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*J. Phys. Chem. B*, **2006**, 110 (49), 25007-25012 • DOI: 10.1021/jp062704m

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# Approximate Analytical Expressions for the Electrical Potential between Two Planar, Cylindrical, and Spherical Surfaces

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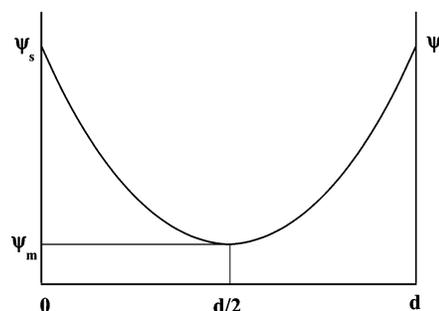
Received: May 2, 2006; In Final Form: September 30, 2006

Approximate analytical expressions for the electrical potential of planar, cylindrical, and spherical surfaces are derived for the case in which the dispersion medium contains counterions only. On the basis of the results for single surfaces, those for two identical surfaces can be derived. The curvature effect of a surface on the electrical potential distribution can be neglected when the order of its radius exceeds  $\sim 100$  times the thickness of the corresponding double layer. If this effect needs to be considered, it can be taken into account by multiplying a correction function by the electrical potential of a planar surface. The electrical potential at the center between two derived surfaces is readily applicable to the evaluation of the electrostatic force per unit area between two surfaces, or the osmotic pressure. For the same set of parameters, the magnitudes of the osmotic pressure for various types of surfaces rank as follows: planar surface > cylindrical surfaces > spherical surfaces.

## 1. Introduction

Colloidal dispersion is ubiquitous in human life and industrial operations. Due to its versatile applications in modern technologies, both theoretical and experimental studies have been extremely plentiful in the past few decades. Among relevant topics, the stability of a colloidal dispersion, which is closely related to the electrostatic force between two colloidal particles, has drawn the attention of many researchers. To evaluate that force, the corresponding spatial distribution of electrical potential must be known. According to Gouy–Chapman theory, the equilibrium electrical potential can be described by the so-called Poisson–Boltzmann equation.<sup>1,2</sup> Unfortunately, the only exactly solvable case of this equation is for a single, infinite planar surface of constant potential immersed in a dispersion containing symmetric electrolytes. Other than that, it needs to be solved numerically, semianalytically, or approximately.<sup>3–14</sup> Often, the condition of low surface potential is assumed so that the original Poisson–Boltzmann equation can be linearized, which can be readily solved for simple geometries.

Salt-free dispersions comprise a special colloidal system in which the liquid phase contains only counterions dissociated from the surface of the dispersed entities. A typical example in practice includes a dispersion of polyelectrolytes, the molecule of which comprises monomers carrying dissociable functional groups, in an electrolyte-free liquid medium. Biopolymers such as DNA and RNA are typical polyelectrolytes. Polyacrylic acid (PAA), often used to make diapers, is an example of polyelectrolytes encountered in daily life. The dissociation of the functional groups on a polyelectrolyte molecule yields a highly charged backbone containing co-ions. Some dissociated counterions are attracted by the surface of that backbone and remain

