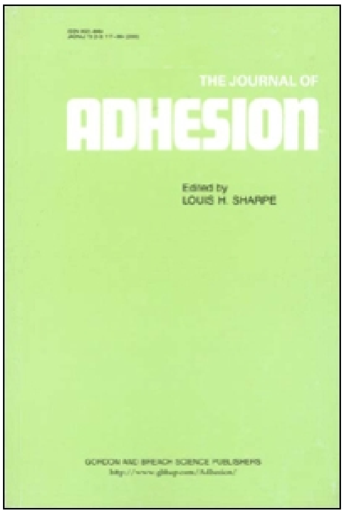

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A NEW MODEL FOR THE ELECTRICAL DOUBLE LAYER INTERACTION BETWEEN TWO SURFACES IN AQUEOUS SOLUTIONS

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A NEW MODEL FOR THE ELECTRICAL DOUBLE LAYER INTERACTION BETWEEN TWO SURFACES IN AQUEOUS SOLUTIONS

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A new theoretical model is developed to evaluate the total potential energy of interaction between two charged flat plates in aqueous solutions. Instead of using the Boltzmann distribution to predict the ionic concentrations of counterion and coion, which is not correct for small confined spaces, this modified model determines the ionic concentrations of counterion and coion based on the Poisson equation, the Nernst equation, and the mass conservation condition. Instead of the approximations used in the traditional model, the osmotic pressure is directly evaluated based on the ionic concentration distributions predicted by this new model. Finally, the total interaction energy is examined and compared with that predicted by the traditional model. It has been found that for high ionic concentration solutions, the traditional model tends to overestimate the total interaction energy due to the approximations employed in simplifying the osmotic pressure. However, for dilute solutions, the traditional model tends to underestimate the total interaction energy at small separation distance due to the misuse of the Boltzmann distribution in calculating the ionic concentration.

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INTRODUCTION

The understanding of adhesion of charged surfaces in aqueous electrolyte solutions is of great importance for a wide spectrum of applications in applied science and engineering. The adhesion phenomena in ionic solutions are dependent, at least, on electrostatic and van der Waals forces, as outlined in the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1].

One general prediction of the DLVO theory is that charged surfaces will attract each other at a small separation distance (*i.e.*, the primary energy minimum) because of the attractive van der Waals forces being dominant over the electrostatic repulsion forces at small separation distance [2]. However, it has been found that the experimentally measured repulsive forces between charged surfaces at close separations could not be explained by the DLVO theory [3–6]. A possible reason that the DLVO theory fails to explain the large repulsive forces is the misuse of the Poisson–Boltzmann equation, or the misuse of the Boltzmann distribution in determining the ionic concentration field. One must realize that the derivation of the Boltzmann distribution requires an infinitely large aqueous phase so that the electrical potential is zero in the liquid far away from the charged surface and that the ionic concentrations in the region far away from the charged surface are equal to the original bulk ionic concentration [7, 8]. However, due to the presence of the charged solid–liquid interface, there exists an excess of counterions and a deficit of coions in the electrical double layer (EDL) region. Therefore, it should be expected that there exists a deficit of counterions and a surplus of coions in the bulk liquid outside of the electrical double layer. The conventional Boltzmann distribution cannot show this logical expectation. This is because a key underlying assumption of the Boltzmann distribution is an infinitely large liquid phase. It is understandable that if the size of the system is sufficiently large, bulk ionic concentration is sufficiently high, or both, such a deficit and such a surplus are negligible and the Boltzmann distribution is acceptable.

However, when the separation distance between two charged surfaces is sufficiently small (*i.e.*, in the case of EDL overlapping, which causes the electrostatic repulsive interaction), and the solution is a dilute electrolyte solution, the excess of counterions and the deficit of coions in the EDL region will result in a significant change in the concentrations of counterion and coion in the region outside the EDL. In order to satisfy the conservation condition that the total ion number is constant in a given system, the concentration of counterion in the liquid region away from the charged surfaces is expected to be lower than the original bulk concentration due to the accumulation of counterions in the EDL region close to the charged surfaces. The concentration of coions in the liquid region away from the charged surfaces is expected to be higher than the original bulk concentration due to the deficit of coions in the EDL region close to the charged surfaces. Consequently, neither the concentration of counterions nor the concentration of coions at the middle plane of these two charged surfaces is equal to the original bulk concentration. Therefore, the assumption that the ionic concentration in the liquid region in the middle between two charged surfaces is equal to the original bulk concentration, which is used to derive the Boltzmann distribution, is not correct. Thus, the DLVO theory, which involves the use of the Boltzmann distribution, cannot properly predict the electrostatic repulsive energy and hence the total interaction energy.

The objective of this study is to develop a new model to investigate the EDL repulsive energy and to evaluate the total potential energy of interaction (*i.e.*, the EDL repulsive interaction and the van der Waals attractive interaction) between two charged surfaces. Instead of using the Boltzmann distribution, the ionic number conservation condition and the Nernst equation are used in this new model to find the ionic concentration field in the liquid between two charged surfaces. A correct boundary condition for the potential field at the middle plane of these two surfaces is developed and applied to this model. The ionic concentration field and electrical potential field are obtained by numerically solving this model. The total potential energy is then examined using the obtained ionic concentration from the developed model.

