

# Approximate Expression for the Critical Coagulation Concentration of a General Electrolyte Solution

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The critical coagulation concentration of a colloidal dispersion for the case of a general electrolyte solution is estimated under the conditions of constant surface potential. By combination of the Langmuir approximation and the Debye–Huckel approximation, explicit expressions for the electrical potential, the osmotic pressure, and the electrical energy are derived, and the results are used to estimate the critical coagulation concentration of ionic species. The influence of the valence of ionic species on this concentration is discussed. We show that the Schultz–Hardy rule is invalid, in general, and that the effect of co-ions can be too large to be ignored.

## 1. Introduction

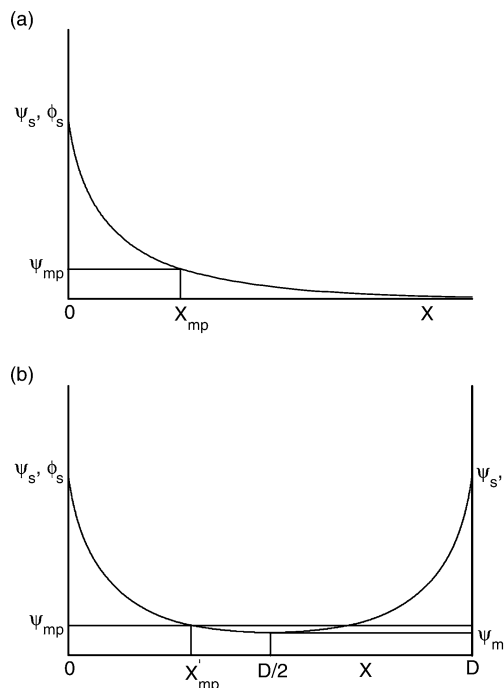
The electrical interaction between two double layers plays the key role in colloid and interface science. The stability of a colloidal dispersion, for example, depends largely upon this type of interaction. One of the key steps to evaluate the electrical interaction between two double layers is to solve the spatial variation of electrical potential, which, under appropriate conditions, is described by the Poisson–Boltzmann equation. In practice, obtaining an explicit analytical solution of this equation is highly desirable because further mathematical treatment is necessary in the subsequent evaluation of electrical energy. Unfortunately, because of its nonlinear nature, the only exactly solvable problem so far is the case of an isolated, infinitely planar surface in a symmetric electrolyte solution. Other than this case, the exact solution needs to be obtained numerically, which involves improper integral and singularity problems; relevant calculations can be laborious, especially when the result is used in a subsequent analysis such as the evaluation of electrical energy. The difficulty of solving a Poisson–Boltzmann equation is often circumvented by assuming that the potential of a charged surface is low. In this case, the Poisson–Boltzmann equation can be approximated by a linearized equation, which is readily solvable for various types of surfaces. However, the level of surface potential assumed also limits the applicability of the solution thus obtained. Another approach is to derive an approximate analytical solution. Hsu and Kuo, for instance, derived an approximate analytical solution of the Poisson–Boltzmann equation for a planar<sup>1</sup> and for cylindrical and spherical surfaces.<sup>2</sup> Zhang<sup>3</sup> obtained a series solution for two dissimilar, planar parallel surfaces in a symmetric electrolyte solution. Luo et al.<sup>4</sup> solved piecewisely the Poisson–Boltzmann equation for the case of two dissimilar, planar parallel surfaces

in a symmetric electrolyte solution. Their idea is that, for a point sufficiently far from a charged surface, because the potential is low, solving a linearized Poisson–Boltzmann equation is sufficient. On the other hand, for a point near the surface, Langmuir approximation,<sup>5</sup> where the contribution of coions to the space charge density is usually negligible relative to that of counterions, is applicable, and the simplified Poisson–Boltzmann equation becomes solvable.

Critical coagulation concentration, the minimum concentration of ionic species to induce coagulation, is one of the basic properties of a colloidal dispersion. For some counterions, it was correlated experimentally that this concentration is proportional to the inverse sixth-power of their valence, the so-called Schultz–Hardy rule, which was interpreted theoretically by the well-known Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory.<sup>6</sup> More detailed observations revealed that the Schultz–Hardy rule is not general; in fact, the dependence of critical coagulation concentration on the valence of counterions is of a complicated nature. This is not surprising because the derivation of the classic DLVO theory involved several assumptions, which may not be satisfied in practice. One of these is the superposition of the electrical potential at the midpoint between two charged surfaces. The same assumption was also made in the other modifications of the DLVO theory.<sup>7,8</sup> In the classic treatment, the superposition of electrical potential is unavoidable because the exact analytical solution of the corresponding Poisson–Boltzmann equation was unknown. One possible approach to solve this problem is to follow the treatment of Luo et al.<sup>4</sup>