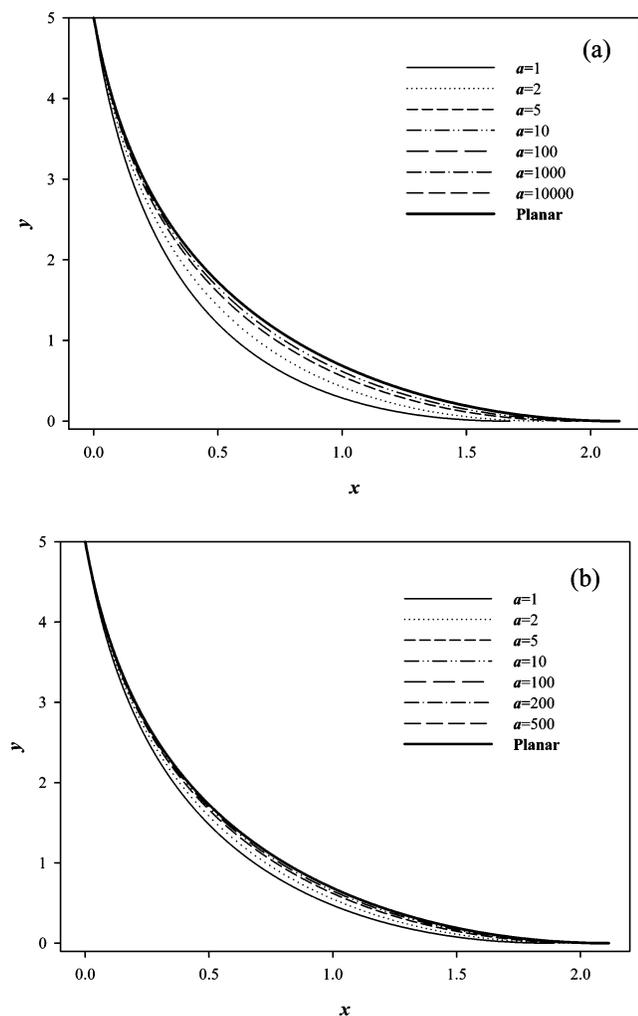


**Figure 1.** Schematic representation of the potential  $\psi$  between two identical surfaces where  $d$  is the closest distance between the surfaces,  $\psi_s$  is the surface potential, and  $\psi_m$  is the potential at the center between two surfaces ( $r - \theta a_0 = d/2$ ).

in an ionic state over the surface, and then a thermodynamic equilibrium is established. The so-called counterion condensation was proposed by Manning<sup>15</sup> and justified by Oosawa.<sup>16</sup> Manning's theory was discussed and/or modified experimentally<sup>17,18</sup> and theoretically<sup>19–23</sup> by many investigators.

In general, the behavior of polyelectrolytes in a polar medium is mainly governed by the electrostatic interaction between polyelectrolyte molecules.<sup>18,24,25</sup> Takahashi et al.<sup>26</sup> studied the influence of various types of charge distribution on protein surface on the complexation between protein and polyelectrolyte in a salt-free, aqueous dispersion. On the basis of Monte Carlo simulations, Wang et al.<sup>22</sup> predicted the effective charge on a polyelectrolyte molecule in a salt-free medium taking the effect of counterion condensation into account. Stevens and Kremer<sup>27</sup> adopted molecular dynamics simulation to investigate the physical properties of linear, flexible polyelectrolytes in a salt-free medium. The same approach was adopted by Messina et al.<sup>28</sup> in evaluating the strong electrostatic interactions between spherical colloids. The interactions between counterions and

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**Figure 2.** Spatial variation in scaled electrical potential  $y$  for (a) a spherical surface and (b) a cylindrical surface, at various scaled radii,  $a$ , for the case in which  $y_s = 5.0$  and  $b = 1$ .

colloidal surface under both the ground and ionized states of a colloid were discussed. Applying an integral equation approach, Anta and Lago<sup>29</sup> analyzed the total correlation functions of colloid–colloid, colloid–counterion, and counterion–counterion pairs; the effective potential between colloids was reported, and the existence of net attractions between colloids which may lead to phase instability was studied. Considering a salt-free colloidal dispersion, Ohshima analyzed the electrical potential and the electrokinetic phenomenon of rigid spheres,<sup>30–32</sup> soft spheres,<sup>33,34</sup> and an array of parallel soft cylinders.<sup>35</sup> The electrical force between two planar, parallel surfaces covered by an impenetrable membrane layer,<sup>36</sup> and the electrical potential for a spherical particle covered by a polymer layer<sup>37</sup> was also reported in the literature. Using a cell model, Chiang et al.<sup>38</sup> modeled the electrokinetic phenomenon of a dispersion of polyelectrolytes.

In a previous study,<sup>39</sup> we analyzed the critical coagulation concentration of a salt-free dispersion where the electrical potential between two identical planar surfaces was determined analytically. Although the assumption of planar geometry is satisfactory at the onset of coagulation, where two entities are very close to each other, the behavior of the electrical potential between two nonplanar surfaces deserves further study. The analyses for the electrical potential for nonplanar surfaces are ample in the literature, ranging from pure numerical to approximate analytical solutions; however, most of them are

focused on a single entity. In a study of the electrical potential for the case of symmetric electrolytes, Tuinier<sup>40</sup> and Lin et al.,<sup>41</sup> for example, solved the Poisson–Boltzmann equation for a single surface of planar, cylindrical, and spherical geometry. A parameter was proposed to measure the curvature effect of a surface, and the electrical potential in these cases was expressed by a similar expression. In this study, the electrical potentials for two planar, cylindrical, and spherical surfaces are derived for a salt-free dispersion medium and the results are used to evaluate the electrostatic force between two surfaces in the normal direction per unit area, or the osmotic pressure. The influences of the curvature of a surface and its potential and the valence of counterions on the electrical potential distribution between two surfaces are discussed.

