The Stability Ratio for a Dispersion of Particles Covered by an Ion-Penetrable Charged Membrane

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The electrostatic interaction between two particles covered by an ion-penetrable charged membrane suspended in an arbitrary electrolyte solution is estimated. A perturbation method is employed to solve the governing nonlinear Poisson–Boltzmann equation. The approximate analytical expression derived for potential distribution yields a sufficiently accurate estimate. Both the stability ratio and the critical coagulation concentration of the counterions of the system under consideration are derived. The results of a numerical simulation reveal that the stability ratio decreases with an increase in the size of a particle and increases with the total amount of fixed charges in the membrane phase. For a constant total amount of fixed charges and particle size, the stability ratio increases with a decrease in the thickness of the membrane. We show that monodispersed particles are more stable than polydispersed particles.

Key Words: stability ratio, spherical particles; critical coagulation concentration, counterions; Poisson–Boltzmann equation, nonlinear; membrane, ion-penetrable, charged; electrical potential distribution, approximate, analytical.

I. INTRODUCTION

One of the key characteristics of a dispersed colloidal suspension is its stability ratio, defined as (rate of fast coagulation)/(rate of slow coagulation). The numerator denotes the rate of coagulation in the absence of an interaction energy barrier, and the denominator is that in the presence of an interaction energy barrier. Here, the interaction energy includes the electrostatic repulsive energy and the van der Waals attractive energy (1). The estimation of the former requires knowledge about the electrostatic potential distribution between two charged surfaces, which is governed by the Poisson–Boltzmann equation (PBE). This equation in its general form is nonlinear. Although there exists some fundamental inconsistency in the PBE which arises from the origin of the corresponding Poisson equation, the deviation from the exact value is tolerable for conditions often encountered in practice (2). The solution to a general PBE is nontrivial, except for limited cases. The degree of difficulty depends largely on the geometry of a charged surface, the types of electrolyte in the liquid phase, and the boundary conditions on the surface. In practice, either drastic assumptions are made and a simplified PBE is solved, or it is solved numerically.

Previous efforts on the estimation of the stability ratio of a dispersed system were mainly based on rigid surfaces (e.g., 3–5). Although this model is appropriate for most of the inorganic colloids, it can be unrealistic for some of the dispersed entities in practice. These include biocolloids and particles covered by an artificial membrane (6–11). A typical example of the former is human erythrocytes, the peripheral zone of which contains a glycoprotein layer about 15 nm thick. This zone possesses some ionogenic groups and forms the outer boundary of the lipid layer (12, 13). An example of the latter is dispersed entities in polymer-induced flocculation. Here, an entity comprises a rigid core and a layer of adsorbed polymer molecules, which often bear fixed charges. In an analysis of the interaction between an ion-penetrable particle and a rigid particle, Terui et al. (14) derived expressions for the interaction potential and the electrostatic interaction force between particles. The analysis was extended to various combinations of two types of particles, and expressions for critical coagulation concentration of counterions were derived (15). These analyses (14, 15) were based on a low level of surface potential, symmetric electrolyte, and uniformly distributed fixed charges in the surface layer of a particle.

In a recent study the electrostatic interactions between spherical particles coated with an ion-penetrable charged membrane immersed in an electrolyte solution at a low electrostatic potential were analyzed (16). The result obtained was adopted to estimate both the stability ratio and the critical coagulation concentration of counterions. If the potential is low, the governing PBE can be approximated by a linear expression, which is readily solvable. In the present study, the linear model of (16) is extended to a general case in which both the level of potential and the type of electrolyte are arbitrary.

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Key Words: stability ratio, spherical particles; critical coagulation concentration, counterions; Poisson–Boltzmann equation, nonlinear; membrane, ion-penetrable, charged; electrical potential distribution, approximate, analytical.
II. MODELING

By referring to Fig. 1, we consider a spherical particle composed of a rigid core and an ion-penetrable, charged membrane immersed in an \( a:b \) electrolyte solution. Denote the dimensionless sizes of the rigid core and the membrane as \( X_0 \) and \( d \), respectively. Here, \( X_0 = \kappa r_0 \), where \( r_0 \) and \( \kappa \) are the size of the rigid core and the reciprocal Debye length, respectively. Without loss of generality, we assume that the fixed charges in the membrane are negative and distributed uniformly.

