Simplifications of the Poisson–Boltzmann Equation for the Electrostatic Interaction of Close Hydrophilic Surfaces in Water

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Received November 27, 2000; accepted February 27, 2001

Simple solutions of the Poisson–Boltzmann (PB) equation for the electrostatic double-layer interaction of close, planar hydrophilic surfaces in water are evaluated. Four routes, being the weak overlap approximation, the Debye–Hückel linearization based on low electrostatic potentials, the Ettelaie–Buscall linearization based on small variations in the potential, and a new approach based on the fact that concentrations are virtually constant in the gap between close surfaces, are discussed. The Ettelaie–Buscall and constant-concentration approach become increasingly accurate for closer surfaces and are exact for touching surfaces, while the weak overlap approximation is exact for an isolated surface. The Debye–Hückel linearization is valid as long as potentials remain low, independent of separation. In contrast to the Ettelaie–Buscall approach and the weak overlap approximation, the Debye–Hückel linearization and constant-concentration approach can also be used for systems containing multivalent ions. Simulations in which the four approaches are compared with the PB equation for the constant-charge model, the constant-potential model, as being used in the DLVO theory, and the charge-regulation model are presented.

Key Words: Poisson–Boltzmann equation; Debye–Hückel equation; colloidal stability; surface forces; DLVO theory; charge regulation.

INTRODUCTION

The interaction of close hydrophilic surfaces in water determines colloid stability, the behavior of materials like clays and biological membranes, and the adsorption behavior of ions in porous materials. In many such systems, the interaction force is based on electrostatic double-layer repulsion and Van der Waals attraction. The electrostatic interaction can be described at thermodynamic equilibrium and for thermodynamically ideal systems by the second-order differential Poisson–Boltzmann (PB) equation (1, 2). The PB equation neglects such nonidealities as ion–ion correlations and ion-size effects and assumes a continuum of charges in the solution as well as on the surface. However, for surfaces that come increasingly close the electrostatic potential increases, resulting in increasing ion concentra-

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0021-9797/01 $35.00

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the midplane potential \( \phi_m \) as function of separation. When \( \phi_m \) is known for that separation, the electrostatic repulsive force, electrostatic potential, and ionic concentrations at all distances from the surface are obtained explicitly (8). This is the exact solution, valid at all separations, but it is difficult to solve (9). Therefore, this article focuses on simplifications of the PB equation.

Like the Ninham–Parsegian solution, the weak-overlap approximation, based on the Gouy–Chapman equation for isolated surfaces, and the Ettelaie–Buscall approach, valid for low field strengths, can be used for systems of monovalent ions. The Debye–Hückel equation, based on a low electrostatic potential (e.g., \(<10 \text{ mV}\)), and a new approach based on constant ion concentrations over the gap between the surfaces can be used for mixtures of ions of all valencies. The constant-concentration route is based on the observation in numerical simulations of the PB equation that when surfaces are close (less than a few nanometers apart) the gradients in ionic concentration are virtually zero. As a result, simple expressions for the electrostatic repulsion as a function of separation follow. The Ettelaie–Buscall and constant-concentration approximations are exact in the limit of touching opposing surfaces, and are valid up to a certain separation, the value of which depends on several parameters. In the simulations, these techniques could typically be used up to 1–4 nm. The Ettelaie–Buscall simplification is valid up to separations larger than those of the constant-concentration assumption and in some cases up to an infinite separation. The weak overlap approximation works from infinity down to a certain separation: the Debye–Hückel simplification works as long as the electrostatic potential remains low.

Under Theory, the Poisson–Boltzmann theory, as well as the several approximations for solving the PB equation with focus on the electrostatic repulsive force between equal, plane parallel, close surfaces, is summarized. Each of the three boundary conditions of the PB equation (constant surface charge, constant surface potential, charge regulation) is considered. Under Results and Discussion predictions of the different approximations are compared with the exact PB solution.