## 2. Analysis

We begin the analysis by considering a single surface and then generalizing the results obtained to the case of two surfaces.

**A. Single Surface.** We consider a positively charged surface in a salt-free liquid medium, which contains counterions dissociated from the functional groups on the surface of the particle. Let  $b$  and  $C_b^0$  be the absolute value of the valence of counterions and its bulk molar concentration, respectively, and  $\epsilon$  be the permittivity of the liquid phase. For this case, the electrical potential  $\psi$  for a planar, cylindrical, and spherical surface can be described by the Poisson–Boltzmann equation

$$\frac{d^2\psi(r)}{dr^2} + \frac{\omega}{r} \frac{d\psi(r)}{dr} = \frac{bFC_b^0}{\epsilon} \exp\left[\frac{bF\psi(r)}{RT}\right] \quad (1)$$

where  $r$  is the distance from a planar surface or the radial distance from the center of a cylindrical or spherical surface. The shape index  $\omega$  is 0, 1, or 2 for planar, cylindrical, or spherical surfaces, respectively.  $F$ ,  $R$ , and  $T$  are the Faraday constant, the gas constant, and the absolute temperature, respectively. Let  $a$  equal  $\kappa a_0$  and be the scaled radius of a cylindrical or a spherical surface, where  $a_0$  is the radius of a cylindrical or spherical surface. Let  $y$  equal  $F\psi/RT$  and be the scaled electrical potential. Let  $x$  equal  $\kappa r - \theta\kappa a_0$  and  $\kappa r - \theta a$  and be the scaled distance from the particle surface, where  $\kappa = (2IF^2/\epsilon RT)^{1/2}$  is the Debye–Hückel parameter and  $I = C_b^0 b^2/2$  is the ionic strength.  $\theta = 0$  for a planar surface, and  $\theta = 1$  for a cylindrical or a spherical surface. In terms of these scaled symbols, eq 1 can be rewritten as

$$\frac{d^2y}{dx^2} + \frac{\omega}{x+a} \frac{dy}{dx} = \frac{1}{b} e^{by} \quad (2)$$

We consider the following boundary conditions:

$$y = y_s, x = 0 \quad (3)$$

$$y = 0 \text{ as } x \rightarrow \infty \quad (4)$$

where  $y_s = F\psi_s/RT$ ,  $\psi_s$  being the surface potential. If  $\omega = 0$ , it can be shown that the solution to eq 2 subject to eqs 3 and 4 is<sup>39</sup>

$$y_{\text{planar}} = \frac{1}{b} \ln \left\{ \sec^2 \left[ -\frac{1}{\sqrt{2}}x + \tan^{-1} (e^{by_s} - 1)^{1/2} \right] \right\} \quad (5)$$

where  $y_{\text{planar}}$  is the scaled electrical potential for a planar surface. For a spherical surface, where  $\omega = 2$ , we define  $u$  as being equal to  $[1 + (x/a)]y$ , and eq 2 can be rewritten as

$$\frac{d^2u}{dx^2} = \frac{1+x/a}{b} \exp\left(\frac{bu}{1+x/a}\right) \quad (6)$$

The corresponding boundary conditions are

$$u = u_s, x = 0 \quad (7)$$

$$u = 0 \text{ as } x \rightarrow \infty \quad (8)$$

If the radius of a surface is sufficiently large and the distance in which we are interested is relatively small, then  $x/a \ll 1$ , and eq 6 can be approximated by

$$\frac{d^2u}{dx^2} = \frac{1}{b} e^{bu} \quad (9)$$

Solving this equation subject to eqs 7 and 8 yields

$$u = \frac{1}{b} \ln \left\{ \sec^2 \left[ -\frac{1}{\sqrt{2}}x + \tan^{-1}(e^{by_s} - 1)^{1/2} \right] \right\} \quad (10)$$

In terms of  $y$  and  $x$ , we have

$$y_{\text{spherical}} = \left( \frac{1}{1+x/a} \right)^{1/b} \ln \left\{ \sec^2 \left[ -\frac{1}{\sqrt{2}}x + \tan^{-1}(e^{by_s} - 1)^{1/2} \right] \right\} \quad (11)$$

where  $y_{\text{spherical}}$  is the scaled electrical potential for a spherical surface.