THEORETICAL MODEL

Attraction Energy

The total potential energy of interaction is the sum of the repulsive energy and the attraction energy. Consider two identical, charged flat surfaces in an aqueous solution, as illustrated in Figure 1. The attraction force or the van der Waals force can be evaluated by [9]

$$F_A = \frac{A}{6\pi D^3}, \tag{1}$$

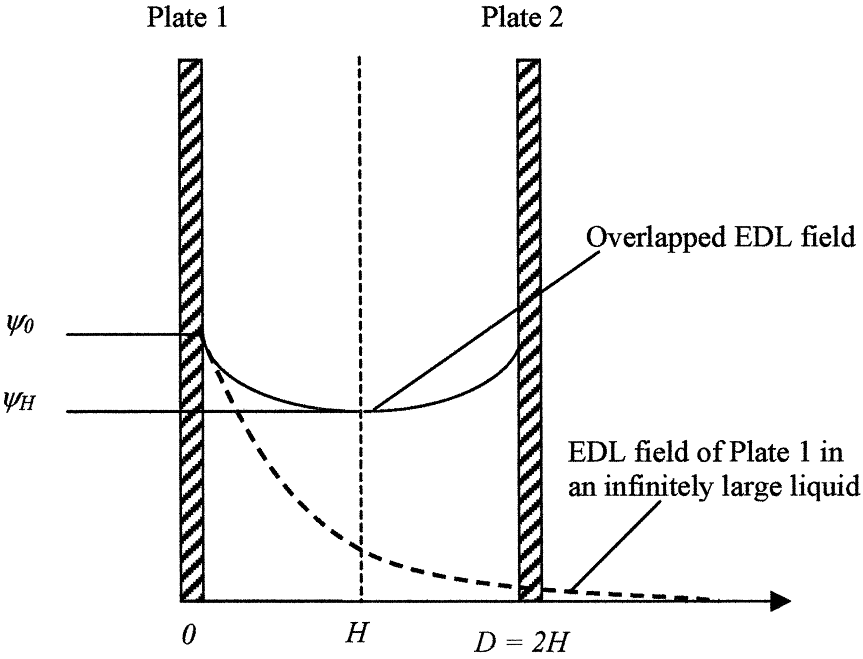


FIGURE 1 Schematic of two charged flat surfaces in an aqueous solution.

where F_A is the attraction force, A is the Hamaker constant chosen as $A = 2.2 \times 10^{-20} J$ in this study, and D is the separation distance between the two flat plates. The attraction energy can be obtained by integrating Equation (1) over the separation distance,

$$W_A = -\frac{A}{12\pi D^2}. \tag{2}$$

Repulsive Energy

The repulsive interaction occurs when two electrical double layers of the same sign begin to overlap. It can be analyzed by examining the osmotic pressure, which develops due to the accumulation of ions between the plates. Thermodynamically, we know

$$\left(\frac{dP}{dx}\right)_T = \sum n_i \left(\frac{d\mu_i}{dx}\right)_T, \tag{3}$$

where n_i is the number density of the ith ion. The chemical potential of an ion may be written as

$$\mu_i = z_i e\psi + k_b T \ln n_i, \tag{4}$$

Where z_i is the valence of the ith ion, e is the elemental charge, ψ is the electrostatic potential at any point between the two surfaces, k_b is the Boltzmann constant, and T is the absolute temperature. Inserting Equation (4) into Equation (3) and considering a constant temperature, we obtain

$$\frac{dP}{dx} = \sum \left(z_i e n_i \frac{d\psi}{dx} + k_b T \frac{dn_i}{dx} \right). \tag{5}$$

The electrical potential field is described by the Poisson equation,

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\varepsilon\varepsilon_0}, \tag{6}$$

where $\rho_e = \sum z_i e n_i$ is the net charge density. The Poisson equation can be rearranged as follows:

$$\sum z_i e n_i = -\varepsilon\varepsilon_0 \frac{d^2\psi}{dx^2}. \tag{7}$$

Using the relationship

$$\frac{d}{dx}\left(\frac{d\psi}{dx}\right)^2 = 2\left(\frac{d\psi}{dx}\right)\left(\frac{d^2\psi}{dx^2}\right), \tag{8}$$

Equation (7) can be rewritten as

$$\sum z_i e n_i \left(\frac{d\psi}{dx}\right) = -\frac{\varepsilon_0\varepsilon}{2}\frac{d}{dx}\left(\frac{d\psi}{dx}\right)^2. \tag{9}$$

Substituting Equation (9) into Equation (5), we get

$$\frac{dP}{dx} = -\frac{\varepsilon_0\varepsilon}{2}\frac{d}{dx}\left(\frac{d\psi}{dx}\right)^2 + \sum \left(k_b T \frac{dn_i}{dx} \right). \tag{10}$$

The pressure change at a point x, when the two plates are brought from infinity $(x' = \infty, P = 0, d\psi/dx = 0)$ to a separation distance, D, can be evaluated by

$$P_x(D) = -\frac{1}{2}\varepsilon\varepsilon_o \left(\frac{d\psi}{dx}\right)^2 \Bigg|_{x(D)} - \sum k_b T \left(n_{ix}^{\infty} - n_{ix(D)} \right). \tag{11}$$

In order to describe the osmotic pressure in terms of the ionic concentration distribution, Equation (11) can be further analyzed by introducing a relationship between potential gradient and ionic concentration. The chemical equilibrium condition, usually referred to as the Nernst equation [10],

$$\frac{1}{n_i}\frac{dn_i}{dx} = -\frac{z_i e}{k_b T}\frac{d\psi}{dx}, \tag{12}$$

can be rewritten as

$$\sum \frac{dn_i}{dx} = -\sum \frac{z_i e n_i}{k_b T}\frac{d\psi}{dx}. \tag{13}$$