**THEORY**

**Poisson–Boltzmann Equation**

For a constant permittivity, \( \varepsilon_r \), and neglecting polarization effects, Maxwell's first law simplifies to the Poisson equation (plane parallel geometry)

\[
\frac{d^2 \phi}{dx^2} = -\frac{F}{\varepsilon_r \varepsilon_0} \sum_i z_i c_i,
\]

where \( x \) is the coordinate perpendicular to the surface (m), \( \phi \) the electrostatic potential (V), \( \varepsilon_r \) the relative permittivity (for water, \( \varepsilon_r = 78 \)), \( \varepsilon_0 \) the permittivity of vacuum (8.854 \times 10^{-12} \text{ C/V⋅m} \), \( F \) Faraday's constant (96,485 C/mol), \( z_i \) the charge number of a given ionic species \( i \), and \( c_i \) the volumetric concentration of ions in solution (mol/m^3) for each of these species.

For thermodynamically ideal systems at equilibrium, the distribution of ions is given by the Boltzmann equation

\[
c_i = C_{\infty,i} \exp \left( -\frac{z_i e \Phi}{RT} \right),
\]

where the subscript \( \infty \) refers to the (neutral) bulk solution (where \( \phi \) is set to 0), \( R \) is the gas constant (8.3144 J/(mol⋅K)), and \( T \) is temperature (here, 298 K is used).

Overall charge neutrality results (for positive \( x \) pointing from the solution to the surface) with Eq. [1] in

\[
\sigma = \varepsilon_r \varepsilon_0 \frac{d \phi}{dx},
\]

where \( \sigma \) is the surface charge (C/m^2) and the subscript 0 refers to the surface. At equilibrium and for thermodynamically ideal behavior of all ions, the repulsive pressure \( P_R \) (Pa) between equal and parallel flat surfaces is given by (1)

\[
P_R = RT \sum_i \left( C_{\infty,i} - C_{\infty,\infty} \right),
\]

where the subscript \( \infty \) refers to the midplane conditions.

To solve this set of equations, the constant-potential model (DLVO theory) assumes a certain, constant surface potential, \( \phi_0 \), and the constant-charge model a certain, constant surface charge, \( \sigma \). The charge-regulation model requires an additional expression for \( \sigma \) in terms of the concentrations of ions at the surface "0." Here an expression for amphiphilic surfaces that implements competitive adsorption by one type of cation and one type of anion is used (5, 10). In this case the hydroxyl surface sites \([\text{OH}]_0 \) either dissociate in \( [\text{O}^-]_0 \) sites or react with the oxonium ions in solution (H\(_2\)O\(^+\), symbol H\(^+\)) to form positive \([\text{OH}^+]_0 \) sites. The [O\(^-\)]\(_0\) sites may react with cations (C\(^{n+}\)) to form [O\(_0\)C\(^n\)\(_0\)]\(_0\) sites and the [OH\(^-\)]\(_0\) sites with anions (A\(^-\)) to form [OH\(_2\)A]\(_0\) sites. All four reactions are governed by equilibrium constants, \( K^- = K^+ = K^C = K^A \), respectively (5, 10). For a 1:1 salt, the resulting expression for the surface charge is (3, 5, 10)

\[
\sigma = F \cdot c_{0,\text{tot}} K^- = c_{0,H} = c_{0,C} = c_{0,A} \frac{c_{0,H}^2}{c_{0,C} + c_{0,A}} (K^- + K^+) = K^- + c_{0,H} K^+ + c_{0,H} K^- K^+ + c_{0,H} c_{0,A} K^+ K^- K^A
\]

where \( c_{0,\text{tot}} \) is the total amount of surface sites available (mol/m^2).

For a 2:1 salt (the cation being divalent, such as for CaCl\(_2\)), the result is

\[
\sigma = \frac{F \cdot K^C c_{0,H}^2}{4 c_{0,C} (K^-)^2} \left( \frac{c_{0,H}}{c_{0,H}} + \frac{K^-}{K^+} + \frac{c_{0,A} c_{0,H}}{K^+} \right) \left( \frac{1}{\sqrt{\left( \frac{K^- + 1}{c_{0,H}} + \frac{K^+ c_{0,H}}{K^+} \right)^2 + 8 c_{0,C} (K^-)^2 c_{0,\text{tot}}}} \right)
\]

\[
= \frac{K^- c_{0,H}}{c_{0,H} K^+ + K^A K^+}.
\]
However, other forms of Eqs. [5] and [6] can be used without changing the essential idea of this report.