In this study, the approach of Luo et al.<sup>4</sup> is modified so that a general electrolyte solution can be considered. Attempts are made to derive approximate analytical expressions for the electrical potential, the osmotic pressure, and the electrical energy for the case of two planar, parallel surfaces. These results are used to estimate the critical coagulation concentration of

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**Figure 1.** Schematic representation of present model under consideration. (a) A single surface and (b) two identical surfaces.

ionic species. In particular, the effects of the valence of counterions and that of co-ions on the critical coagulation concentration are discussed.

## 2. Analysis

The analysis is begun by considering first a single surface followed by an extension to the case of two parallel surfaces.

**A Single Surface.** Referring to Figure 1a, we consider a positively charged surface with a surface potential  $\phi_s$  immersed in a general  $a$ – $b$  electrolyte solution,  $a$  and  $b$  being respectively the valences of cations and anions. Here, we assume that the double layer surrounding a particle is thin relative to its linear size and that the local curvature of the surface of the particle is insignificant, that is, it can be treated as planar. As pointed out by Hsu and Tseng,<sup>9</sup> this is usually satisfied when the concentration of electrolyte is near the critical coagulation concentration. In this case, the spatial variation in the scaled electrical potential  $\psi$  can be described by the one-dimensional Poisson–Boltzmann equation

$$\frac{d^2\psi}{dX^2} = \frac{e^{b\psi} - e^{-a\psi}}{a + b} \quad (1)$$

where  $\psi = F\phi/RT$  and  $X = \kappa x$ .  $F$ ,  $R$ , and  $T$  are respectively the Faraday constant, the gas constant, and the absolute temperature,  $\phi$  and  $x$  are respectively the electrical potential and the distance from the surface, and  $\kappa = (bC_b^0(a + b)F^2/\epsilon RT)^{1/2} = (2IF^2/\epsilon RT)^{1/2}$  is the Debye–Huckel parameter,  $C_b^0$  and  $\epsilon$  are respectively the molar concentration of anions and the permittivity of the dispersion medium, and  $I = bC_b^0(a + b)/2$  is the ionic strength. Under the Debye–Huckel condition,  $\psi$  is low and eq 1 can be approximated by

$$\frac{d^2\psi}{dX^2} = \kappa^2\psi \quad (2)$$

This equation is readily solvable, and it is known that the solution is sufficiently accurate for  $a\psi$  and/or  $b\psi$  up to the order

of unity. On the other hand, if  $\psi$  is high, because the  $e^{-a\psi}$  on the right-hand side of eq 1 is much smaller than  $e^{b\psi}$ , therefore, it can be neglected. The resultant equation can be solved analytically by the so-called Langmuir approximation.<sup>5</sup> Because  $\psi$  decays rapidly with the distance away from the surface, these results suggest that eq 1 can be solved approximately by combining the above two approaches: Langmuir approximation is used for the description of the  $\psi$  near the surface, and the result under Debye–Huckel condition is used for the  $\psi$  far away from the surface. To this end, we define  $X_{mp}$  as the scaled distance at which the results based on these two approaches match each other, and the potential at this position is  $\psi_{mp}$ . We choose  $\psi_{mp}$  as the inverse of the larger value of  $a$  and  $b$ , that is,  $\psi_{mp} = 1/\max[a, b]$ . On the basis of the above discussions, eqs 1 and 2 are solved subject to the following conditions

$$\psi = \psi_s \quad X = 0 \quad (3)$$

$$\psi = \psi_{mp} \quad X = X_{mp} \quad (4)$$

$$\frac{d\psi}{dX}\bigg|_{X=X_{mp}^-} = \frac{d\psi}{dX}\bigg|_{X=X_{mp}^+} \quad X = X_{mp} \quad (5)$$

$$\psi \rightarrow 0 \quad \text{and} \quad \frac{d\psi}{dX} \rightarrow 0 \quad \text{as} \quad X \rightarrow \infty \quad (6)$$

where  $\psi_s = F\phi_s/RT$ . Equation 5 implies that the electrical field is continuous at the match point. Solving eqs 1 and 2 subject to eqs 3–6, we obtain