For a cylindrical surface ( $\omega = 1$ ), we define

$$v = \frac{y}{K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right] e^{a(1+x/a)}} \quad (12)$$

Substituting this expression into eq 2 gives

$$K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right] e^{a(1+x/a)} \frac{d^2v}{dx^2} + K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right] \left\{ \frac{1}{a \left( 1 + \frac{x}{a} \right)} - 2 \frac{K_1 \left[ a \left( 1 + \frac{x}{a} \right) \right]}{K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right]} + 2 \right\} e^{a(1+x/a)} \frac{dv}{dx} + K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right] \left\{ \frac{1}{a \left( 1 + \frac{x}{a} \right)} - \left[ 2 + \frac{1}{a \left( 1 + \frac{x}{a} \right)} \frac{K_1 \left[ a \left( 1 + \frac{x}{a} \right) \right]}{K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right]} + 2 \right\} e^{a(1+x/a)} v = \frac{1}{b} e^{K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right] e^{a \left( 1 + \frac{x}{a} \right) b v}} \quad (13)$$

where  $K_0$  is the zero-order modified Bessel function of the second kind and  $K_1$  is the first-order modified Bessel function of the second kind. If  $x/a \ll 1$  and  $a \gg 1$ , then  $\{K_1[a(1+x/a)]\}/\{K_0[a(1+x/a)]\} \rightarrow 1$  and  $1/[a(1+x/a)] \rightarrow 0$ . Therefore eq 13 can be approximated by

$$K_0(a) e^{a \frac{d^2v}{dx^2}} = \frac{1}{b} e^{K_0(a) e^{bv}} \quad (14)$$

or

$$\frac{d^2[K_0(a) e^a v]}{dx^2} = \frac{1}{b} e^{K_0(a) e^{bv}} \quad (15)$$

The corresponding boundary conditions are

$$K_0(a) e^a v = K_0(a) e^a v_s = y_s, x = 0 \quad (16)$$

$$K_0(a) e^a v = 0, \text{ as } x \rightarrow \infty \quad (17)$$

Solving eq 15 subject to these conditions gives

$$K_0(a) e^a v = \frac{1}{b} \ln \left\{ \sec^2 \left[ \frac{-1}{\sqrt{2}}x + \tan^{-1}(e^{bK_0(a) e^a v_s} - 1)^{1/2} \right] \right\} \quad (18)$$

Note that this expression is similar to the result for a planar surface. In terms of  $y$  and  $x$ , we have

$$y_{\text{cylindrical}} = \left\{ \frac{K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right]}{K_0(a)} \right\} \frac{e^x}{b} \ln \left\{ \sec^2 \left[ -\frac{1}{\sqrt{2}}x + \tan^{-1}(e^{by_s} - 1)^{1/2} \right] \right\} \quad (19)$$

where  $y_{\text{cylindrical}}$  is the scaled electrical potential for a cylindrical surface.

**B. Two Surfaces.** In relation to Figure 1, let us consider the case of two identical surfaces where  $d$  is the closest distance between them, and  $D (= \kappa d)$  is the scaled value of  $d$ . We assume the following boundary conditions:

$$y = y_s, x = 0 \quad (20)$$

$$y = y_m, x = \frac{D}{2} \quad (21)$$

where  $y_m = F\psi_m/RT$ ,  $\psi_m$  being the potential when  $r = (d/2) + \theta a_0$ . It can be shown that the solution to the Poisson–Boltzmann equation for a planar surface subject to these conditions is<sup>39</sup>

$$y_{\text{planar}} = \frac{1}{b} \ln \left( e^{by_m} \sec^2 \left\{ -\sqrt{\frac{e^{by_m}}{2}}x + \tan^{-1} [e^{b(y_s - y_m)} - 1]^{1/2} \right\}, 0 \leq x \leq \frac{D}{2} \right) \quad (22)$$

where  $y_m$  is the scaled electrical potential at the center between two surfaces. Equation 22 implies that  $y_m$  is the root of

$$-\sqrt{\frac{e^{by_m}}{2}} \frac{D}{2} + \tan^{-1} [e^{b(y_s - y_m)} - 1]^{1/2} = 0 \quad (23)$$

If  $\exp[b(y_s - y_m)] \gg 1$ , since  $\tan^{-1} \{ \exp[b(y_s - y_m)] - 1 \}^{1/2}$  can be approximated by  $\pi/2 - \exp[b(y_m - y_s)/2]$ , eq 23 leads to

$$y_{m,\text{planar}} = \frac{-2}{b} \ln \left( \frac{D}{\sqrt{2\pi^2}} + \frac{2}{\pi} e^{-by_s/2} \right) \quad (24)$$