**Monovalent Ions Only**

When only monovalent ions are present, Eqs. [1] and [2] result in

$$\frac{dE}{dx} = -\frac{d^2\phi}{dx^2} = -2c_\infty \frac{F}{\varepsilon_0 \varepsilon_\infty} \sinh \frac{F \phi}{RT}$$

[7]

based on

$$\sum_i z_i c_i = -2c_\infty \sinh \frac{F \phi}{RT}$$

[8]

with $c_\infty$ being the ionic strength of the bulk solution (mol/m³)

$$c_\infty = \frac{1}{2} \sum_i z_i^2 c_{\infty,i}.$$

[9]

For a system of monovalent ions only, the repulsion $P_R$ based on the midplane potential $\phi_m$ is given by combination of Eqs. [2], [4], and [9], resulting in (13–15)

$$P_R = 2RT c_\infty \left( \cosh \left( \frac{F \phi_m}{RT} \right) - 1 \right).$$

[10]

**Gouy–Chapman Equation for Isolated Surfaces and 1:1 Salts**

The Gouy–Chapman equation is the solution of Eqs. [1] and [2] for an isolated planar surface valid for symmetric salts (1, 2, 6, 11). For a 1:1 salt the solution of Eq. [7] is

$$\phi = \frac{2RT}{F} \ln \left( 1 + \exp(-\kappa \cdot x^*) \tan \left( \frac{F \phi_\infty}{RT} \right) \right)$$

[11]

with $x^*$ being the distance from the surface ($x$ without superscript will be the distance from the midplane, $m$), $\phi_\infty$ the surface potential at infinite separation, $\text{tanh}(x) = \sinh(x)/\cosh(x)$, $\sinh(x) = 1/2(e^x - e^{-x})$, $\cosh(x) = 1/2(e^x + e^{-x})$, and $\kappa$ the inverse of the Debye length

$$\kappa = \sqrt{\frac{2F^2 c_\infty}{\varepsilon_0 \varepsilon_\infty RT}}.$$

[12]

Equation [11] can be differentiated and combined with Eq. [3] to give the surface charge $\sigma$ (1, 2, 6, 12)

$$\sigma = 2\sqrt{2\varepsilon_0 RT c_\infty} \sinh \left( \frac{F \phi_\infty}{2RT} \right).$$

[13]


For monovalent ions and isolated surfaces, the above equations suffice for calculating the surface charge, as well as the potential and ion concentration as a function of distance from the (isolated) surface for the constant-potential, constant-charge, and charge-regulation models.

**The Weak Overlap Approximation**

The results for an isolated surface (ion concentrations, potentials) can be used in the weak overlap approximation (1) to determine the electrostatic repulsion between surfaces that are far apart. To that end, Eq. [11] is used to generate a midplane potential $\phi_m$ for a given separation $2x_0^*$ ($x^* = x_0^*$) and a given $\phi_\infty$ (obtained for the constant-charge and charge-regulation models via Eq. [13]). The value of $\phi_m$ is doubled (1, 17) and this value is used in Eq. [10].

**Debye–Hückel Assumption**

For low potentials $\phi$ (e.g., <10 mV), Eq. [7] can be simplified to the Debye–Hückel equation (6)

$$\frac{d^2\phi}{dx^2} = \kappa^2 \phi.$$  

[14]

Equation [14] is not only valid for monovalent ions, but can be used for any mixture of multivalent ions, with the definition of $\kappa$ as in Eq. [12]. This result is most easily derived when the Debye–Hückel linearization of Eq. [2],

$$c_i = c_{\infty,i} (1 - \frac{z_i^2 F}{RT}\phi),$$

[15]

is implemented directly in Eq. [1], resulting in

$$\frac{d^2\phi}{dx^2} = -\frac{F}{\varepsilon_0 \varepsilon_\infty} \sum_i \left( z_i^2 c_{\infty,i} - \sum_j \left( \frac{z_i^2 z_j^2 F \phi}{RT} \right) \right)$$

$$\frac{F^2 \phi}{\varepsilon_0 \varepsilon_\infty RT} \sum_i \left( z_i^2 c_{\infty,i} \right) = \kappa^2 \phi.$$  

[16]

Using the boundary conditions,

$$x = 0 \text{ (midplane): } \phi = \phi_m, \quad \frac{d\phi}{dx} = 0,$$

[17]

the solution of Eq. [14] for the potential, $\phi$, and surface charge, $\sigma$, between two flat, parallel, and equal plates, is (13, 14)

$$\phi = \phi_m \cosh(\kappa x),$$

[18]

$$\sigma = e_\infty \varepsilon_0 \kappa \phi_m \sinh(\kappa x).$$

[19]