The electrical potential distribution in spherical geometry is described by the PBE

\[
\frac{d^2 \psi}{dX^2} + \frac{2}{X} \frac{d \psi}{dX} = \frac{g + iN}{a + b}, \quad i = 0, 1, \tag{1}
\]

where \( \psi = \phi/k_B T, \ g = [\exp(b\psi) - \exp(-a\psi)], \ X = \kappa r, \ k^2 = e^2 a (a + b) n_0^u / \epsilon_0 k_B T, \) and \( N = ZN_A N_0 / an_0^u. \) In these expressions, \( \phi \) denotes the electrical potential; \( e \) is the elementary charge; \( N_0 \) and \( Z \) are, respectively, the density and the valence of the charged groups in the membrane \(-ZeN_A N_0 \) is the density of fixed charges); \( N_A \) represents the Avogadro number; \( \epsilon_0 \) and \( \epsilon_r \) are the relative permittivities of the solution and the vacuum, respectively; \( n_0^u \) is the number concentration of cations in the bulk liquid phase; \( k_B \) and \( T \) are, respectively, the Boltzmann constant and the absolute temperature; \( i \) represents a region index \((i = 0 \) denotes the double-layer region, \( i = 1 \) the membrane phase); and \( r \) is the distance measured from the center of a particle. The boundary conditions associated with [1] are assumed to be

\[
\psi \to 0 \quad \text{and} \quad (d\psi/dX) \to 0 \quad \text{as} \quad X \to \infty \quad \tag{1a}
\]

\[
\psi \big|_{x=(X_0+d)^-} = \psi \big|_{x=(X_0+d)^+} = \psi_d \quad \tag{1b}
\]

\[
(d\psi/dX) \big|_{x=(X_0+d)^-} = (d\psi/dX) \big|_{x=(X_0+d)^+} \quad \tag{1c}
\]

\[
\psi \to \psi_c \quad \text{and} \quad (d\psi/dX) \to 0 \quad \text{as} \quad X \to X_0. \tag{1d}
\]

In these expressions, \( \psi_c \) and \( \psi_d \) are, respectively, the dimensionless electrical potential at the outer boundary of the rigid core of a particle and that at the membrane-liquid interface. Suppose that \( \psi \) can be expanded in the perturbation series

\[
\psi = \sum_{i=0}^{\infty} \frac{h_i}{X^i} \approx h_0 + \left( \frac{h_1}{X} + \frac{h_2}{X^2} \right). \tag{2}
\]

Substituting [2] into [1] with \( i = 0 \) and solving the resultant expression give the electrical potential distribution for the double-layer region (Appendix A),

\[
h_0 = \left( \frac{2}{a} \right) \ln \left\{ \frac{1 + [\tanh(a\psi_d/4)]}{1 - [\tanh(a\psi_d/4)]} \times \exp[-k_3(X - X_0 - d)] \right\} \tag{3}
\]

\[
h_1 = \left( \frac{1}{ak_3} \right) \sinh \left( \frac{ah_0}{2} \right) \left[ \tanh^2 \left( \frac{a\psi_d}{4} \right) - \tanh^2 \left( \frac{ah_0}{4} \right) - 2 \ln \left( \frac{\tanh(a\psi_d/4)}{\tanh(ah_0/4)} \right) \right] \tag{4}
\]

\[
h_2 = X(h_0) \frac{a \sinh(ah_0/2)}{8k_3} \left[ u \int_0^{h_0} h_3 \sinh(ah_0/2) \frac{dh_0}{X(h_0)} + \int_{h_0}^{\psi_0} u h_3 \sinh(ah_0/2) \frac{dh_0}{X(h_0)} \right], \tag{5}
\]

where \( k_3, u, \) and \( X(h_0) \) are defined in Appendix A.

If the membrane is sufficiently thick, the dimensionless Donnan potential \( \psi_{D0n} \) and \( \psi_d \) are related by (Appendix A)
\[
\left(\frac{2}{a+b}\right)^{1/2} \left\{ \frac{1}{b} \left[ \exp(b\psi_d) - 1 \right] + \frac{1}{a} \left[ \exp(-a\psi_d) - 1 \right] \right\}^{1/2} \\
- \frac{1}{X_0 + d} \left\{ \frac{4}{a} \tanh \left( \frac{a\psi_d}{4} \right) \right\} + \frac{4}{(X_0 + d)^2} \\
\times \left[ \frac{\tanh^2(a\psi_d/4) - 2 \ln[\cosh(a\psi_d/4)]}{k_5\sinh(a\psi_d/2)} \right] \\
= \left(\frac{2}{a+b}\right)^{1/2} \left\{ \frac{1}{b} \left[ \exp(b\psi_d) - \exp(b\psi_{\text{Don}}) \right] \right\}^{1/2} \\
+ \frac{1}{a} \left[ \exp(-a\psi_d) - \exp(-a\psi_{\text{Don}}) \right] \\
+ N(\psi_d - \psi_{\text{Don}}) \right\}^{1/2} \\
- \frac{4}{X_0 + d} \\
\times \left\{ \frac{1}{a} \tanh \left( \frac{a(\psi_d - \psi_{\text{Don}})}{4} \right) \right\} + \frac{4}{(X_0 + d)^2} \\
\times \left\{ \frac{\tanh^2[a(\psi_d - \psi_{\text{Don}})/4] - 2 \ln[\cosh[a(\psi_d - \psi_{\text{Don}})/4]]}{k_5\sinh[a(\psi_d - \psi_{\text{Don}})/2]} \right\}. \quad [6]
\]