Substituting Equations (7) and (8) into Equation (13) yields

$$\sum \frac{dn_i}{dx} = \frac{1}{2}\frac{\varepsilon\varepsilon_0}{k_b T}\frac{d}{dx}\left(\frac{d\psi}{dx}\right)^2. \tag{14}$$

Integrating Equation (14) from the middle plane between the two flat plates separated by a distance, D, to a position, x, we obtain

$$\frac{1}{2}\varepsilon\varepsilon_0\left(\frac{d\psi}{dx}\right)^2\Bigg|_{x(D)} = k_b T\left(\sum n_{ix(D)} - \sum n_{i\_mid(D)}\right), \tag{15}$$

where $\sum n_{i\_mid(D)}$ is the total ionic concentration at the middle plane of the two flat plates with a separation distance of D. It should be noted that a symmetric boundary condition, $x = x_{mid}, d\psi/dx = 0$, has been applied here. Substituting Equation (15) into Equation (11), we have

$$P_{x(D)} = k_b T \sum \left(n_{i\_mid(D)} - n_{ix}^{\infty}\right). \tag{16}$$

Because $P_{x_{(D)}}$ is a uniform pressure across the gap (independent of position, x) acting on the electrolyte ions and the surfaces we will drop off the subscript x in Equation (16), that is,

$$P_{(D)} = k_b T \sum \left(n_{i\_mid(D)} - n_i^{\infty}\right). \tag{17}$$

Note that $n_{i\_mid(D)}$ is the electrolyte concentration at the middle plane when the separation distance is a finite value, D. n_i^{∞} is the electrolyte concentration at the middle plane when the surfaces are separated infinitely far away. In analogy to the ideal gas law, $P = \mathrm{RT}\rho$, we can easily understand that $k_b T n$ is a pressure: the higher the density the higher the pressure. Similarly, $k_b T \sum \left(n_{i\_mid(D)} - n_i^{\infty}\right)$ is a pressure difference caused by the density difference; the higher the density difference; the higher the pressure difference. This pressure difference is usually referred to as the osmotic pressure. n_i^{∞} is the original electrolyte concentration, which is constant for a given system. The determination of osmotic pressure depends on how one determines the ionic concentration fields of electrolyte solution at the middle plane when the separation distance is a finite value, D.

Traditional Treatment

In the traditional treatment, the Boltzmann distribution,

$$n_i = n_i^{\infty} \exp\left(-\frac{z_i e\psi}{k_b T}\right), \tag{18}$$

is applied to Equation (17) to find the osmotic pressure. For a 1:1 electrolyte such as KCl or NaCl, it can be expressed as

$$P(D) = k_b T n_\infty \left[(e^{-e\psi_{mid}/K_b T} - 1) + (e^{+e\psi_{mid}/K_b T} - 1)\right]. \tag{19}$$

Equation (19) may be further simplified under certain assumptions [9]:

$$P(D) \approx \frac{e^2 \psi_{mid}^2 n_\infty}{k_b T}, \tag{20}$$

where n_∞ is the bulk concentration and ψ_{mid} is the electrical potential at the middle plane. It can be shown that the potential at the middle plane is approximately [2]

$$\psi_m \approx \frac{8 k_b T \gamma}{e} \exp\left[-\frac{\kappa D}{2}\right], \tag{21}$$

where $\gamma = \tanh(ze\psi_0/4k_bT)$ and ψ_0 is the electrical potential at the solid–liquid interface. Using the above equations, we can show that the osmotic pressure is given by

$$P(D) = 64 k_b T n_\infty \gamma^2 e^{-\kappa D}. \tag{22}$$

This equation gives the electrical double layer interaction for weak overlapped EDL fields between two identically charged surfaces of constant surface potential. The interaction free energy per unit surface area corresponding to the above pressure can be obtained by integrating the pressure, P, with respect to the separation distance, D:

$$W(D) = \frac{64 k_b T n_\infty \gamma^2}{\kappa} e^{-\kappa D}. \tag{23}$$

It should be pointed out that the Boltzmann distribution, Equation (18), is derived by employing the boundary condition that requires the liquid to be infinitely large. This condition cannot be satisfied for two charged flat plates with a very small separation distance. As we explained in the Introduction, the ionic concentrations at the middle plane of these two flat plates no longer obey the Boltzmann distribution.

A Modified Model

As discussed above, a correct model for evaluating osmotic pressure should be derived without using the Boltzmann equation, Equation (18). The Poisson equation, Equation (6), and the chemical equilibrium conditions, Equation (12), are valid for the system considered here. Integrating Equation (12) from the middle plane, where

$$x = H, \quad n_+|_H = n_+^H, \quad n_-|_H = n_-^H, \quad \psi|_H = \psi_H, \tag{24}$$

to a point between two flat plates yields

$$n_i = n_i^H \exp\left[\frac{z_i e}{k_b T}(\psi_H - \psi)\right],$$

where n_i^H is the concentration of the ith ion at the middle plane and ψ_H is the unknown electrical potential at the middle plane. Further applying the Debye-Hückel approximation yields

$$n_i = n_i^H\left[1 + \frac{z_i e}{k_b T}(\psi_H - \psi)\right]. \tag{25}$$

Substituting Equation (25) for both counterion and coion into Equation (6) leads to

$$\frac{d^2\psi}{dy^2} - \frac{e}{\varepsilon\varepsilon_0 k_b T}(n_+^H + n_-^H)\psi = \frac{e}{\varepsilon\varepsilon_0}\left[(n_-^H - n_+^H) - \frac{e}{k_b T}(n_-^H + n_+^H)\psi_H\right]. \tag{26}$$