Under the Debye–Hückel assumption, an analytical expression for $P_R$ as a function of the half-separation, $x_0$, is found for the
FIG. 1. Electrostatic repulsion $P_R$ as a function of separation $2 \cdot \chi_0$ for 1:1 salt. Squares are exact PB solution; lower dashed line is the weak overlap approximation (WOA), upper dashed line the constant-concentration approach (CCo), solid lines the Ettelaie–Buscall (EB) or Debye–Hückel (DH) approach. Data in Table 1; equations in Table 2. (a) Constant-potential model based on $\phi_0 = \phi_{0,\infty}$, (b) constant-charge model based on $\sigma = \sigma_{\infty}$, and (c) charge-regulation model.

The constant-potential model by combining Eq. [18] with [10]

$$P_R = 2RT \varepsilon_{\infty} \left( \cosh \left( \frac{F \phi_0}{RT \cosh(\kappa \chi_0)} \right) - 1 \right). \quad [20]$$

as well as for the constant-charge model by combining Eq. [10] and [19]

$$P_R = 2RT \varepsilon_{\infty} \left( \cosh \left( \frac{F \sigma}{\varepsilon_{\infty} RT \kappa \sinh(\kappa \chi_0)} \right) - 1 \right). \quad [21]$$

Equations [20] and [21] can be used for a system of monovalent ions for sufficiently low (surface) potentials. Therefore, in the constant-potential model and for a low enough potential, $\phi_0$, Eq. [20] can be used down to contact (zero separation) as can be observed in Fig. 1a and Fig. 2a. In the constant-charge model, the electrostatic potential in the gap between two surfaces increases when the separation decreases (infinite potential in the limit of touching surfaces). Therefore, Eq. [21] will always break down below a certain separation, as can be observed in Fig. 1b and Fig. 2b.
For the charge-regulation model, explicit expression such as Eqs. [20] and [21] are not found, but for a given half-separation, $x_0$, $\phi_m$ can be solved from a transcendental equation, after which Eq. [10] can be used to determine the repulsion $P_R$. The transcendental equation is different for different surface charging equations; if we use Eq. [5] together with Eqs. [2], [18], and [19], we obtain

$$\phi_m = \left(\frac{\sigma}{\varepsilon_F \varepsilon_0 \sinh(\kappa x_0)}\right)^{-1} \cdot \frac{F \cdot c_{\infty, \sigma}}{c_{\infty, H} \gamma^2 - K^- K^+} \div \left(\frac{K^- K^+ + K^- K^+ (K^+)^{-1} c_{\infty, C} \gamma + K^+ c_{\infty, H} \gamma}{c_{\infty, H} \gamma^2 + (K^+)^{-1} c_{\infty, L} c_{\infty, \sigma} \gamma}\right)$$

with

$$\gamma = \exp\left(-\frac{F \phi_m}{kT \cosh(\kappa x_0)}\right).$$

which can be solved by iteration.

**Gregory Simplification of the Debye–Hückel Equation**

For a system of monovalent ions and for a known surface potential (as in the constant-potential model), Gregory (13) derived (his Eq. [16])

$$P_R = 2RTc_{\infty}\left(\sqrt{1 + \left(\frac{F \phi_0}{kT}\right)^2 \cosh^2(\kappa x_0) - 1}\right).$$

which—for a low $\phi_0$ or a high $x_0$—simplifies to (Eq. [15] in (13); Eq. [8] in (18))

$$P_R = \frac{c_{\infty} F^2 \phi_0^2}{RT \cosh^2(\kappa x_0)}.$$  \(\text{[25]}\)

Equation [25] can also be derived from Eq. [20], again for a low $\phi_0$ or a high $x_0$. The Gregory route of simplifying Eq. [10] to

$$P = \frac{c_{\infty} F^2 \phi_0^2}{RT}$$

can also be used for a known surface charge $\sigma$ (constant-charge model) by combining Eqs. [19] and [26] resulting in

$$P_R = \frac{\sigma^2}{2 \varepsilon_F \varepsilon_0 \sinh^2(\kappa x_0)}.$$  \(\text{[27]}\)

which—for a low $\sigma$ or a high $x_0$—can also be derived from Eq. [21].