The electrostatic interaction energy between two particles \(I_{el}(R)\) can be estimated by substituting [2]–[5] into [B16] (see Appendix B) to yield

\[
I_{el}(R) = \frac{16\pi}{ak^2} \sum_{n=1}^{2} \{ P_{n,n'} \sum_{i=1}^{3} \{ A_i \exp[k_i(2t - 1) \}
\times (X_{0,n} + d_n - R) \}], \quad n \neq n', \quad [7]
\]

where the subscripts \(n\) and \(n'\) denote particles \(n\) and \(n'\), respectively, \(d_n\) is the dimensionless thickness of the membrane phase of particle \(n\), and \(R\) is the dimensionless center-to-center distance between two particles (Fig. 2). The values of \(A_1, A_2, A_3, A_4, \) and \(P_{n,n'}\) are defined by

\[
A_1 = (3 + \alpha_1)(X_{0,n} + d_n)\cosh[k_3(X_{0,n} + d_n)] \\
- (3 + \alpha_1)X_{0,n}\cosh[k_3X_{0,n}] - \left( \frac{3}{k_3} + \alpha_1 \right) \\
\times (X_{0,n} + d_n)\sinh[k_3(X_{0,n} + d_n)] \\
+ \left( \frac{3}{k_3} + \alpha_1 \right) \times X_{0,n}\sinh(k_3X_{0,n}) \quad [7a]
\]

\[
A_2 = - \left[ \frac{4}{27k_3} + \frac{2}{9a_4} (\alpha_2^2 - 2\alpha_2\alpha_3) \right] \tanh^2 \left( \frac{a\psi_{\text{Don}}}{4} \right) \\
\times \{ 3k_3(X_{0,n} + d_n)\cosh[3k_3(X_{0,n} + d_n)] \\
- 3k_3X_{0,n}\cosh(3k_3X_{0,n}) \\
- \sinh[3k_3(X_{0,n} + d_n)] + \sinh(3k_3X_{0,n}) \} \quad [7b]
\]

\[
A_3 = \left[ \frac{3}{32a_4} (2\alpha_2^2 - 2\alpha_2) \right] \tanh^4 \left( \frac{a\psi_{\text{Don}}}{4} \right) \\
\times \{ 5k_3(X_{0,n} + d_n)\cosh[5k_3(X_{0,n} + d_n)] \\
- 5k_3X_{0,n}\cosh(5k_3X_{0,n}) \\
- \sinh[5k_3(X_{0,n} + d_n)] + \sinh(5k_3X_{0,n}) \} \quad [7c]
\]

\[
\alpha_1 = \left( \frac{1}{2} \right) \tanh^2 \left( \frac{a\psi_{\text{Don}}}{4} \right) + k_3(X_{0,n} + d_n) - 3 + \frac{\alpha_5}{\alpha_4} \quad [7d]
\]

\[
\alpha_2 = \tanh^2 \left( \frac{a\psi_{\text{Don}}}{4} \right) + \ln \left[ \frac{1}{2} \left[ 1 + \cosh \left( \frac{a\psi_{\text{Don}}}{2} \right) \right] \right] \quad [7e]
\]

\[
\alpha_3 = \frac{\coth(a\psi_{\text{Don}}/2) - 1}{2} \times \ln \left[ \frac{1}{2} \left[ 1 + \cosh \left( \frac{a\psi_{\text{Don}}}{2} \right) \right] \right] \quad [7f]
\]

\[
\alpha_4 = 600\frac{\chi}{\lambda}(X_{0,n} + d_n) \quad [7g]
\]
\[ \alpha_s = \alpha_0 \alpha_1 \sinh^2 \left( \frac{\alpha \psi_{0, n}}{4} \right) \]
\[ + \left[ 2\alpha_0^2 \alpha_1 + \frac{1}{2} \alpha_1^2 + \alpha_2 \right] \times \sinh^4 \left( \frac{\alpha \psi_{0, n}}{4} \right) \]
\[ P_{n,n'} = L_n \left[ n \tanh \left( \frac{\alpha \psi_{0, n}}{4} \right) \right] \times \exp \left[ k_3 (X_{0,n} + d_n - X_{0,n'} - d_{n'}) \right], \quad [7i] \]

where the energy density \( L_n \) is defined in Appendix B.

The electrostatic interaction force between two particles, \( f_{el}(R) \), can be calculated by

\[ f_{el}(R) = -\kappa \frac{dI_{el}}{dR} \]
\[ = \frac{\kappa I_{el}}{R} + \frac{16\pi}{ak_3^2 \kappa^2 R} \sum_{n=1}^{2} \left\{ P_{n,n'} \sum_{r=1}^{3} \{ A_r (2t - 1) \times \exp \left[ k_3 (2t - 1) (X_{0,n} + d_n - R) \right] \} \right\} \]
\[ = \frac{\kappa (k_3 R + 1)}{R} I_{el} + \frac{32\pi}{ak_3^2 \kappa^2 R} \sum_{n=1}^{2} \left\{ P_{n,n'} \sum_{r=1}^{3} \{ A_r (t - 1) \times \exp \left[ k_3 (t - 1) (X_{0,n} + d_n - R) \right] \} \right\}, \quad n \neq n'. \quad [8] \]

Note that if \( R \to \infty \), both \( I_{el} \) and \( f_{el} \) vanish, as expected.