The boundary conditions for Equation (26) are

$$x = 0, \quad \psi = \psi_0, \tag{27a}$$

$$x = H, \quad \psi = \psi_H. \tag{27b}$$

Equation (26) together with the above boundary conditions can be solved analytically, and the solution is given by

$$\psi(x) = \frac{(\psi_H - B - \psi_0)\sinh(\sqrt{A}(x - H))}{\sinh(\sqrt{A}H)} + \frac{B\sinh(\sqrt{A}x)}{\sinh(\sqrt{A}H)} - B + \psi_H, \tag{28}$$

where the parameters A and B are defined as

$$A = \frac{e^2}{\varepsilon k_b T}\left(n_+^H + n_-^H\right), \tag{29a}$$

$$B = \frac{k_b T}{e}\frac{n_-^H - n_+^H}{n_-^H + n_+^H}. \tag{29b}$$

Applying the symmetric boundary condition at the middle plane,

$$x = H, \quad \frac{d\psi}{dx} = 0, \tag{30}$$

to Equation (28), we obtain

$$\psi(x) = \frac{-B\cosh\left(\sqrt{A}H\right)\sinh\left(\sqrt{A}(x-H)\right)}{\sinh\left(\sqrt{A}H\right)} + \frac{B\sinh\left(\sqrt{A}x\right)}{\sinh\left(\sqrt{A}H\right)} - B\cosh\left(\sqrt{A}H\right) + \psi_0. \tag{31}$$

The concentrations of counterion and coion can be determined by substituting Equation (31) into Equation (25):

$$n_+ = n_+^H\left\{1 + \frac{eB}{k_b T}\left[\frac{\cosh\sqrt{A}H\sinh\left[\sqrt{A}(x-H)\right]}{\sinh\sqrt{A}H} - \frac{\sinh\sqrt{A}x}{\sinh\sqrt{A}H} + 1\right]\right\}, \tag{32a}$$

$$n_- = n_-^H\left\{1 - \frac{eB}{k_b T}\left[\frac{\cosh\sqrt{A}H\sinh\left[\sqrt{A}(x-H)\right]}{\sinh\sqrt{A}H} - \frac{\sinh\sqrt{A}x}{\sinh\sqrt{A}H} + 1\right]\right\}. \tag{32b}$$

From Equations (31), (32), and (29), it can be seen that in addition to the geometrical variable x, the distributions of the potential and ionic concentrations are functions of two unknown parameters, n_+^H, and n_-^H. In order to determine these two unknowns, we need to apply the ionic number conservation conditions to this system, which is similar to that reported in Ren and Li [11]. The method is outlined belows.

Mass Conservation Equation

According to the site-dissociation model [12], the H_3O^+ and OH^- ions in the aqueous solution play a direct potential-determining role at the inorganic oxide-aqueous-solution interface. Either H_3O^+ or OH^- ions will be adsorbed onto the surface, and the surface can become charged either positively or negatively, depending on the pH value of the solution. The surface charge density can be evaluated by

$$\sigma_0 = \frac{eN_s\delta \sinh\left(\tilde{\psi}_N - \tilde{\psi}_0\right)}{1 + \delta \sinh\left(\tilde{\psi}_N - \tilde{\psi}_0\right)}, \tag{33}$$

where N_s is the site density on oxide surfaces, and $\tilde{\psi}_0$ is the nondimensional surface potential, given by

$$\tilde{\psi}_0 = \frac{e\psi_0}{kT}. \tag{34}$$

$\tilde{\psi}_N$ is the nondimensional Nernst potential given by

$$\tilde{\psi}_N = 2.303(pH_z - pH), \tag{35}$$

where pH_z is the pH value when the solid surface reaches the point of zero charge (p.i.z.) [12], and δ in Equation (33) is a parameter defined as

$$\delta = 2.0 \cdot 10^{-\frac{\Delta pK}{2}}, \tag{36}$$

where ΔpK is the dissociation constant difference [12]. The selection of the material properties such as pH_z and ΔpK, etc., was done in a manner similar to that of Healy and White [12]. The parameters used in this paper are also listed in Table 1.

It should be realized that the counterions in the solution include K^+ and H_3O^+ ions, and the coions include Cl^- and OH^-. Applying the mass conservation principle for these ions in the half space (from the surface to the middle plane), we have

$$\int_0^H n^+ dx = \int_0^H n_{K^+}\, dx + \int_0^H n_{H_3O^+}\, dx, \tag{37a}$$

TABLE 1 Property Parameters

Parameters	Value
N_s	5×10^{18} site/m^2
pH_z	5.8
pH	6.7
ΔpK	10.0

$$\int_{0}^{H} n^{-}\,dx = \int_{0}^{H} n_{Cl^{-}}\,dx + \int_{0}^{H} n_{OH^{-}}\,dx. \tag{37b}$$

Consider that the original bulk ionic concentration of the simple $z:z = 1:1$ eletrolyte solution is $n_{K^{+}}^{\infty} = n_{Cl^{-}}^{\infty} = n^{\infty}$. For simplicity, we assume no specific adsorption of KCl ions on the surface; all K^{+} and Cl^{-} ions are in the solution. Applying the mass conservation principle to the half space (from the surface to the middle plane), we have

$$\int_{0}^{H} n_{K^{+}}\,dx = \int_{0}^{H} n_{Cl^{-}}\,dx = n^{\infty}H. \tag{38}$$