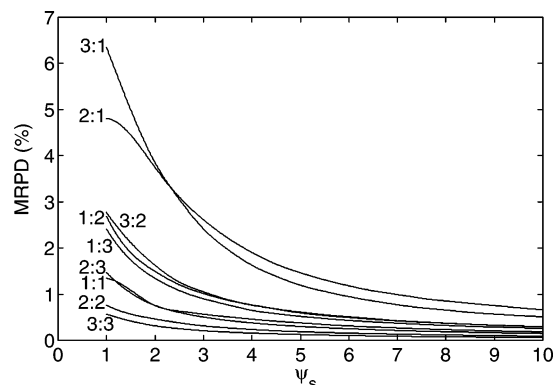
$$\psi = \frac{1}{b} \ln \left\{ \left[ e^{b\psi_{mp}} - \frac{b(a+b)}{2} \psi_{mp}^2 \right] \sec^2 \left\{ - \left[ \frac{b}{2(a+b)} e^{b\psi_{mp}} - \frac{b^2}{4} \psi_{mp}^2 \right]^{1/2} X + \tan^{-1} \left[ \frac{e^{b\psi_s}}{e^{b\psi_{mp}} - [b(a+b)/2] \psi_{mp}^2} - 1 \right]^{1/2} \right\} \right\} \quad 0 \leq X \leq X_{mp} \quad (7)$$

$$\psi = \psi_{mp} e^{-(X-X_{mp})} \quad X_{mp} \leq X \quad (8)$$

where

$$X_{mp} = \left[ \frac{b e^{b\psi_{mp}}}{2(a+b)} - \frac{b^2}{4} \psi_{mp}^2 \right]^{-1/2} \left\{ \tan^{-1} \left[ \frac{e^{b\psi_s}}{e^{b\psi_{mp}} - [b(a+b)/2] \psi_{mp}^2} - 1 \right]^{1/2} - \tan^{-1} \left[ \frac{e^{b\psi_{mp}}}{e^{b\psi_{mp}} - [b(a+b)/2] \psi_{mp}^2} - 1 \right]^{0.5} \right\} \quad (9)$$

The performance of the approximate solution obtained is illustrated in Figure 2, where the variation of the mean relative percentage deviation in  $\psi$  based on eqs 7 and 8 from the corresponding exact numerical solution, MRPD, as a function of  $\psi_s$  for various types of electrolyte solution is plotted. This figure reveals that MRPD decreases rapidly with the increase in  $\psi_s$ ; that is, the higher the surface potential, the more accurate the approximate solution. In general, the performance of the approximate solution is satisfactory. For symmetric electrolyte solution ( $a = b$ ), in particular, MRPD is below 1.5% for the range of surface potential examined. The deviation arises mainly from the negligence of the higher-order terms in the linearization procedure to arrive at eq 2.



**Figure 2.** Variation of mean relative percentage deviation in  $\psi$ , MRPD, as a function of  $\psi_s$  at various  $a:b$  for the case when  $X \leq 3$ .

**Two Identical Surfaces.** Consider next the case of two identical, planar parallel surfaces, both are positively charged with a constant scaled surface potential  $\psi_s$ , as illustrated in Figure 1b. Let  $d$  be the distance between two surfaces and  $\psi_m$  be the scaled potential on the midplane between them. Because the solution for the case when  $\psi_s$  is low, that is,  $\psi_s \leq \psi_{mp}$ , can be solved directly from eq 2, we assume  $\psi > \psi_{mp}$ . Two cases need to be considered, namely,  $\psi_m \geq \psi_{mp}$  and  $\psi_m \leq \psi_{mp}$ .

*Case 1.*  $\psi_m \geq \psi_{mp}$ . In this case,  $d \leq d_{mp}$ , where  $d_{mp}$  is the value of  $d$  at which  $\psi_m = \psi_{mp}$ . Following the procedure as that applied for the case of one surface, it can be shown that

$$\psi = \frac{1}{b} \ln \left\{ e^{b\psi_m} \sec^2 \left\{ - \left[ \frac{b}{2(a+b)} e^{b\psi_m} \right]^{1/2} X + \tan^{-1} \left[ \frac{e^{b(\psi_s - \psi_m)} - 1}{2} \right]^{1/2} \right\} \right\} \quad 0 \leq X \leq D/2 \quad (10)$$

where  $D = \kappa d$  and  $\psi_m$  is the root of the equation

$$\left[ \frac{b}{2(a+b)} e^{b\psi_m} \right]^{-1/2} \tan^{-1} [e^{b(\psi_s - \psi_m)} - 1]^{1/2} - \frac{D}{2} = 0 \quad (11)$$