The stability ratio can be regarded as the reciprocal collision efficiency which leads to coagulation. It can be measured by the ratio of particle fluxes without and with an energy barrier \( \lambda \). Therefore the kinetic property can be described by the interaction energy between two particles. According to Fuchs (18) and Overbeek (19), the stability ratio of the system under consideration, \( W \), can be estimated by

\[ W = \int_1^\infty \left( \frac{1}{R_i} \right) \exp \left( \frac{I_{el}}{k_BT} \right) dR_i, \quad [9] \]

where \( R_i = R/D_2 \), and \( I_{el} \) is the total interaction energy between two particles. The latter includes the electrostatic repulsion energy and the van der Waals attraction energy. On the basis of [7], [8], [C2e], [C3], and [C5a], it can be shown that the value of \( R \) at which \( I_{el} \) has its primary maximum, \( R_{max} \), is

\[ R_{max} \approx [\beta_6 + (\beta_7 + \beta_8) 1/2]^{1/2} \]
\[ + [\beta_6 - (\beta_7 + \beta_8) 1/2]^{1/2} - \frac{\beta_3}{3}, \quad [10] \]

where

\[ \beta_3 = \beta_2 - 2D_2 - \frac{A_{132}}{12D_3 \beta_1} \quad [10a] \]
\[ \beta_6 = \frac{(9\beta_3 \beta_4 - 27\beta_5 - 2\beta_3)}{54} \quad [10b] \]
\[ \beta_7 = \frac{(3\beta_3 - \beta_5)}{9} \quad [10c] \]
\[ \beta_8 = D_2 \beta_2 \quad [10d] \]
\[ \beta_4 = D_2 (D_2 - 2\beta_2) \quad [10e] \]
\[ \beta_2 = \frac{16\pi}{ak_3^2 \kappa^2 \beta_1} \sum_{n=1}^{2} \left\{ \sum_{r=1}^{3} \{ A_r \times \exp \left[ k_3 (2t - 1) \right] \times (X_{0,n} + d_n) \} \right\}, \quad n \neq n'. \quad [10f] \]
\[ \beta_1 = \frac{16\pi}{ak_3^2 \kappa} \sum_{n=1}^{2} \left\{ \sum_{r=1}^{3} \{ A_r (2t - 1) \times \exp \left[ k_3 (2t - 1) (X_{0,n} + d_n) \right] \} \right\}, \quad n \neq n'. \quad [10g] \]

In these expressions, \( A_{132} \) denotes the Hamaker constant, and \( D_2 \) and \( D_3 \) are defined in [C2c] and [C2b], respectively (see Appendix C). Substituting [7], [C1], [C2e], [C5a], and [10] into [C4] yields

\[ W \equiv \exp \left\{ \left[ I_{el}(R_{max}) - \frac{A_{132}D_3}{12(R_{max} - D_2)} \right] / k_BT \right\}. \quad [11] \]

The critical coagulation concentration (CCC) can be determined by

\[ I_{el}(R_c) - \frac{A_{132}D_3}{12(R_c - D_2)} = 0 \quad [12] \]
\[ f_{el}(R_c) + \frac{kA_{132}D_3}{12(R_c - D_2)^2} = 0, \quad [13] \]

where \( R_c \) is the dimensionless center-to-center distance between two particles at the CCC. Solving these equations yields
RESULTS

Phase. This figure suggests that particle at various densities of fixed charges in the membrane of the cation and anion, respectively. The ratio method is satisfactory.

This table, the performance of the present perturbation estimated by solving \([1]\) numerically. As can be seen from the exact values, potential distribution estimated by \([2]\) from the exact values, \(Q\) is defined by \(100\% \frac{\left[ \sum_{j=1}^{n+1} \left( \psi_j - \psi \right) \right]}{n!}, \) where \(a\) and \(b\) are the valences of the cation and anion, respectively.

\[
R_c \equiv \gamma + \left[ \gamma (\gamma + D_2) \right]^{1/2}, \tag{14}
\]

where

\[
\gamma = D_2 - \frac{A_{132} D_1}{12\beta_1}. \tag{14a}
\]

The CCC for counterions can be estimated by substituting [14] into either [12] or [13].

III. DISCUSSION

Table 1 shows the average percentage deviation in the potential distribution estimated by [2] from the exact values, estimated by solving [1] numerically. As can be seen from this table, the performance of the present perturbation method is satisfactory.