When an aqueous solution is in contact with an oxide surface, either H_3O^{+} or OH^{-} ions will attach to the solid surface depending on the pH value of the solution. For most oxide surfaces pHz, the pH value at the point of zero charge, is between 5 and 6 [12]. If we assume the pH value of the aqueous solution is 6.7, the oxide surface will be negatively charged due to the attachment of OH^{-}. At higher pH values, the surface potential may be larger than 25 mV at room temperature and thus the linear (Debye-Hückel) approximation used in this model development may be invalid. Therefore, we limit the pH value in this model to around 6.7 and consider that the oxide solution interface is negatively charged; that is, some OH^{-} ions are attached to the solid surfaces. This process will affect the balance between H_3O^{+} and OH^{-} ions in the solution. It is well known that water can dissociate into H_3O^{+} and OH^{-} ions. The process can be expressed as

$$2H_2O \leftrightarrow H_3O^{+} + OH^{-}. \tag{39}$$

The equilibrium between liquid water and the ions yields a constant known as the dissociation constant of water, K_w, which is defined as [13]

$$K_w = [H_3O^{+}][OH^{-}], \tag{40}$$

where $[H_3O^{+}]$ and $[OH^{-}]$ are the ionic concentrations. If the unit of ionic concentration is chosen as M (mol/L), K_w has a value of 10^{-14} at 25°C, which means in any aqueous solution at 25°C, the product of $[H_3O^{+}]$ and $[OH^{-}]$ must be equal to 10^{-14}. Normally, the ionic concentrations of H_3O^{+} and OH^{-} ions are given by $[H_3O^{+}] = 10^{-pH}$ and $[OH^{-}] = 10^{pH-14}$. When the solution is in contact with the solid surface, the concentration of OH^{-} ion will decrease due to the adsorption on the solid surface. In order to reach the equilibrium condition as show in Equation (40) again, a certain amount of water molecules will dissociate into H_3O^+ and OH^- ions. The total ionic number concentrations can be expressed as

$$\int_0^H n_{H_3O^+} dy = n^0_{H_3O^+} H + N_d, \tag{41}$$

$$\int_0^H n_{OH^-} dy = n^0_{OH^-} H + N_d - \left|\frac{\sigma_0}{e}\right|, \tag{42}$$

where N_d is the amount of water molecules dissociated into H_3O^+ and OH^- ions, $n^0_{H_3O^+}$ and $n^0_{OH^-}$ are the original ionic number concentration with a unit of m^{-3}, which can be calculated by [12]

$$n^0_{H_3O^+} = N_a 10^3 [\mathrm{H_3O^+}], \tag{43a}$$

$$n^0_{OH^-} = N_a 10^3 [\mathrm{OH^-}], \tag{43b}$$

where N_a is the Avogadro number. If we define the average concentrations of H_3O^+ and OH^- ions, $\bar{n}_{\mathrm{H_3O^+}}$ and $\bar{n}_{\mathrm{OH^-}}$, through the following equations,

$$\bar{n}_{\mathrm{H_3O^+}} = \frac{1}{\mathrm{H}} \int_0^{\mathrm{H}} n_{\mathrm{H_3O^+}}\, dy, \tag{44a}$$

$$\bar{n}_{\mathrm{OH^-}} = \frac{1}{\mathrm{H}} \int_0^{\mathrm{H}} n_{\mathrm{OH^-}}\, dy, \tag{44b}$$

Equations (44a) and (44b) can be rewritten as

$$\bar{n}_{\mathrm{H_3O^+}} \mathrm{H} = n^0_{\mathrm{H_3O^+}} \mathrm{H} + N_d, \tag{45a}$$

$$\bar{n}_{\mathrm{OH^-}} \mathrm{H} = n^0_{\mathrm{OH^-}} \mathrm{H} + N_d - \left|\frac{\sigma_0}{e}\right|. \tag{45b}$$

If we assume that the average ionic concentrations of H_3O^+ and OH^- ions also obey the equilibrium condition, Equation (40), the product of ionic number concentration can be described by

$$\bar{n}_{\mathrm{H_3O^+}} \cdot \bar{n}_{\mathrm{OH^-}} = N_a^2 \cdot 10^6 \cdot K_w. \tag{46}$$

The number of water molecules dissociated into H_3O^+ and OH^- ions, N_d, can be determined by Equations (33)–(36), (43), (45), and

(46). Finally, the mass conservation of ions in the half space, Equations (37a) and (37b), can be further expressed as

$$\int_{0}^{\mathrm{H}} n^{+}\,dx = n^{\infty}\mathrm{H} + \bar{n}_{\mathrm{H_3O^+}}\mathrm{H}, \tag{47a}$$

$$\int_{0}^{\mathrm{H}} n^{-}\,dx = n^{\infty}\mathrm{H} + \bar{n}_{\mathrm{OH^-}}\mathrm{H}. \tag{47b}$$

The assumption given by Equation (46) may introduce some errors in calculating the unknown constants involved in Equations (31) and (32). A more general treatment is to determine the local concentrations of the H_3O^+ and OH^- ions first and then calculate the integration in Equations (37a) and (37b). However, it should be realized that the mathematics involved in such a process is too complicated. Furthermore, the purpose of introducing Equations (47a) and (47b) is to calculate the unknown constants in Equations (31), (32a), and (32b). Although the values of these constants may not be very accurate as the result of our approximation, Equation (46), the approximation will not introduce significant effects on the distributions of the electrical potential and ionic concentrations that are determined by the functions given in Equations (31), (32a), and (32b).