**Etelaie–Buscall Assumption for 1:1 Salts**

Ettelaie and Buscall (14, 15) approximate Eq. [7] for low gradients in potential

$$\frac{d^2 \phi}{dx^2} = 2c_{\infty} \frac{F}{\varepsilon_F \varepsilon_0} \left(\sinh F \phi_m \frac{F}{RT} + \frac{F}{RT} (\phi - \phi_m) \cosh F \phi_m \frac{F}{RT}\right).$$  \(\text{[28]}\)
.. similar approximation (but around \( \phi_0 \)) was made in Ref. (19). Solving Eq. [28] with the boundary condition, Eq. [17], gives the potential, \( \phi \), and surface charge, \( \sigma \),

\[
\phi = \phi_m + \frac{RT}{F} \tanh \left( \frac{F \phi_m}{RT} \left( \cosh \left( x_0 \kappa \sqrt{\cosh \frac{F \phi_m}{RT}} \right) - 1 \right) \right).
\]

\[\sigma = \sqrt{2c_\infty RT \varepsilon_0 \varepsilon \cosh \frac{F \phi_m}{RT}} \times \tanh \left( \frac{F \phi_m}{RT} \right) \times \sinh \left( x_0 \kappa \sqrt{\cosh \frac{F \phi_m}{RT}} \right).
\]

For the constant-potential model (given \( \phi_0 \)), Eq. [29] can be rewritten with Eq. [10] to give a lengthy, but explicit expression of the half-separation \( x_0 \) as a function of repulsion, \( P_R \); alternatively, Eq. [29] can be solved iteratively. Similarly, for the constant-charge and charge-regulation models, Eq. [30] can be written to give a lengthy but explicit expression of \( x_0 \) vs \( P_R \) or can be solved iteratively (for the charge-regulation model in combination with Eqs. [2], [5], and [29]).

**Constant-Concentration Assumption for Mixtures of Ions of Different Valencies**

In numerical calculations of the PB equation, Eq. [1], it was discovered that at close separations the concentrations \( c_i \) did not change much over the width of the gap. When concentrations \( c_i \) are indeed independent of place (thus the same at "m" and at "0"), integration of Eq. [1] with boundary condition, Eq. [17], gives the potentials, \( \phi \), and surface charge, \( \sigma \),

\[
\phi = \phi_m - \frac{1}{2} \sum_i z_i c_i,
\]

\[
\sigma = -x_0 F \sum_i z_i c_i.
\]

These constant-concentration solutions are based on constant concentrations \( c_i \) over the gap (from the midplane "m" to the surface "0"). Thus, it assumes a constant potential \( \phi \) in Eq. [2]. However, in Eq. [31], a gradient of \( \phi \) over the gap is essential. Indeed, the constant-concentration solution is valid only when the second term on the RHS of Eq. [31] is small compared to \( \phi_0 \) and \( \phi_m \).

In all three models for the surface condition (constant potential, constant charge, charge regulation), constant-concentration solutions are most easily obtained by generating a list of midplane potentials \( \phi_m \), and determining for each \( \phi_m \), entry the (midplane) concentrations \( c_i \) using Eq. [2] and the repulsion \( P_R \) using Eq. [4]. The corresponding \( x_0 \) value is determined for the constant-potential model by rearranging Eq. [31], resulting in

\[
x_0 = \sqrt{\frac{2\varepsilon_0 (\phi_m - \phi_0)}{F \sum_i z_i c_i}}.
\]

In the constant-charge model, the midplane–surface separation, \( x_0 \), is given by rearranging Eq. [32]. For the charge-regulation model, combination of Eqs. [2], [5]/[6], [31], and [32] relates the half-separation \( x_0 \) to the midplane concentrations.

**Constant-Concentration Assumption for Monovalent Ions**

When only monovalent ions are present, several simplifications can be made to the constant-concentration solution, resulting in a direct relation between \( x_0 \) and \( P_R \). For the constant-potential model, combination of Eqs. [8] (\( \phi = \phi_m \)), [10], and [33] gives an explicit expression for \( x_0 \) as function of \( P_R \)

\[
x_0 = \sqrt{\varepsilon_0 \left( \phi_m - \frac{RT}{F} \cosh \left( \frac{P_R}{2RTc_\infty} + 1 \right) \right) / \left( \cosh \frac{P_R}{2RTc_\infty} + 1 \right)}.
\]

The repulsion \( P_R \) as a function of \( x_0 \) is found by solving Eq. [34] iteratively.