Substituting this expression into eq 22 yields the scaled electrical potential for two planar surfaces. A comparison between the results for the three types of single surface, eqs 5, 11, and 19, suggests that the result for a nonplanar surface can be deduced from that for a planar surface by multiplying a correction function. Following this analogy, the scaled electrical potential for two nonplanar surfaces is derived directly from that for two planar surfaces. For two spherical surfaces, using the modified expression  $u = (1+x/a)y$  and the boundary conditions

$$u = u_s = y_s, x = 0 \quad (25)$$

$$u = u_m = y_m \left(1 + \frac{D}{2a}\right), x = \frac{D}{2} \quad (26)$$

we arrive at the following approximate expression:

$$y_{\text{spherical}} = \frac{1}{b \left(1 + \frac{x}{a}\right)} \ln \left\{ e^{b y_m (1+D/2a)} \sec^2 \left[ -\sqrt{\frac{e^{b y_m (1+D/2a)}}{2}} x + \tan^{-1} \left( e^{b [y_s - y_m (1+D/2a)]} - 1 \right)^{1/2} \right] \right\}, 0 \leq x \leq \frac{D}{2} \quad (27)$$

Equation 27 implies that  $y_m$  is the root of

$$-\sqrt{\frac{e^{b y_m (1+D/2a)}}{2}} x + \tan^{-1} \left\{ e^{b [y_s - y_m (1+D/2a)]} - 1 \right\}^{1/2} = 0 \quad (28)$$

Following the treatment for planar surfaces, if  $\exp\{b[y_s - y_m(1 + D/2a)]\} \gg 1$ , the second term on the left-hand side of eq 28 can be approximated by  $\pi/2 - \exp\{1/2 b[y_m(1 + D/2a) - y_s]\}$ , and solving the resultant expression for  $y_m$  yields

$$y_{m,\text{spherical}} = \frac{-2}{b} \left( \frac{1}{1 + \frac{D}{2a}} \right) \ln \left( \frac{D}{\sqrt{2\pi^2}} + \frac{2}{\pi} e^{-b y_s/2} \right) \quad (29)$$

For two cylindrical surfaces, if we let  $v^*$  equal  $y([K_0(a)]/[K_0(a(1 + x/a))])e^{-x}$ , which is the correction function for a single cylindrical surface, then the boundary conditions for the corresponding Poisson–Boltzmann equation become

$$x = 0, v^* = v_s^* = y_s \frac{K_0(a)}{K_0(a)} = y_s \quad (30)$$

$$v^* = v_m^* = y_m \frac{K_0(a)}{K_0(a + \frac{D}{2})} e^{-D/2}, x = \frac{D}{2} \quad (31)$$

Following the treatment of spherical surfaces, that is, after substituting  $v_s^*$  and  $v_m^*$  into the corresponding governing equation and checking the consistency of the boundary conditions, we can show that an approximate electrical potential between two parallel cylindrical surfaces is

$$y_{\text{cylindrical}} = \left\{ \frac{K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right]}{K_0(a)} \right\} \frac{e^x}{b} \ln \left[ \frac{e^{b y_m} K_0(a)}{K_0 \left( a + \frac{D}{2} \right)} e^{-D/2} \sec^2 \left( -\sqrt{\frac{e^{b y_m} K_0(a)}{2}} e^{-D/2} x + \tan^{-1} \left\{ e^{b \left[ y_s - y_m \frac{K_0(a)}{K_0 \left( a + \frac{D}{2} \right)} \right]} - 1 \right\}^{1/2} \right) \right], 0 \leq x \leq \frac{D}{2} \quad (32)$$

where  $y_m$  is the root of

$$-\sqrt{\frac{e^{b y_m} \frac{K_0(a)}{K_0 \left( a + \frac{D}{2} \right)} e^{-D/2}}{2}} x + \tan^{-1} \left\{ e^{b \left[ y_s - y_m \frac{K_0(a)}{K_0 \left( a + \frac{D}{2} \right)} \right]} - 1 \right\}^{1/2} = 0 \quad (33)$$

Equations 27 and 32 are accurate when a particle is large enough that the symmetric condition of the spatial distribution of electrical potential is satisfied. If  $\exp\{b[y_s - y_m\{K_0(a)/[K_0(a + D/2)]]e^{-(D/2)}\} \gg 1$ , the second term on the left-hand side of eq 33 can be approximated by  $\pi/2 - \exp\{1/2 b[y_m\{K_0(a)/[K_0(a + D/2)]]e^{-(D/2)} - y_s\}$ , and solving the resultant expression for  $y_m$  gives

$$y_{m,\text{cylindrical}} = \frac{-2}{b} \left[ \frac{K_0 \left( a + \frac{D}{2} \right)}{K_0(a)} \right] \frac{D}{2} \ln \left( \frac{D}{\sqrt{2\pi^2}} + \frac{2}{\pi} e^{-b y_s/2} \right) \quad (34)$$