Numerical Scheme

Once the unknown parameters, n_{+}^{H} and n_{-}^{H}, are determined by numerically solving Equations (43)–(47), Equations (31) and (32) can be solved to obtain the potential and ionic concentration fields in the liquid between two charged flat surfaces. This allows the osmotic pressure to be calculated by Equation (17). The repulsive energy can be obtained by integrating the osmotic pressure over the separation distance and then the total potential energy of interaction can be calculated by adding repulsive energy and attractive energy together.

It should be pointed out that this new model used correct boundary conditions to obtain the ionic concentrations instead of using the Boltzmann distribution that is not valid for such a small system, as discussed earlier. In addition, this model did not use the approximations in evaluating the osmotic pressure that are used in the traditional treatment. Since the osmotic pressure is uniform across the separation distance, the repulsive energy can be obtained by multiplying the calculated osmotic pressure by the separation distance, D. The total interaction energy is the sum of both the repulsive energy and the attraction energy.

RESULTS AND DISCUSSIONS

Figures 2–4 show the comparison of the model-predicted total interaction energy between the traditional model (Equation (23)) and the modified model for 10^{-3} M, 10^{-4} M, and 10^{-5} M KCl solution, respectively. It should be noted that the new model developed here considers the contribution of the dissociated water ions to the repulsive energy and, in turn, the total interaction energy. However, the traditional model, Equation (23), does not consider this contribution. In order to compare these two models in predicting the total interaction energy, the contribution of the dissociated water ions to the repulsive energy has been added in the traditional model, as shown in these plots.

Figures 2 and 3 show that the traditional model predicts a higher total interaction energy as compared with the modified model. This is because of the approximations [2] used in the traditional model (Equation (23)) to simplify the calculation of the osmotic pressure. A key mathematical approximation used in the calculation of the osmotic

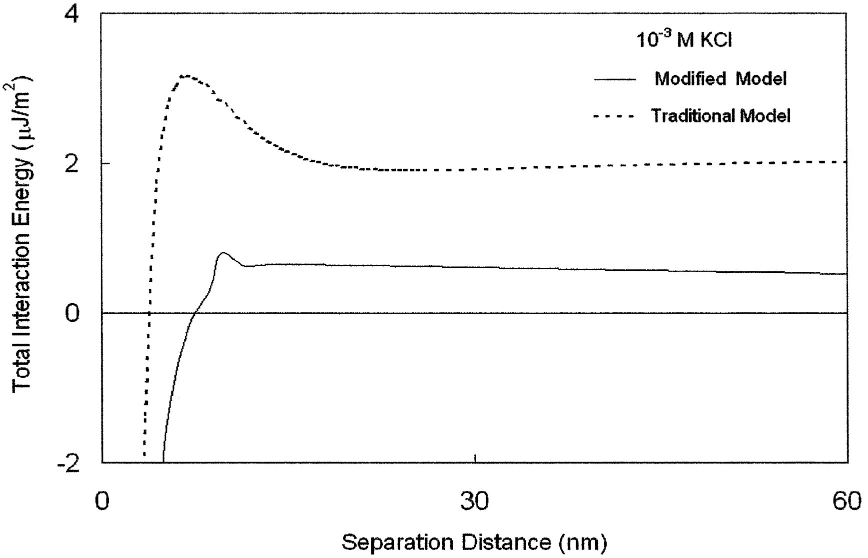


FIGURE 2 Comparison of the total potential energy of interaction between the traditional model prediction and the modified model prediction for 10^{-3} M KCl solution.

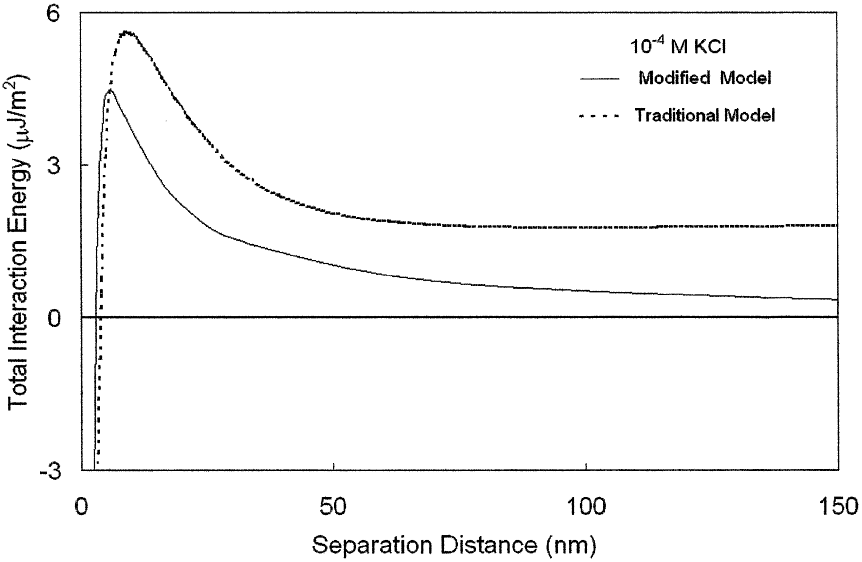


FIGURE 3 Comparison of the total potential energy of interaction between the traditional model prediction and the modified model prediction for 10^{-4} M KCl solution.