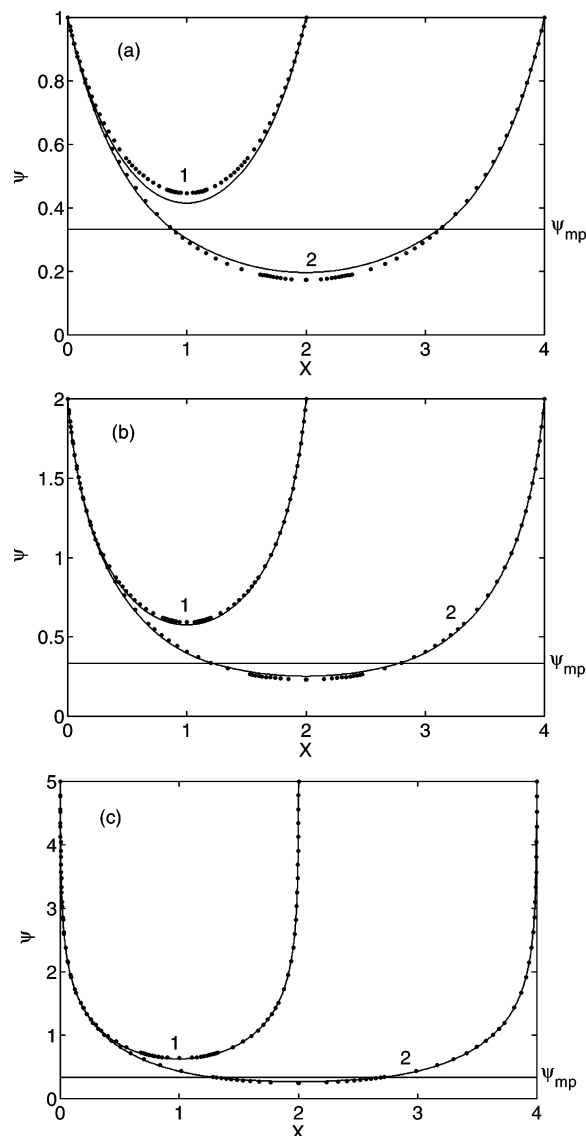
Note that because the electrical potential is symmetric about  $X = D/2$ , only the result in the range  $0 \leq X \leq D/2$  needs to be shown.

*Case 2.*  $\psi_m \leq \psi_{mp}$ . In this case,  $d \geq d_{mp}$ , and it can be shown that the solution to the Poisson-Boltzmann equation is

$$\psi = \frac{1}{b} \ln \left\{ \left[ e^{b\psi_{mp}} - \frac{b(a+b)}{2} (\psi_{mp}^2 - \psi_m^2) \right] \sec^2 \left\{ - \left[ \frac{b}{2(a+b)} e^{b\psi_{mp}} - \frac{b^2}{4} (\psi_{mp}^2 - \psi_m^2) \right]^{1/2} X + \tan^{-1} \left[ \frac{e^{b\psi_s}}{e^{b\psi_{mp}} - \frac{b(a+b)}{2} (\psi_{mp}^2 - \psi_m^2)} - 1 \right]^{1/2} \right\} \right\} \quad 0 \leq X \leq X'_{mp} \quad (12)$$

$$\psi = \psi_m \cosh(X - D/2) \quad X'_{mp} \leq X \leq D/2 \quad (13)$$

where  $X'_{mp} = (D/2) - \text{sech}^{-1}(\psi_m/\psi_{mp})$  is the value of  $X$



**Figure 3.** Variation of  $\psi$  as a function of  $X$  at different  $D$  for various  $\psi_s$  for the case when  $a:b = 1:3$ . Curve 1,  $D = 2$ ; curve 2,  $D = 4$ . Solid curves represent the present model; discrete symbols represent the exact numerical result. (a)  $\psi_s = 1$ , (b)  $\psi_s = 2$ , (c)  $\psi_s = 5$ .

at the match point for the case of two surfaces and  $\psi_m$  is the root of the equation

$$\left[ \frac{b}{2(a+b)} e^{b\psi_m} - \frac{b^2}{4} (\psi_{mp}^2 - \psi_m^2) \right]^{-1/2} \left\{ \tan^{-1} \left[ \frac{e^{b\psi_s}}{e^{b\psi_{mp}} - \frac{b(a+b)}{2} (\psi_{mp}^2 - \psi_m^2)} - 1 \right]^{1/2} - \tan^{-1} \left[ \frac{e^{b\psi_{mp}}}{e^{b\psi_{mp}} - \frac{b(a+b)}{2} (\psi_{mp}^2 - \psi_m^2)} - 1 \right]^{1/2} \right\} + \text{sech}^{-1}(\psi_m/\psi_{mp}) - \frac{D}{2} = 0 \quad (14)$$