Figure 3 illustrates the simulated variation in the stability ratio \(W\) as a function of the linear size of the rigid core of a particle at various densities of fixed charges in the membrane phase. This figure suggests that \(W\) decreases with increases in \(X_0\). This is consistent with the classic DLVO theory together with the Fuchs model (1), and the result for the case of low potential (16). For a fixed \(X_0\), the greater the density of fixed charges \(N_0\), the greater the \(W\). This is expected, since the greater the \(N_0\), the greater the electrostatic repulsive force between two particles.

Figure 4 shows the effect of membrane thickness on the stability ratio at a constant total amount of fixed charges and particle size. As can be seen from Fig. 4, the stability ratio increases with decreases in the membrane thickness. This is because at a constant total amount of fixed charges, the smaller the thickness of membrane, the more concentrated the fixed charges, and the greater the electrostatic repulsion energy. Figure 4 also suggests that the stability ratio increases with the total amount of fixed charges, as expected.

**TABLE 1**

<table>
<thead>
<tr>
<th>(N_0 (M))</th>
<th>(10^{-3})</th>
<th>(5 \times 10^{-3})</th>
<th>(10^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.77</td>
<td>4.84</td>
<td>5.61</td>
</tr>
<tr>
<td>2</td>
<td>3.13</td>
<td>4.27</td>
<td>4.85</td>
</tr>
<tr>
<td>4</td>
<td>2.32</td>
<td>3.50</td>
<td>4.39</td>
</tr>
<tr>
<td>6</td>
<td>2.17</td>
<td>3.28</td>
<td>3.96</td>
</tr>
</tbody>
</table>

\(Q\) for the case \(Z = 1, d = X_0/4, \) ionic strength \(= 10^{-3} M, \) \(\epsilon_\text{r} = 78, \) and \(T = 298.15 K, \) \(\) equally spaced points in the range \([X_0 + d, X_0 + d + 3]\) are chosen, and the potentials at these points are evaluated. \(Q\) is defined by \(100\% [\sum_{j=1}^{n+1} \left( \psi_j - \psi \right) / (\psi^* - \psi)] / n!\), where \(a\) and \(b\) are the valences of the cation and anion, respectively.

\[
\psi - \psi^* \approx \gamma + \gamma (\gamma + D_2)^{1/2},
\]

where

\[
\gamma = D_2 - \frac{A_{132} D_1}{12\beta_1}.
\]

Figure 5 illustrates the variation in the stability ratio as a function of the size ratio of two interacting particles, \((X_{0,1} + d_1)/(X_{0,2} + d_2),\) at a fixed mean size of two particles, \((X_{0,1} + d_1)/(X_{0,2} + d_2))^{1/2}.\) This figure shows that the smaller the size ratio \((\) the greater the difference in the sizes of two
particles), the smaller the stability ratio. In other words, monodispersed particles are more stable than polydispersed particles. This can be deduced from Eqs. [C2]–[C2d]. The smaller the size ratio, the smaller the value of \( I \). For the case \( \delta \) of the van der Waals attraction energy, and the smaller the stability ratio.

Under certain conditions, the results of the present study can be either simplified or reduced to those reported in the literature. We consider five special cases.

3.1. Two Identical Particles

If the interacting particles are identical, then \( X_{0,1} = X_{0,2} = X_0, d_1 = d_2 = d, \psi_{d,1} = \psi_{d,2} = \psi_d, P_{d,1} = P_{d,2} = P(X_0, d, \psi_d), A_t = A_t(X_0, d, \psi_d), t = 1, 2, 3, \) and [7] gives

\[
I_{d}(H) = \frac{32\pi}{\kappa^3 k^2 x^2} P(X_0, d, \psi_d) \\
\times \sum_{t=1}^{3} \left\{ A_t(X_0, d, \psi_d) \right\} \\
\times \exp[k_3(2t - 1)(X_0 + d - R)]. \tag{15}
\]

3.2. A Spherical Particle and a Flat Surface

If particle 1 is spherical and particle 2 becomes a flat surface, [7] reduces to

\[
I_{d}(H) = \frac{24\pi}{\kappa^3 k^2} L_1 \left[ \tanh \left( \frac{a \psi_d}{4} \right) \right] \left[ 1 - \exp(-k_3 d_2) \right] \\
\times \exp[k_3(X_{0,1} + d_1 - D_3 H)], \tag{16}
\]

where \( H \) is the dimensionless surface-to-surface distance between the particle and the surface.

3.3. Two Parallel Flat Surfaces

In the case of two parallel flat surfaces, it can be shown that

\[
I_{d}(H) = \frac{8\pi}{3k^4} \sum_{n=1}^{3} \left\{ L_n \left[ \tanh \left( \frac{a \psi_d}{4} \right) \right] \\
	imes \left\{ 3 \left[ 1 - \exp(-k_3 d_2) \right] \exp(-k_3 D_3 H) \right\} \right\}. \tag{17}
\]

3.4. Rigid Particles and 1:1 Electrolytes

For 1:1 electrolytes and rigid particles, [3]–[5] reduce to those derived by Dukhin et al. (20).