Equations 24, 29, and 34 indicate that, apart from a correction function, the electrical potential at the center between two surfaces has the same form. We conclude that for both a single surface and two surfaces, the electrical potentials a certain distance along the normal direction of a surface for the three types of surfaces considered all have the same form, subject to a correction function. We have

$$y_{\text{spherical}}(x) = \frac{1}{1 + \frac{x}{a}} y_{\text{planar}}(x) \quad (35)$$

$$y_{\text{cylindrical}}(x) = \frac{K_0 \left[ a \left( 1 + \frac{x}{a} \right) \right]}{K_0(a)} e^x y_{\text{planar}}(x) \quad (36)$$

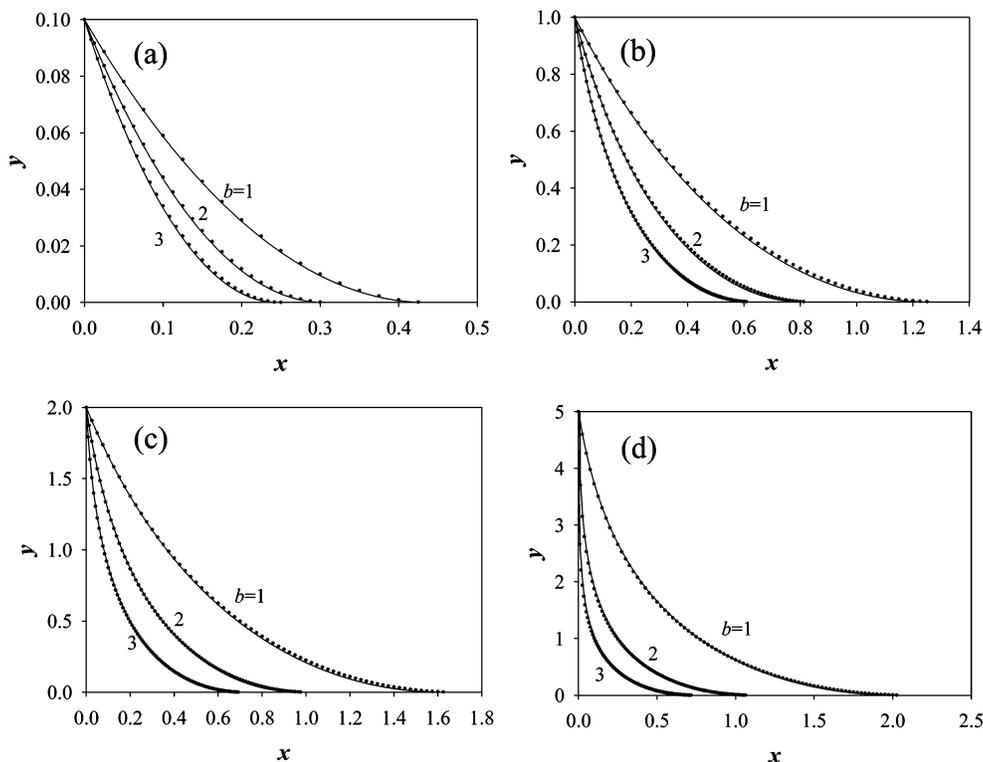
Note that for the case of symmetric electrolytes these expressions are consistent with those in the literature,<sup>40,41</sup> except that the latter are available for single surfaces only.

Once  $y_m$  is known, the electrostatic force between two surfaces in the normal direction per unit area, or the osmotic pressure,  $p$ , can be evaluated by

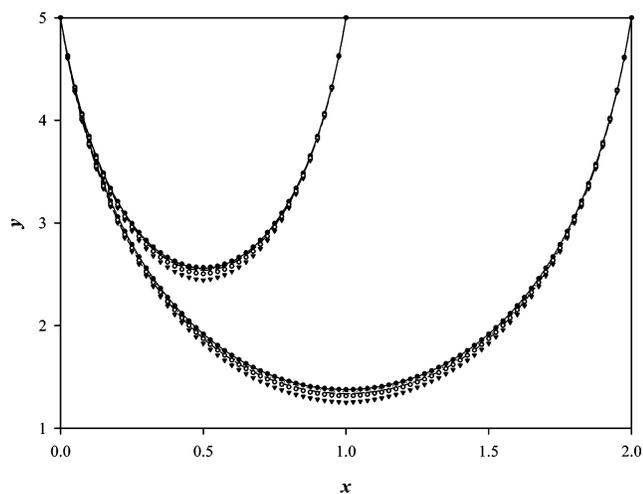
$$\frac{p}{IRT} = \frac{2}{b^2} (e^{b y_m} - 1) \quad (37)$$