The performance of the present results is illustrated in Figure 3 in which the spatial variations of  $\psi$  at various levels of  $\psi_s$  are presented for both  $D < D_{mp}$  and  $D > D_{mp}$ , where

$$D_{\text{mp}} = \kappa d_{\text{mp}} = 2 \left[ \frac{b}{2(a+b)} e^{b\psi_{\text{mp}}} \right]^{-1/2} \tan^{-1} [e^{b(\psi_s - \psi_{\text{mp}})} - 1]^{1/2} \quad (15)$$

is obtained from eq 11. Figure 3 reveals that the performance of the approximate solution obtained is satisfactory, in general. As in the case of one surface, the higher the  $\psi_s$ , the more accurate is the approximate result.

For the case when  $D \leq D_{\text{mp}}$  (or  $\psi_m \geq \psi_{\text{mp}}$ ), if  $e^{b(\psi_s - \psi_m)} \gg 1$ , then because  $\tan^{-1} [e^{b(\psi_s - \psi_m)} - 1]^{1/2} \cong \pi/2 - e^{0.5(\psi_m - \psi_s)}$ , eq 11 yields

$$e^{(1/2)b\psi_m} = \frac{1}{\left[ \frac{b}{2\pi^2(a+b)} \right]^{1/2} D + \frac{2}{\pi} e^{-(1/2)b\psi_s}} \quad (16)$$

On the basis of this expression, it can be shown that the osmotic pressure  $p$  and the electrical energy between two surfaces  $V_{\text{edl}}$  can be expressed respectively as

$$\frac{p}{IRT} = \frac{2}{b(a+b)} \left( \frac{b}{a} e^{-a\psi_m} + e^{b\psi_m} - \frac{b}{a} - 1 \right) \quad D \leq D_{\text{mp}} \quad (17)$$

$$\begin{aligned} \frac{\kappa V_{\text{edl}}}{IRT} = & - \int_{\infty}^D \frac{p}{IRT} dD = 4\psi_{\text{mp}}^2 e^{-(D_{\text{mp}} - 2X_{\text{mp}})} + \\ & \left[ \frac{\pi^2 b(a+b)}{2} \right]^{1/2} \left[ - \frac{4}{a(a+b)(2a+b)} e^{-(a+(1/2)b)\psi_m} + \right. \\ & \frac{4}{b^2(a+b)} e^{(1/2)b\psi_m} + \frac{4}{ab^2} e^{-(1/2)b\psi_m} + \\ & \left. \frac{4}{a(a+b)(2a+b)} e^{-(a+(1/2)b)\psi_{\text{mp}}} - \frac{4}{b^2(a+b)} e^{(1/2)b\psi_{\text{mp}}} - \right. \\ & \left. \frac{4}{ab^2} e^{-(1/2)b\psi_{\text{mp}}} \right] \quad D \leq D_{\text{mp}} \quad (18) \end{aligned}$$

On the other hand, if  $D \geq D_{\text{mp}}$  (or  $\psi_m \leq \psi_{\text{mp}}$ ),  $\psi_m$  can be approximated by a linear superposition of the result for a single surface and  $p$  can be expressed as

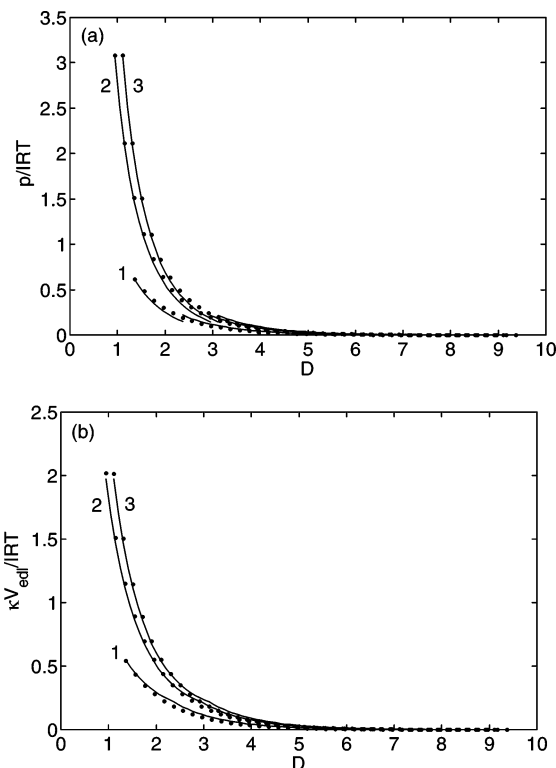
$$\begin{aligned} \frac{p}{IRT} = & \frac{2}{b(a+b)} \left( \frac{b}{a} e^{-a\psi_m} + e^{b\psi_m} - \frac{b}{a} - 1 \right) \cong \psi_m^2 = \\ & 4\psi_{\text{mp}}^2 e^{-(D-2X_{\text{mp}})} \quad D \geq D_{\text{mp}} \quad (19) \end{aligned}$$