3.5. Single Particle

Suppose that the radius of one of the two interacting particles approaches zero, i.e., \( X_{0,1} + d_1 \rightarrow 0, n = 1 \) or 2. Then \( \delta \rightarrow 0 \) and \( \psi_d \) does not exist. In this case, [7] implies that \( I_{d}(R) \rightarrow 0 \) and \( I_{d,aw} \rightarrow 0 \) by [B2].

**APPENDIX A**

Substituting [2] into [1] and collecting terms of the same order in \( X \), we obtain the potential distribution in the double-layer region,

\[
\frac{d^2 h_0}{dx^2} = \frac{g_0 + iN}{a + b} \tag{A1}
\]

\[
\frac{d^2 h_1}{dx^2} = \frac{-2}{X} \frac{dh_0}{dx} \tag{A2}
\]

\[
\frac{d^2 h_2}{dx^2} = \frac{-2}{X} \frac{dh_2}{dx} + \frac{2}{X^2} h_2 \tag{A3}
\]
where $g_0 = g(h_0)$. The boundary conditions associated with these equations are

$$h_i$ and $(dh_i/dX) \to 0$ as $X \to \infty$, \hspace{1em} v = 0, 1, 2, \ldots \hspace{1em} [A4]$$

$$h_0 \to \psi_0, \hspace{1em} h_e \to 0$ as $X \to (X_0 + d)$, \hspace{1em} v = 1, 2, \ldots \hspace{1em} [A5]$$


$$k_3 = \begin{cases} [k_1 - (k - 2)k_2]/k_1, & \text{if } k \leq 4 \\ [2k_1 + (k - 2)k_2]/k_1, & \text{if } k > 4 \end{cases} \hspace{1em} [A6]$$

where $k_1 = 2/[k^{1/2}[(k/2)^{2/(k-2)} - 1]]$, $k_2 = 2/k^{1/2}$, and $k = 2 + 2b/a$ (17). Similarly, solving [A2] and [A3] subject to [A4] and [A5] gives [4] and [5] with

$$u = \frac{\cosh(\alpha \psi_a/2)}{\sinh^2(\alpha \psi_a/2)} - \frac{\cosh(\alpha \psi_e/2)}{\sinh^2(\alpha \psi_e/2)}$$

$$- \ln \left[ \frac{\tanh(\alpha \psi_e/4)}{\tanh(\alpha \psi_a/4)} \right] \hspace{1em} [A7]$$

$$X(h_0) = \frac{1}{2k_3} \ln \left[ \frac{(\cosh(\alpha \psi_a/2) + 1)(\cosh(\alpha \psi_a/2) - 1)}{(\cosh(\alpha \psi_a/2) - 1)(\cosh(\alpha \psi_a/2) + 1)} \right]$$

$$+ X_0 + d \hspace{1em} [A8]$$


Differentiating [2] with respect to $X$ and applying [A5], we obtain

$$\left( \frac{d\psi}{dX} \right)_{X_0+d} = \sum_{i=0}^{\infty} \left[ \left( \frac{dh_i}{dX} \right)_{X_0+d} \right] [X^v]_{X_0+d}$$

$$= \frac{1}{2} \left( \frac{dh_0}{dX} \right)_{X_0+d} + \frac{X_0 + d}{X_0 + d} \left( \frac{dh_1}{dX} \right)_{X_0+d}$$

$$+ \frac{1}{(X_0 + d)^2} \left( \frac{dh_2}{dX} \right)_{X_0+d} \hspace{1em} [A9]$$

Integrating [A1]–[A3] with $i = 0$, subject to [A4] and employing [A5], we have

$$\left( \frac{dh_0}{dX} \right)_{(X_0+d)^+} = \frac{2}{a + b} \left\{ \frac{1}{b} \left[ \exp(b\psi_a) - 1 \right] \right\}^{1/2}$$

$$\left( \frac{dh_1}{dX} \right)_{(X_0+d)^+} = - \frac{4}{a} \tanh \left( \frac{a \psi_a - \psi_e}{4} \right) \hspace{1em} [A11]$$

$$\left( \frac{dh_2}{dX} \right)_{(X_0+d)^+} = - \frac{4 \tanh^2(\alpha \psi_a/4)}{k_3 \sinh(\alpha \psi_a/2)} \hspace{1em} [A12]$$

Equation [1d] can be rewritten in terms of $h_e$ as

$$\left( \frac{dh_0}{dX} \right) \to 0, \left( \frac{dh_1}{dX} \right) \to 0, \hspace{1em} h_0 \to \psi_e, \hspace{1em} \text{as } X \to X_0, \hspace{1em} v = 1, 2, \ldots \hspace{1em} [A13]$$