For the constant-charge model, an explicit expression of \( P_R \) in terms of \( x_0 \) (and vice versa) can be obtained by combining Eqs. [3], [8], [10], and [32], resulting in

\[
P_R = 2RTc_\infty \left( \sqrt{\frac{\sigma^2}{4x_0 F c_\infty} + 1} - 1 \right).
\]

Equation [35] correctly predicts that \( P_R \) is zero at an infinite separation, that \( P_R \) is zero for a zero surface charge (as for a pH at the isoelectric point), and that \( P_R \to \infty \) for \( x_0 \to 0 \) in a constant-charge model with a nonzero surface charge. This follows from the condition of overall charge neutrality, which implies that the amount of ions in the gap between the surfaces is always above 0 to compensate for the surface charge. This implies that the width of the gap (2 \cdot \varepsilon_0) must be above 0 at all times.

For \( \sigma \cdot (2x_0 F c_\infty)^{-1} \ll 1 \), Eq. [35] simplifies to

\[
P_R = \frac{RT \sigma^2}{4x_0^2 F^2 c_\infty},
\]

which also follows from Eq. [27] for low \( k \cdot x_0 \) (\( \sinh(x) \to x \)). For \( \sigma \cdot (2x_0 F c_\infty)^{-1} \gg 1 \), Eq. [35] simplifies to (Eq. [30] in Ref. (19); Eq. [1223] in Ref. (1))

\[
P_R = \frac{RT}{x_0 F c_\infty} |\sigma|.
\]

**RESULTS AND DISCUSSION**

For monovalent ions, simulation results for the four simplifications are compared with each other and with the exact PB solution in Fig. 1 for alumina surfaces in water based on experimental conditions (20), see Table 1. Figure 1a describes the constant-potential model, Fig. 1b the constant-charge model,
and Fig. 1c the charge-regulation model. The exact PB solution is given as squares and is the benchmark for the different approximate techniques (see Table 2): For large separations (>4 nm), the repulsion is the same for all three models (constant potential, constant charge, charge regulation). The weak overlap approximation exactly describes the repulsion at these distances. At lower separations the repulsion for the constant-charge, constant-potential, and charge-regulation models start to deviate from each other while the weak overlap approximation predicts an intermediate value (i.e., describes none of the models).

For the experimental case considered (Table 1), the Debye–Hückel equation works well for the constant-potential model, Eq. [20], at all separations (zero to infinite separation), while it gives a good prediction down to 0.5 nm for the constant-charge model, Eq. [21], and the charge-regulation model, Eq. [22]. That the Debye–Hückel equation fails for lower separations is because of the increasing electrostatic potentials in the constant-charge and charge-regulation models at these separations, for which the assumption made in the Debye–Hückel equation, sinh(ϕF/RT) ≈ ϕF/RT, becomes increasingly inaccurate.

Indeed, in the constant-charge model the surface potential increases to ∞ when surfaces approach, while the maximum potential (when surfaces make contact) in the charge-regulation model is given by Eq. [17] in Ref. (10), namely

\[ \phi_{\max} = \frac{RT}{F} \ln(10) ( \phi_{\text{HPE}} - \phi_{\text{H}}) . \]  

Equation [38], together with the surface potential at infinite separation (for 1:1 salt determined by combining Eqs. [2], [5], and [13], see Table 1), predicts that for the charge-regulation model the surface potential increases 60-fold for the case of Fig. 1 (ϕmax = 370 mV) and 40-fold for the case of Fig. 2 (ϕmax = −65 mV).

Incidentally, this significant increase of potential also shows why for low separations (below a few nanometers) the constant-potential model (DLVO theory) predicts so much lower electrostatic repulsions than the constant-charge and charge-regulation models (5, 10).

The Ettelaie–Buscall solution works excellent for the constant-potential model, the constant-charge model, and the charge-regulation model. It is exact in the limit of touching surfaces.