On the basis of this equation, we have

$$\frac{\kappa V_{\text{edl}}}{IRT} = - \int_{\infty}^D \frac{p}{IRT} dD = 4\psi_{\text{mp}}^2 e^{-(D-2X_{\text{mp}})} \quad D \geq D_{\text{mp}} \quad (20)$$

Figure 4 shows the simulated variation of the scaled osmotic pressure and the scaled electrical energy as a function of  $D$  at various levels of  $\psi_s$ . In general, the performance of the approximate expressions derived is satisfactory. As is in the case of electrical potential, the higher the level of  $\psi_s$ , the more accurate the present approximate results. Figure 4a indicates that the osmotic pressure predicted by eqs 17 and 19 has a discontinuous point at  $D_{\text{mp}}$ , at which the maximum deviation occurs. This discontinuity does not appear in Figure 4b for the case of electrical energy. This discontinuity in the osmotic pressure also occurred in the analysis of Luo et al.<sup>4</sup>

**Critical Coagulation Concentration.** The results obtained are readily applicable to the evaluation of the critical coagulation



**Figure 4.** Variation of  $p/IRT$  (a) and  $\kappa V_{\text{edl}}/IRT$  (b) as a function of  $D$  at various  $\psi_s$  for the case when  $a:b = 1:3$  and  $C_b^0 = 1 \times 10^{-3}$  M. Curve 1,  $\psi_s = 1$ ; curve 2,  $\psi_s = 2$ ; curve 3,  $\psi_s = 5$ . Solid curves represent the present model; discrete symbols represent the exact numerical result.

concentration (CCC) of ionic species. The following conditions need to be satisfied at CCC<sup>10</sup>

$$p - \frac{\kappa^3 A}{6\pi D_c^3} = 0 \quad (21)$$

$$V_{\text{edl}} - \frac{\kappa^2 A}{12\pi D_c^2} = 0 \quad (22)$$

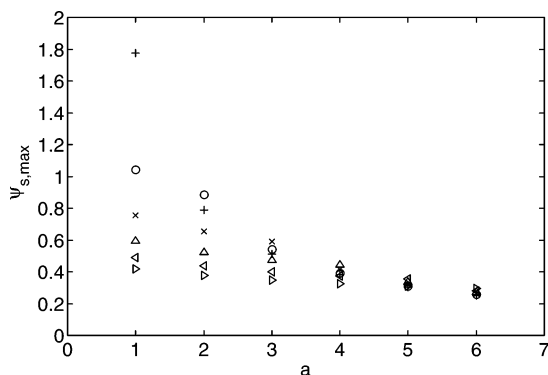
where  $A$  is the Hamaker constant and  $D_c$  is the value of  $D$  when the total energy between two surfaces achieves the maximum value of zero at  $C_b^0 = \text{CCC}$ . For the case when  $D_c \leq D_{\text{mp}}$ , CCC can be determined from eqs 16–18, 21, and 22. However, solving these equations simultaneously is nontrivial, and a try-and-error procedure seems necessary. If  $D_c \geq D_{\text{mp}}$ , solving eqs 19–22 gives  $D_c = 2$  and

$$\text{CCC} = C_b^0 = \frac{9216\pi^2 e^{-4} \epsilon^3 R^5 T^5 \psi_{\text{mp}}^4 e^{4X_{\text{mp}}}}{A^2 F^6 b(a+b)} \cong \frac{\psi_{\text{mp}}^4 e^{4X_{\text{mp}}}}{b(a+b)} = S_3 \quad (23)$$