Integrating [A1]–[A3] with $i = 1$ subject to [A13] and applying [A5], we obtain

$$\left( \frac{dh_1}{dX} \right)_{(X_0+d)^+} = \left\{ \frac{2}{a + b} \right\}^{1/2} \left\{ \frac{1}{b} \left[ \exp(b\psi_a) - \exp(b\psi_e) \right] \right\}$$

$$+ \frac{1}{a} \left[ \exp(-a\psi_a) - \exp(-a\psi_e) \right]$$

$$+ N(\psi_a - \psi_e)^{1/2} \hspace{1em} [A14]$$

$$\left( \frac{dh_2}{dX} \right)_{(X_0+d)^+} = - \frac{4 \tanh^2(\alpha \psi_a - \psi_e/4)}{k_3 \sinh(\alpha \psi_a/2)} \hspace{1em} [A15]$$

If the membrane phase is sufficiently thick, there is no net charge as $X \to X_0$, and $\psi$ approaches $\psi_{Don}$, the dimensionless Donnan potential. In this case, letting $i = 1$ in [1] yields

$$g(\psi_{Don}) + N = 0 \hspace{1em} [A17]$$

$\psi_{Don}$ can be estimated by solving this equation. On the basis of [1b], [A9], [A10]–[A12], and [A14]–[A16], [6] can be recovered.

**APPENDIX B**

Let $E$ be the strength of electric field. We have

$$\nabla \cdot (\phi E) = \phi \nabla \cdot E + E \cdot \nabla \phi \hspace{1em} [B1]$$

where $\nabla$ is the differential operator. Since $E = -\nabla \phi$, the PBE can be written as
\[ \nabla \cdot \mathbf{E} = - \nabla \cdot \nabla \phi = - \left[ \sum_{i=1}^{M} \frac{e_i e}{\epsilon_0} \exp(-z_i \psi) - i \rho_{fix} \right]. \]  

where \( n_i^0 \) and \( z_i \) denote, respectively, the number concentration of the \( i \)th ion species in the bulk liquid phase and its valence, \( M \) is the number of ion species, and \( \rho_{fix} \) represents the density of fixed charges evaluated by

\[ \rho_{fix} = Z e N_A N_0. \]  

For the present system, the density of internal energy, \( u_{el} \), is identical to the electric field energy, i.e.,

\[ u_{el} = \left( \frac{\epsilon_0 e_i}{2} \right) \mathbf{E} \cdot \mathbf{E}. \]  

For dilute solutions the density of entropy, \( s_{el} \), is

\[ s_{el} = - \left( \frac{k_B}{2} \right) \sum_{i=1}^{M} n_i \ln \left( \frac{n_i}{n_i^0} \right), \]  

where \( n_i \) is the number concentration of species \( i \). According to the Gibbs–Helmholtz equation, we have

\[ f_{el} = u_{el} - T s_{el}, \]  

where \( f_{el} \) is the density of electrical free energy. Substituting [B3] and [B4] into this expression, employing the Boltzmann distribution law for ions, and using [B1] and [B2], we have

\[ f_{el} = - \left( \frac{\epsilon_0 e_i}{2} \right) \nabla \cdot (\phi \mathbf{E}) - \frac{i \rho_{fix} \phi}{2}. \]  

Denote the volume of the membrane phase and that of the liquid phase as \( V_1 \) and \( V_2 \), respectively, and let \( V = V_1 + V_2 \). The total free energy of the system, \( F_{el}^1 \), is

\[ F_{el}^1 = \int f_{el} dV. \]  


\[ F_{el}^1 = - \left( \frac{\epsilon_0 e_i}{2} \right) \int_V \nabla \cdot (\phi \mathbf{E}) dV - \frac{1}{2} \int_{V_1} \rho_{fix} \phi dV_1, \]  

where \( dV \) and \( dV_1 \) represent volume elements. Applying the Gauss divergence theorem yields

\[ F_{el}^1 = - \left( \frac{\epsilon_0 e_i}{2} \right) \int_V \phi \mathbf{E} \cdot dA - \frac{1}{2} \int_{V_1} \rho_{fix} \phi dV_1, \]  

where \( \mathbf{n} \) denotes the unit outer normal vector of surface element \( dA \). Since both \( \mathbf{E} \) and \( \phi \) are continuous, and \( d\mathbf{E} \) is bounded, the surface integral in [B9] vanishes, and we have

\[ F_{el}^1 = - \frac{1}{2} \int_{V_1} \rho_{fix} \phi dV_1. \]  

For a rigid surface \( \mathbf{E} \) is not continuous at the solid–liquid interface. Thus, if \( \mathbf{n} \) is parallel to \( \mathbf{E} \), letting \( V_1 = 0 \) in [B9] leads to

\[ F_{el}^1 = \frac{\sigma \phi_0 A}{2}, \]  

where \( \phi_0 \) denotes the surface potential, and \( A \) is the area of the surface.

