–Boltzmann equation not only at constant surface potential but also at constant surface charge. In Figure 5, the double layer repulsion (relative to that predicted by Poisson–Boltzmann equation) is presented for (a) a small constant surface potential $\psi_s = 0.02$ V and (b) a small constant surface charge density $\sigma_s = 0.032$ C/m². Even at the relatively high ionic strength selected ($n/V = 1.0$ M), the decrease of the repulsion is small.

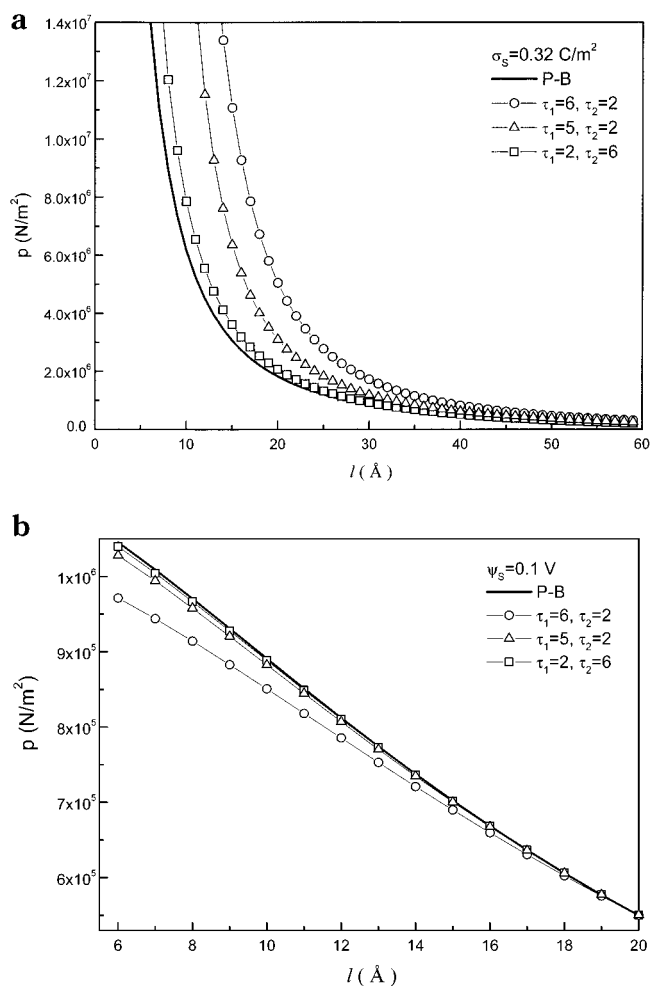


Figure 4. (a) Double layer force per unit area for constant surface charge density ($\sigma_s = 0.32 \text{ C/m}^2$), $n/V = 0.01 \text{ M}$ and $T = 300 \text{ K}$. (b) Double layer force per unit area for constant surface potential ($\psi_s = 0.1 \text{ V}$), $n/V = 0.01 \text{ M}$ and $T = 300 \text{ K}$.

V. Conclusions

The lattice model of Ruckenstein and Schiby,⁴ which accounted for the sizes of the ions, was extended to account for the correlations between the probabilities of occupancy of neighboring sites. In the present model, the excess chemical potential depends strongly on the number of water molecules that hydrate an ion; hence slightly different hydration numbers can lead (at high potentials) to large differences in the double layer repulsion. It was also shown that, at high surface potentials, the thickness of the double layer near a charged surface is increased

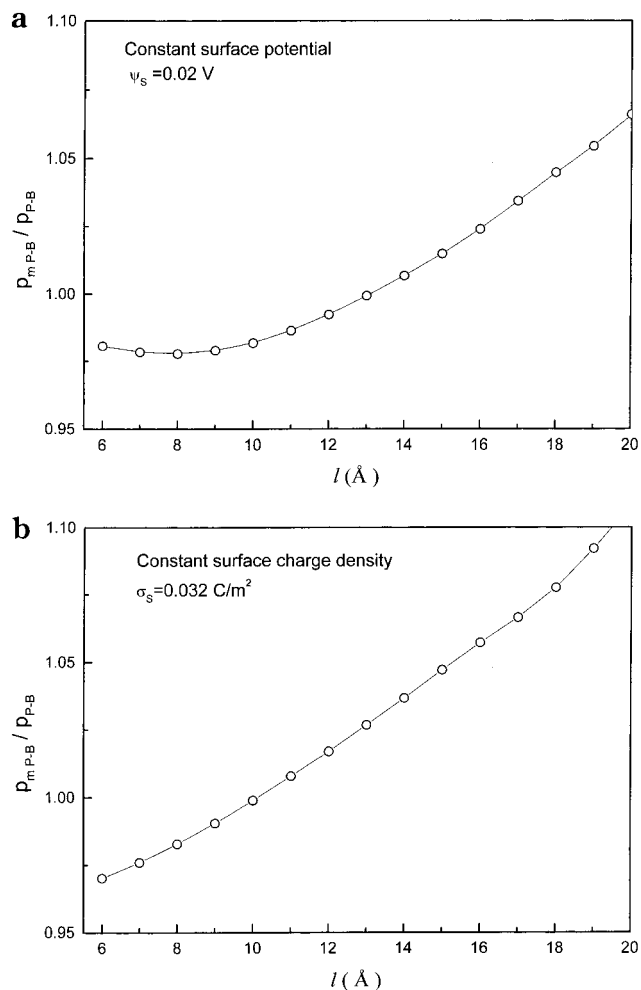


Figure 5. Ratio between the double layer force with site exclusion (modified Poisson–Boltzmann) and the double layer force provided by the Poisson–Boltzmann equation: (a) constant (small) surface potential ($\psi_s = 0.02 \text{ V}$); (b) constant (small) surface charge density ($\sigma_s = 0.032 \text{ C/m}^2$), $n/V = 1.0 \text{ M}$ and $T = 300 \text{ K}$.

(compared to that predicted by the Poisson–Boltzmann equation). However, at low surface potentials the diffuse layer might be slightly compressed, when the co-ions are larger than the counterions. The increase in the effective Debye length (thickness of the double layer) leads to an increase in the double layer repulsion at constant surface charge at any distance but to a slight decrease of the double layer repulsion at constant surface potential and small separation distances and an increase at large separations.

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