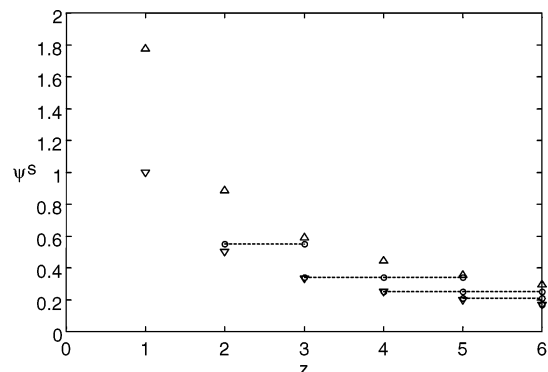
where  $X_{\text{mp}} = X_{\text{mp}}(a, b, \psi_s)$  is expressed in eq 9. Equation 23 is applicable to  $\psi_s$  in the interval  $[\psi_{\text{mp}}, \psi_{s, \text{max}}]$ , where  $\psi_{s, \text{max}}$  is evaluated from eq 11 by letting  $\psi_m = \psi_{\text{mp}}$  and  $D = D_c = 2$ . We obtain

$$\psi_{s, \text{max}} = \frac{1}{b} \ln \left\{ e^{b\psi_{\text{mp}}} \left[ \tan^2 \left[ \frac{b}{2(a+b)} e^{b\psi_{\text{mp}}} \right]^{1/2} + 1 \right] \right\} \quad (24)$$

Figure 5 shows the value of  $\psi_{s, \text{max}}$  as a function of  $a$  for various



**Figure 5.** Variation of  $\psi_{s,\max}$  as a function of  $a$  for various  $b$  for the case when  $D_{\text{mp}} = 2$ . (+)  $b = 1$ , (O)  $b = 2$ , (x)  $b = 3$ , ( $\Delta$ )  $b = 4$ , ( $\nabla$ )  $b = 5$ , (\*)  $b = 6$ .



**Figure 6.** Variation of  $\psi_{s,\max}$  ( $\Delta$ ) and  $\psi_{\text{mp}}$  ( $\nabla$ ) as a function of  $z$ . Dashed curves represent the region in which  $\psi_s$  is applicable to eqs 25 and 26.

types of electrolyte. For symmetric electrolytes,  $a = b = z$ , and eq 23 reduces to

$$\text{CCC} = \frac{4608\pi^2 e^{-4} \epsilon^3 R^5 T^5}{A^2 F^6} \frac{e^{4X_{\text{mp}}}}{z^6} \propto e^{4X_{\text{mp}}} z^{-6} = S_1 z^{-6} \quad (25)$$

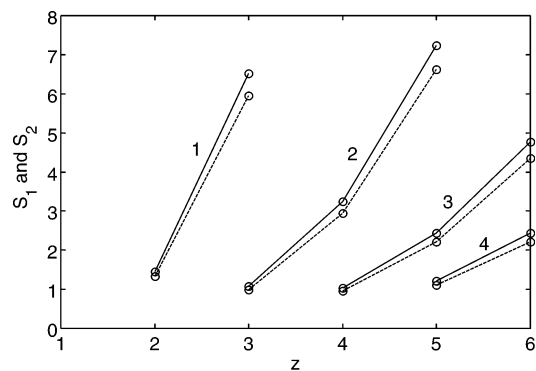
where  $S_1 = e^{4X_{\text{mp}}}$ . Verwey and Overbeek<sup>10</sup> arrived at, on the basis of linear superposition and  $\psi_{\text{m}} \leq \psi_{\text{mp}}$

$$\text{CCC} = \frac{4608\pi^2 e^{-4} \epsilon^3 R^5 T^5}{A^2 F^6} \frac{256 \tanh^4(z\psi_s/4)}{z^6} \propto \frac{256 \tanh^4(z\psi_s/4) z^{-6}}{256 \tanh^4(z\psi_s/4) z^{-6}} = S_2 z^{-6} \quad (26)$$

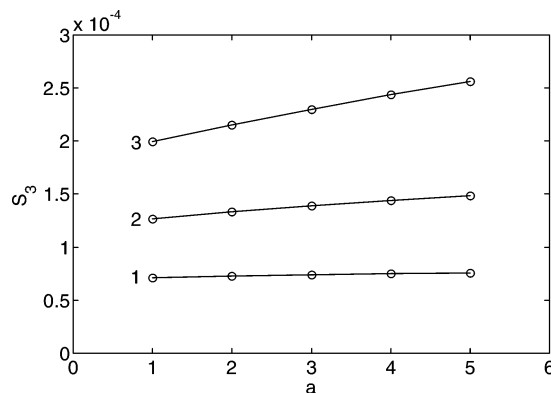
where  $S_2 = 256 \tanh^4(z\psi_s/4)$ . The variations of the lower and the upper limits of the region of  $\psi_s$ , in which eqs 25 and 26 are applicable,  $\psi_{\text{mp}}$ , and  $\psi_{s,\max}$ , as a function of  $z$ , are presented in Figure 6. The range of  $z$  corresponds to a fixed  $\psi_s$  in which eqs 25 and 26 are applicable is also illustrated in this figure. The variations of  $S_1$  and  $S_2$  as a function of  $z$  at several levels of  $\psi_s$  are presented in Figure 7. This figure indicates that both  $S_1$  and  $S_2$  are very sensitive to the variation in  $z$ , which implies that the Schultz–Hardy rule,  $\text{CCC} \propto z^{-6}$ , is invalid if  $\psi_{\text{mp}} \leq \psi_s \leq \psi_{s,\max}$ . Figure 7 also reveals that  $S_1 > S_2$ , in general, and if  $\psi_s$  is sufficiently high,  $S_1 \approx S_2$ . This implies that unless  $\psi_s$  is sufficiently high, eq 26 will underestimate CCC.