The electrostatic energy of a system containing \( K \) particles, \( I_{el}(R) \), can be calculated by

\[ I_{el}(R) = F_{el}^1(R) - F_{el}^1(\infty), \]  

where \( R \) is the set of distances \( R_{n,n'} \), \( n, n' = 1, 2, \ldots, K, n \neq n' \). Suppose that the double layer around a particle is thin. Employing [B10] and [B2a], we obtain

\[ F_{el}^1(R) = \sum_{n=1}^{K} \int_{V_{1,n}} L_0 \phi dV_{1,n}, \]  

\[ F_{el}^1(\infty) = \sum_{n=1}^{K} \int_{V_{1,n}} L_0 \phi_{n,n=1} dV_{1,n}, \]  

\[ \psi = \begin{cases} \psi_{n,j=1} + \sum_{n'} \psi_{n',j=0}, & X_{0,n} < X_n < (X_{0,n} + d_n), \\ \psi_{n,j=0} + \sum_{n'} \psi_{n',j=0}, & (X_{0,n} + d_n) < X_n < X_{n'}, & n, n' = 1, 2, \ldots, K, \\ (X_{0,n'} + d_{n'}) < X_n < X_{n'}, & n, n' = 1, 2, \ldots, K, \\ n' \neq n. & \end{cases} \]  

where \( L_0 = -e_{an} N_A N_0, n k_B T/2, dV_{1,n} = 2\pi X_0^2 \sin \theta dX_X d\theta_X / \kappa^1 \), and \( \theta_X \) is the angle between line segments defined by \( R_{n,n'} \) and \( X_n \). \( F_{el}^1(\infty) \) is the electrostatic free energy for the case any pair of two particles are infinitely apart. Since \( \psi_{n,j=1} \) is a function of \( X_n \), \( F_{el}^1(\infty) \) is independent of \( R \). For a system containing two particles, [B14] reduces to
By referring to Fig. 2, we have [9]. As an approximation, the total interaction energy is

\[ I = \sum_{i=1}^{2} \left( \psi_{1,i=0} + \psi_{2,i=0} \right) \]

(\(X_{0,1} < X_i < (X_{0,1} + d_i)\))

which includes the van der Waals energy \(I_{vdw}\) and the electrostatic energy \(I_{el}\), i.e.,

\[ I = I_{vdw} + I_{el}. \] \[C1\]

We assume that (1)

\[ I_{vdw} = -\frac{A_{132}}{12H} \left[ \frac{1}{1 + D_4H} + \frac{H}{1 + H + D_4H^2} \right] \]

\[ + 2H \ln \left( \frac{H + D_4H^2}{1 + H + D_4H^2} \right), \] \[C2\]

where

\[ D_4 = \frac{D_1}{2D_2} \] \[C2a\]

\[ D_3 = \frac{D_1}{D_2} \] \[C2b\]

\[ D_2 = X_{0,1} + d_1 + X_{0,2} + d_2 \] \[C2c\]

\[ D_1 = 2(X_{0,1} + d_1)(X_{0,2} + d_2) \] \[C2d\]

\[ H = \frac{(R - D_2)}{D_3}, \] \[C2e\]

where \(A_{132}\) denotes the Hamaker constant and \(D_3\) represents the dimensionless reduced radius. The interaction force between particles, \(f_i\), can be evaluated by

\[ f_i = -\left( \frac{\kappa}{D_i} \right) \left( \frac{dI}{dH} \right) \]

\[ = f_{i \alpha} - \left( \frac{\kappa}{D_i} \right) \left( \frac{dI_{vdw}}{dH} \right). \] \[C3\]

The stability ratio of the system, \(W\), can be estimated by [9]. As an approximation, the total interaction energy is replaced with its primary maximum, \(I_{t,max}\), and the integration procedure suggested by Overbeek (19) leads to

\[ W \approx \exp \left( \frac{I_{t,max}}{k_B T} \right). \] \[C4\]

As \(H \to 0\), [C2] reduces to

\[ I_{vdw} = -\frac{A_{132}}{12H} \left[ 1 + H(1 - D_4) + 2H \ln H + \cdots \right] \]

\[ \approx -\frac{A_{132}}{12H}. \] \[C5a\]

If the size of one of the two interacting particles approaches infinity, i.e., \(X_{0,n} \to \infty\), \(n = 1\) or \(2\), [C2] reduces to

\[ I_{vdw} = -\frac{A_{132}}{6} \left[ \frac{1 + 2H}{2H(1 + H)} + \ln \left( \frac{H}{1 + H} \right) \right]. \] \[C5b\]

If the sizes of two interacting particles approach infinity, the problem reduces to the interaction of two parallel planar surfaces. In this case, [C2] gives

\[ I_{vdw} = -A_{132}A_p[12\pi(D_4H)^2], \] \[C5c\]

where \(A_p\) is the average surface area of two particles, and \(D_4H\) represents the dimensionless surface-to-surface distance between two particles.

At the critical coagulation contraction,

\[ I = 0 \quad \text{and} \quad f_i = 0. \]

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