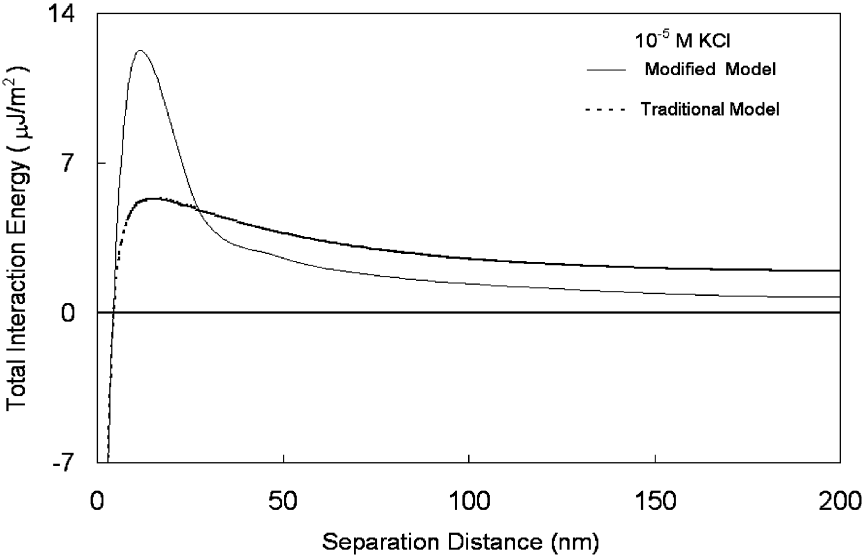


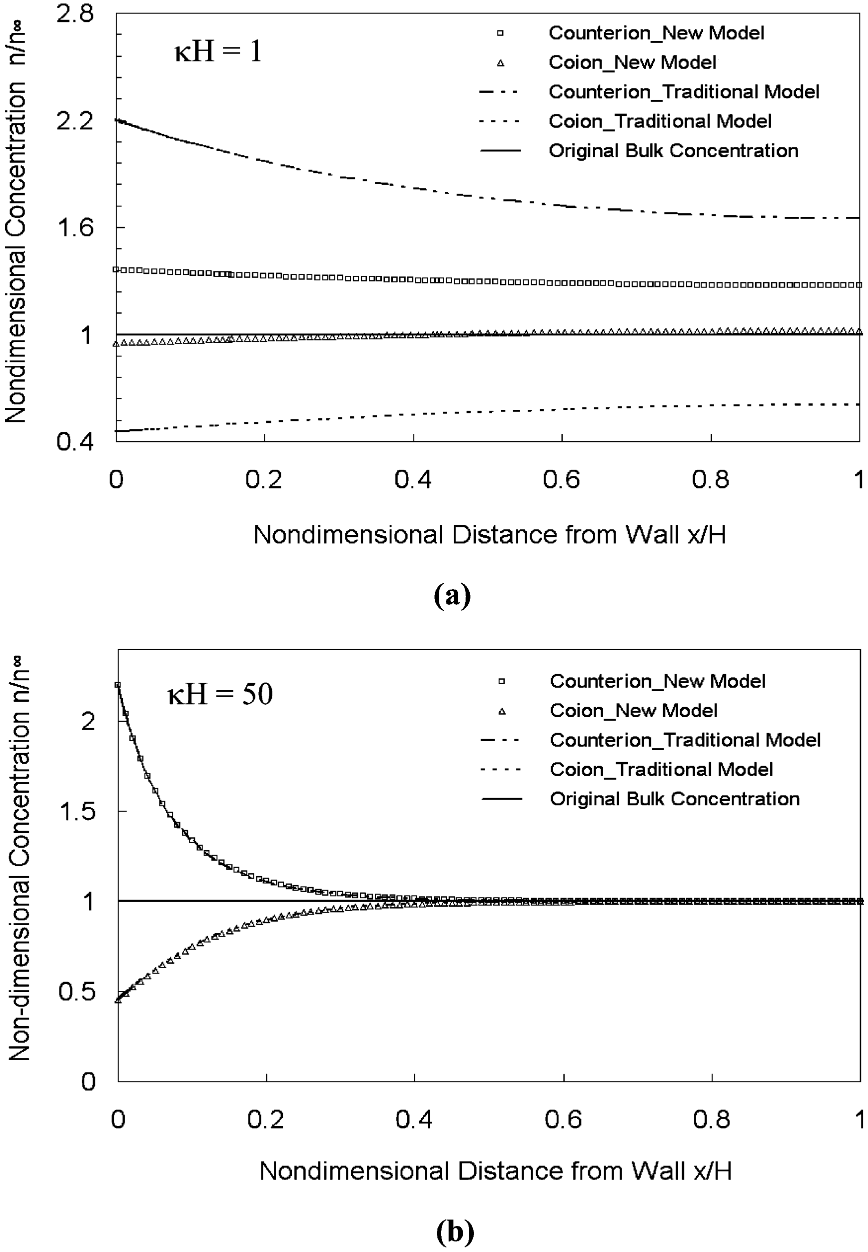
FIGURE 4 Comparison of the total potential energy of interaction between the traditional model prediction and the modified model prediction for 10^{-5} M KCl solution.

pressure in the traditional model is $\tanh x \approx x$. However, we know the following relationship is generally true, $\tanh x \approx x/\left(1+0.5x^2\right)$ 60; x. This assumption leads to an overestimation of the osmotic pressure; consequently, the repulsive energy and the total interaction energy, which are proportional to the osmotic pressure, are overestimated.