The constant-concentration assumption is accurate (<10% deviation) up to a separation of ~2.5 nm for the constant-potential model, Eq. [34], up to 1.5 nm for the charge-regulation model, Eqs. [3], [5], and [32], and up to 1 nm for the constant-charge model, Eq. [35]. The deviation decreases with decreasing separation and, like the Ettelaie–Buscall equation, the constant-concentration assumption is exact in the limit of touching surfaces.

Interestingly, the Debye–Hückel, Ettelaie–Buscall, and constant-concentration solutions never underestimate the electrostatic repulsion, while the weak overlap approximation is always an overestimate for the constant-potential model and an underestimate for the constant-charge and charge-regulation models.

### Table 1

**Overview of Data**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (3)</td>
<td>3.02 ± 0.1 M = 100 mol/m³, ionic strength</td>
</tr>
<tr>
<td>Isoelectric point (pI)</td>
<td>1/2(pK+ + pK−) = 9.25 and</td>
</tr>
<tr>
<td>ΔpK</td>
<td>pK+ − pK− = 3 (8), thus</td>
</tr>
<tr>
<td>K+ = 1.778 × 10^−5 mol/m³ and K− = 1.778 × 10^−8 mol/m³</td>
<td></td>
</tr>
<tr>
<td>Total amount of surface sites c0, tot = 8.3 × 10^−6 mol/m³ (8)</td>
<td></td>
</tr>
<tr>
<td>K = 0.7 mol/m³ (5)</td>
<td></td>
</tr>
<tr>
<td>ϕ0,∞ = 6.02 mV, σ = 4.37 mC/m, κ−1 = 0.954 nm, T = 298 K, ε = 78</td>
<td></td>
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</tbody>
</table>

### Table 2

**Overview of Equations Used in Calculations**

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Constant-potential model</td>
<td>Poisson–Boltzmann, PB, squares, Eqs. [7], [10]</td>
</tr>
<tr>
<td>Weak overlap approximation, WOA, lower dashed line, Eqs. [10], [11]</td>
<td></td>
</tr>
<tr>
<td>Debye–Hückel, DH, solid line, Eq. [20]</td>
<td></td>
</tr>
<tr>
<td>Ettelaie–Buscall, EB, solid line, Eqs. [10], [29]</td>
<td></td>
</tr>
<tr>
<td>Constant-concentration, C1, upper dashed line, Eq. [34]</td>
<td></td>
</tr>
<tr>
<td>(b) Constant-charge model</td>
<td>Poisson–Boltzmann, PB, squares, Eqs. [3], [7], [10]</td>
</tr>
<tr>
<td>Weak overlap approximation, WOA, lower dashed line, Eqs. [10], [11], [13]</td>
<td></td>
</tr>
<tr>
<td>Debye–Hückel, DH, solid line, Eq. [21]</td>
<td></td>
</tr>
<tr>
<td>Ettelaie–Buscall, EB, solid line, Eqs. [10], [30]</td>
<td></td>
</tr>
<tr>
<td>Constant-concentration, C1, upper dashed line, Eq. [35]</td>
<td></td>
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<tr>
<td>(c) Charge-regulation model</td>
<td>Poisson–Boltzmann, PB, squares, Eqs. [2], [3], [5], [7], [10]</td>
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<tr>
<td>Weak overlap approximation, WOA, lower dashed line, Eqs. [2], [5], [10], [11], [13]</td>
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<tr>
<td>Debye–Hückel, DH, solid line, Eq. [10], [22]</td>
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<tr>
<td>Ettelaie–Buscall, EB, solid line, Eqs. [2], [5], [10], [29], [30]</td>
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<tr>
<td>Constant-concentration, C1, upper dashed line, Eqs. [2], [5], [10], [31], [32]</td>
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<thead>
<tr>
<th>Divalent system of Fig. 2</th>
<th>(a) Constant-potential (CP) model</th>
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<tbody>
<tr>
<td>Poisson–Boltzmann, PB, squares, Eqs. [1], [2], [4]</td>
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<tr>
<td>Debye–Hückel, solid line, Eqs. [2], [4], [18]</td>
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<td>Constant-concentration, dashed line, Eqs. [2], [4], [33]</td>
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<tr>
<td>(b) Charge-regulation model</td>
<td>Poisson–Boltzmann, PB, squares, Eqs. [1]–[4]</td>
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<tr>
<td>Debye–Hückel, solid line, Eqs. [2], [4], [19]</td>
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<td>Constant-concentration, dashed line, Eqs. [2], [4], [32]</td>
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models. This information can be used to assess the true repulsion as accurately as possible without the need to solve the PB equation numerically.