### 3. Results and Discussion

In the literature, the only exactly solvable electrical potential near a charged surface immersed in an electrolyte solution is that for the case of a single planar surface in a symmetric electrolyte solution. Here, we show that if no salt is added, an analytical expression for the electrical potential of a planar surface can be derived and, under appropriate conditions, that of a cylindrical or a spherical surface can be obtained directly from the former by multiplying a correction function, which takes the curvature effect of a surface into account. Using the same correction function, the electrical potential for two cylindrical surfaces or two spherical surfaces can also be obtained directly from that for two planar surfaces. This is highly desirable since the nature of a colloidal dispersion depends largely on the interaction between two dispersed entities. In particular, the derived analytical expressions for the electrical potential at the center between two surfaces are readily



**Figure 3.** Spatial variation in scaled electrical potential  $y$  for a spherical surface at various combinations of  $y_s$  and  $b$  for the case in which  $a = 10$ . Solid curves depict numerical results; discrete symbols depict results based on eq 11: (a)  $y_s = 0.1$ , (b)  $y_s = 1.0$ , (c)  $y_s = 2.0$ , and (d)  $y_s = 5.0$ .

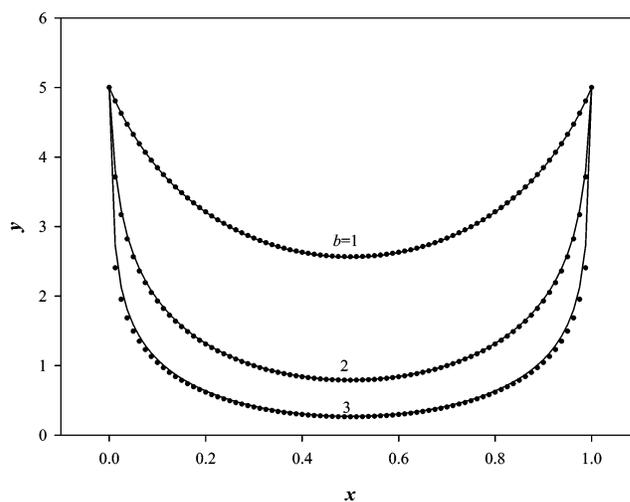


**Figure 4.** Spatial variation in scaled electrical potential  $y$  between two surfaces for two levels of  $D$  (1.0 and 2.0) when  $a = 10$ ,  $y_s = 5.0$ , and  $b = 1$ . Curves depict numerical results of eqs 2, 20, and 21; discrete symbols depict results based on eqs 22, 27, and 32: (—●—) planar surfaces, (···○···) cylindrical surfaces, and (—▼—) spherical surfaces.

applicable to the evaluation of the electrostatic force per unit area between two surfaces, or the osmotic pressure.

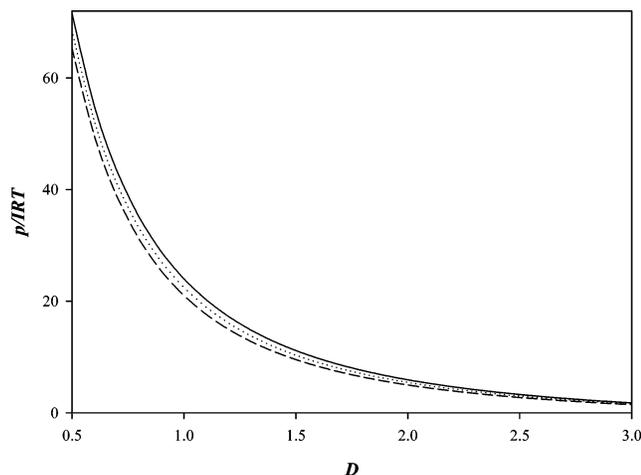
Figure 2 shows the typical spatial variation in the scaled electrical potential,  $y$ , for both a spherical and a cylindrical surface at various scaled radii,  $a$ . As expected, when  $a$  increases, both the electrical potential distribution of a cylindrical surface and that of a spherical surface approach that of a planar surface. The curvature effect of a spherical surface is more significant than that of a cylindrical surface. This effect becomes unimportant, however, when the order of  $a$  exceeds  $\sim 100$ .