Figure 4 shows the comparison of the model-predicted total interaction energy between the traditional model and the modified model for 10^{-5} M KCl solution. Similar to the cases of higher concentration solutions (Figures 2 and 3), the traditional model predicts a higher total interaction energy when the separation distance is larger than $0.3(1/\kappa)$. However, when the separation distance is small, the modified model predicts a higher peak than the traditional model. This is because, for low concentration solutions, the EDL thickness is larger (*i.e.*, $1/\kappa \approx 90$ nm for 10^{-5} M KCl solution). When the separation distance between the two plates is small ($0.3(1/\kappa) = 30$ nm), the EDL field overlaps significantly. In such a situation, the traditional model underestimates the ionic concentration at the middle plane due to the misuse of the Boltzmann distribution. Since the osmotic pressure is proportional to the concentration difference at the middle plane (see Equation (17)), consequently the osmotic pressure is underestimated by the traditional model. Therefore, the repulsive energy and the total interaction energy, which are proportional to the osmotic pressure, are underestimated when the separation distance is small.

The underestimation of ionic concentration at the middle plane for a small separation distance is shown in Figure 5a, which shows the comparison of the model-predicted ionic concentration between the traditional Poisson-Boltzmann model and the modified model for 10^{-5} M KCl solution. It can be seen that the sum of the concentrations of the counterions and the coions at the middle plane ($\kappa \mathrm{H} = 1$) predicted by the modified model (2.30×10^{-5} M KCl) is higher than that predicted by the traditional model (2.26×10^{-5} M KCl). Therefore, the modified model predicts a larger concentration difference at the middle plane than that predicted by the traditional model. According to Equation (17), this will lead to a higher osmotic pressure. As a result, the repulsive energy and then the total potential energy, both of which are proportional to the osmotic pressure, will be predicted to be higher by the modified model than by the traditional model. It is easy to understand that when the separation distance is increased, the difference between these two models decreases and eventually the two models become the same, as shown in Figure 5b.

Figure 6 shows the comparison of the predicted repulsive energy between the traditional model and the modified model. It can be clearly seen that, when the separation distance is small or the EDL



(a)

(b)

FIGURE 5 Comparison of the concentration distributions of counterions and coions between the traditional model predictions and the modified model predictions for 10^{-5} M KCl solution: (a) κH = 1 and (b) κH = 50.

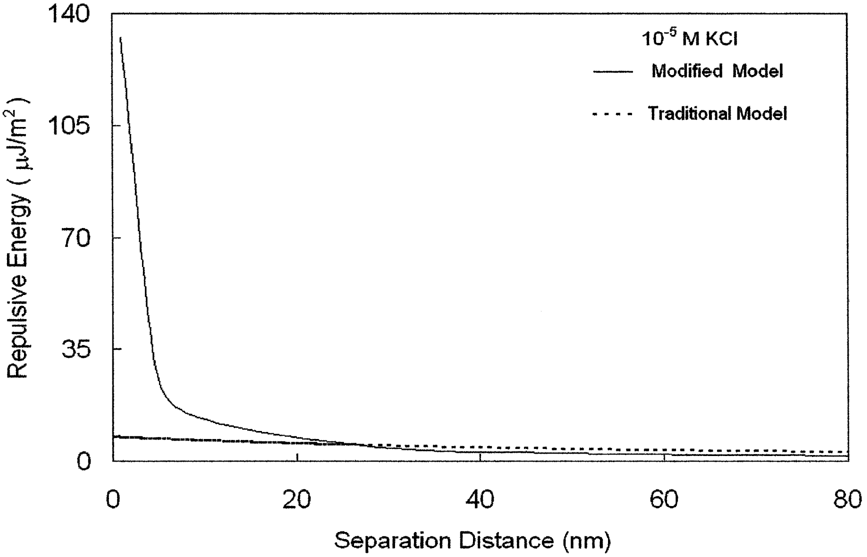


FIGURE 6 Comparison of the repulsive energy between the traditional model predictions and the modified model predictions for 10^{-5} M KCl solution.

fields overlap significantly, the traditional model underestimates the repulsive energy due to the underestimation of the ionic concentrations by use of the Boltzmann distribution, as shown in Figure 5a. Therefore, the traditional model underestimates the total interaction energy (seen in Figure 4) when the separation distance is small, since the total interaction energy is the sum of the repulsive energy and the attraction energy, and the attraction energy is constant for a given system.

SUMMARY

A new theoretical model is developed to evaluate the electrostatic interaction energy between two charged flat surfaces. This modified model does not use the Boltzmann distribution for the ionic concentrations because the boundary conditions used to derive the Boltzmann distribution are not valid for two charged flat plates with a small separation distance. Instead, this modified model employs the Poisson equation, the Nernst equation, and the mass conservation conditions to find the concentrations of counterions and coions. In addition, the approximations used in the traditional treatment to simplify osmotic pressure are not used in this model. The osmotic pressure is directly evaluated based on the ionic concentration distribution predicted by this new model. The total interaction energy is finally examined based on this modified model and is compared with that predicted by the traditional model. It has been found that the traditional model overestimates the total interaction energy for high concentration solutions (10^{-3} M and 10^{-4} M KCl solutions) at the full range of separation distance and overestimates the total interaction energy for low concentration solutions, *e.g.*, 10^{-5} M KCl solution, at relatively larger separation distances. However, it underestimates the peak value of the total interaction energy at a small separation distance for 10^{-5} M KCl solution. This is because the misuse of the Boltzmann distribution leads to underestimation of the ionic concentration difference at the middle plane and, in turn, underestimation of the electrostatic interaction energy.

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