The constant-concentration and Debye–Hückel approximations can also be used for mixtures containing multivalent ions, such as a CaCl₂ solution, see Fig. 2. This simulation is based on experiments (21) for the interaction of silica surfaces, see Table 1. The constant-concentration technique works up to ~4 nm for the constant-potential model (Eqs. (33): <10% deviation at 3.8 nm) and ~2 nm for the constant-charge and charge-regulation models (Eqs. (32) and (32) + (6), respectively: <10% deviation at 1.7 nm). The Debye–Hückel approximation works down to contact for the constant-potential model, Eq. (20), and down to separations of ~2 nm for the constant-charge model, Eq. (21), and the charge regulation model, Eq. (22). Together, the two models describe practically the entire interaction curve (repulsion for each separation). Again, as for the monovalent system of Fig. 1, both techniques systematically overestimate the repulsion, a fact that can be used to estimate the exact repulsion without having to solve the full PB equation.

Several further simplifications of the Debye–Hückel linearization and of the constant-concentration assumption have been presented under Theory for a system of monovalent ions and will be evaluated next. The two simplifications for known surface potential φs, namely Eqs. (24) and (25), were compared with the exact PB solution for the constant-potential model. The two simplifications were as accurate as the Debye–Hückel and Eteläe–Buscall approaches, thus exactly describing the PB equation. For a known surface charge, as in the constant-charge model, Eqs. (27), (36), and (37) can be used. Their predictions for the electrostatic repulsion are compared with the exact solution of the PB equation in Fig. 3 for the constant-charge model. For the case considered (Table 1), Eq. (27) can be used down to a separation of ~2 nm, thus being as accurate as the Debye–Hückel approach, Eq. (21). However, Eq. (36) is much less accurate and Eq. (37) fails completely to describe the repulsion.

Finally, calculations were performed in which the charge regulation model neglected adsorption of the monovalent cat- and anions in the surface charge reaction, Eq. (5); i.e., infinitely high values for K⁺ and K⁻ were used. In that case (data in Table 1), the surface potential at infinite separation was already 192 mV; as a result, the Debye–Hückel approach did not give accurate predictions at all. The constant concentration technique came within a factor of 2 from the true value below separations of 0.2 nm, the Eteläe–Buscall came within a factor of 2 below 1 nm separation, and the weak overlap approximation had 10% deviation at 5-nm separation and 40% deviation at 3-nm separation. Clearly, without competitive adsorption (therefore, with higher surface potentials), the analytical solutions are less accurate or fail completely. This is an important limitation, but it must be noted that competitive adsorption (low surface potentials) can be expected for important systems such as soils and cell membranes, because of the presence of significant concentrations of indifferent ions (especially multivalent ions) that compete for the surface sites.

![Graph](image)

**FIG. 3.** Electrostatic repulsion $\mathcal{R}$ as a function of separation $\zeta$ for 1:1 salt: for the constant-charge model. Squares are exact PB solution, solid line is Eq. (27), dashed line is Eq. (36), and dotted line is Eq. (37). Data in Table 1.

**SUMMARY**

Simplifications of the Poisson–Boltzmann equation for the electrostatic double-layer interaction of equal, plane parallel, close, hydrophilic surfaces in a solution of monovalent and multivalent ions are evaluated. The simplifications can be used for each of the three electrostatic models in use, being the constant-potential model of the DLVO theory, the constant-charge model, and the charge-regulation model. For monovalent ions the Debye–Hückel linearization can be used as well as the weak-overlap approximation, the Eteläe–Buscall linearization, and a solution route based on the fact that ion concentrations are virtually constant in the gap between very close surfaces. The latter two are exact in the limit of touching surfaces, while the weak overlap approximation is exact in the limit of surfaces that are infinitely far apart. For mixtures containing multivalent ions, the Debye–Hückel and constant-concentration routes can be used as well.

**ACKNOWLEDGMENTS**

I thank W. B. S. de Lint (University of Twente, the Netherlands) for his help in the preparation of this manuscript.

**REFERENCES**