If  $\psi_s \leq \psi_{\text{mp}}$ , Debye–Huckel approximation is satisfactory, and the osmotic pressure and the electrical energy can be expressed respectively as

$$\frac{p}{IRT} = \psi_s^2 \text{sech}^2(D/2) \quad (27)$$



**Figure 7.** Variations of  $S_1$  and  $S_2$  as a function of  $z$  at various  $\psi_s$ . Curve 1,  $\psi_s = 0.55$ ; curve 2,  $\psi_s = 0.34$ ; curve 3,  $\psi_s = 0.252$ ; curve 4,  $\psi_s = 0.21$ . Solid curves represent  $S_1$ ; dashed curves represent  $S_2$ .



**Figure 8.** Variation of  $S_3$  as a function of  $a$  at various  $\psi_s$  for the case when  $b = 5$ . Curve 1,  $\psi_s = 0.25$ ; curve 2,  $\psi_s = 0.30$ ; curve 3,  $\psi_s = 0.35$ .

and

$$\frac{\kappa V_{\text{edl}}}{IRT} = \psi_s^2 [1 - \tanh(D/2)] \quad (28)$$

On the basis of eqs 21, 22, 27, and 28, it can be shown that  $D_c$  is the root of  $(D_c - 2) e^{D_c} - 2 e^{-D_c} + D_c - 4 = 0$ , which yields  $D_c \approx 2.218$ . In this case, CCC can be expressed by

$$\text{CCC} = C_b^0 = \frac{144\pi^2 D_c^6 \epsilon^3 R^5 T^5 \psi_s^4}{(e^{D_c} + e^{-D_c} + 2)^2 A^2 F^6} \frac{1}{b(a+b)} \propto \frac{1}{b(a+b)} \quad (29)$$

For symmetric electrolyte, this expression reduces to

$$\text{CCC} = \frac{72\pi^2 D_c^6 \epsilon^3 R^5 T^5 \psi_s^4}{(e^{D_c} + e^{-D_c} + 2)^2 A^2 F^6} \frac{1}{z^2} \propto z^{-2} \quad (30)$$

Figure 8 shows the influence of the valence of co-ions on CCC, measured by the function  $S_3$  defined in eq 23, when the valence of counterions  $b$  is fixed. This figure reveals that for a fixed  $\psi_s$ ,  $S_3$  increases with  $a$ ; that is, the higher the valence of co-ions, the more important its influence on CCC. Also, for a fixed  $a$ ,  $S_3$  increases with the increase in  $\psi_s$ ; that is, the higher the surface potential, the more significant the influence of the valence of co-ions on CCC. For the present case, if  $\psi_s = 0.35$  and  $b = 5$ , the relative percentage deviation of CCC for  $a \neq 5$  from that for  $a = 5$  is about 4.9, 10.3, 16.0, and 22.2% for  $a$  equals 4, 3, 2, and 1, respectively. In general, because it is not

uncommon for  $\psi_s$  to exceed 0.5, the effect of co-ions on CCC can be too significant to be ignored.

### 3. Conclusion

Explicit expressions for the electrical interaction between two identical, planar parallel surfaces in a general electrolyte solution are derived based on a combination of the Langmuir approximation and the Debye–Huckel approximation. These include the electrical potential, the osmotic pressure, and the electrical energy. The results of numerical simulation reveal that the higher the surface potential the more accurate these expressions are. We show that, for the case of symmetric electrolytes, the Schultz–Hardy rule for the critical coagulation concentration of counterions is invalid, in general, and for the case of asymmetric electrolytes, the influence of the valence of co-ions on the critical coagulation concentration can be appreciable, especially when the surface potential is high.

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