The performance of the approximate analytical expression for a spherical surface, eq 11, is justified in Figure 3, where



**Figure 5.** Spatial variation in scaled electrical potential  $y$  between two planar surfaces for various values of  $b$  when  $y_s = 5.0$  and  $D = 1.0$ . The value of  $\kappa$  is based on  $b = 1$ . Curves depict numerical results of eq 2; discrete symbols depict results based on eq 22.

the exact numerical solution of eq 2 is also presented. In general, the higher the surface potential and/or the valence of counterions, the more accurate the approximate analytical result. The same phenomenon is also observed for a cylindrical surface. If both the radius of a surface and its potential are fixed, the larger the value of  $b$ , the lower the value of  $y$  and the faster the rate of decrease of  $y$  as  $x$  increases. This is true because when the radius of a surface is fixed, the larger the value of  $b$ , the higher the ionic strength and the thinner the double layer. Also, as  $y_s$  increases, the double layer surrounding a surface is compressed and it is easier for counterion condensation to occur,<sup>15,16,39</sup> which yields a faster rate of decrease in  $y$  as  $x$  increases. This phenomenon is also observed for a planar and a cylindrical surface.



**Figure 6.** Variation of scaled osmotic pressure ( $p/RT$ ) as a function of scaled separation distance between two surfaces,  $D$ , when  $y_s = 5.0$  and  $b = 1$ : (—) planar surfaces, (···) cylindrical surfaces, and (---) spherical surfaces.

The spatial variations in scaled electrical potential  $y$  for three types of two surfaces are presented in Figure 4. This figure indicates that under the conditions where  $\exp[b(y_s - y_m)] \gg 1$  for planar surfaces,  $\exp\{b[y_s - y_m(1 + D/2a)]\} \gg 1$  for spherical surfaces, and  $\exp[b(y_s - y_m\{[K_0(a)]/[K_0(a + D/2)]\}e^{-D/2})] \gg 1$  for cylindrical surfaces, the performance of the approximate analytical expressions (eqs 22, 27, and 32) is satisfactory. The influence of the curvature of a surface is clearly seen where the magnitude of  $y$  at a fixed  $x$  follows this order: planar surfaces > cylindrical surfaces > spherical surfaces. The general trends of  $y$  as  $y_s$  and  $b$  vary are the same as those for the case of a single surface, as illustrated in a previous study<sup>39</sup> and Figure 5 where two planar surfaces are considered.

Figure 6 shows the variation of the scaled osmotic pressure ( $p/RT$ ) as a function of the scaled separation distance between two surfaces,  $D$ . The magnitude of ( $p/RT$ ) follows this order: planar surfaces > cylindrical surfaces > spherical surfaces (which arises from the fact that the mean distance between two symmetric surface elements on each surface is the longest for two spherical surfaces, followed by that for two cylindrical surfaces and that for two planar surfaces). This can also be justified by Figure 4 where the magnitude of  $y_m$  follows this order: planar surfaces > cylindrical surfaces > spherical surfaces.

#### 4. Conclusion

In summary, the Poisson–Boltzmann equation describing the electrical potential distribution of planar, cylindrical, and spherical surfaces immersed in a salt-free medium is solved semianalytically, and the results are extended to the case of two identical surfaces. We show that the curvature effect of a surface can be taken into account by considering a correction function. Analytical expressions for the electrical potential at the center between two surfaces are also derived which can be readily applied to the evaluation of the osmotic pressure. The results of numerical simulations reveal the following. (a) The curvature effect of a spherical surface is more significant than that of a cylindrical surface. This effect becomes unimportant, however, if the radius of a surface exceeds  $\sim 100$  times the thickness of its double layer. (b) In general, the higher the surface potential and/or the valence of counterions, the more accurate the approximate analytical result that is derived. (c) If both the radius of a surface and its potential are fixed, the higher the

valence of counterions, the lower the electrical potential and the faster the rate of its decrease as the distance from the surface increases. (d) For a fixed surface potential and counterion valence, the rate of decrease in the electrical potential as the distance from a surface increases follows this order: planar surface > cylindrical surface > spherical surface. (e) For a fixed surface potential, counterion valence, and separation distance between two surfaces, the magnitude of the osmotic pressure for various types of surface follows this order: planar surfaces > cylindrical surfaces > spherical surfaces.

**Acknowledgment.** This work is supported by the National Science Council of the Republic of China.

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