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NOTE

Effect of Particle Size on Critical Coagulation Concentration

The variation of the electrical interaction energy between two spherical particles as a function of particle size is investigated. We show that, for a fixed electrolyte concentration, the larger the particle, the greater the primary maximum of the total interaction energy; i.e., larger particles are less probable to coagulate than smaller particles. On the other hand, the smaller the particle, the higher the critical coagulation concentration (CCC). If the radius of a particle is larger than 1 μm, CCC is independent of particle size. For larger particles, DLVO theory will overestimate CCC, and the reverse is true for smaller particles. Also, the higher the surface potential, the more serious the deviation. If the radius of a particle is sufficiently large, DLVO theory predicts that, $\kappa h_m = 1$, κ and h_m being, respectively, the reciprocal Debye length and the closest surface-to-surface distance between two particles. On the other hand, we show that $\kappa h_m \cong 8/7$. The deviation of the DLVO theory arises from applying the superposition principle in the estimation of the electrical potential.

Key Words: **critical coagulation concentration**; **DLVO theory**; **particles, spherical.**

The critical coagulation concentration (CCC) is one of the most significant characteristics of a colloidal dispersion. It is defined as the minimum concentration of counterions to induce instability of a colloidal dispersion. Experimental observations reveal that CCC is related to the valence of counterion, Z. The well-known empirical result, the Schulze–Hardy rule, states that it is inversely proportional to Z^{-6} (1). This rule was elaborated through consideration of the electrostatic interactions between two charged particles by the DLVO theory (2). Two types of interactions are considered in the theoretical derivations: the van der Waals attraction interaction and the electrical repulsion interaction. Although criticisms have been raised concerning its rigorousness and completeness, the DLVO theory is one of the most successful achievements in colloidal and interface science and is widely adopted to interpret experimental data.

The derivation of the DLVO theory was based on the assumptions that the thickness of the electrical double layer surrounding a charged particle in an electrolyte solution is much smaller than the linear size of the particle, and the electrical interaction energy can be estimated through the superposition principle. The former implies that CCC is independent of the size of a particle, and the latter assumes that two interacting particles can be considered independently. However, experimental observations reveal that these assumptions are not necessarily adequate. The coagulation of polystyrene latex performed by Ottewill and Shaw (3), for example, showed that CCC varies with particle size. Apparently, the assumptions made in the DLVO theory deserve further discussion. This is conducted in the present note.

The analysis is begun by a brief summary of the DLVO theory. We assume that the total interaction energy between two spherical particles, V, consists of the van der Waals interaction energy, V_{VDW}, and the electrical interaction energy, V_{DL}. Other non-DLVO interactions, such as the solvent–structural interaction, are neglected. We have

$$V = V_{\mathrm{VDW}} + V_{\mathrm{DL}}. \qquad [1]$$

If the thickness of the electrical double layer surrounding a particle is much smaller than the radius of a particle, and the ratio (surface-to-surface distance/radius) is very small, an analytic form for the van der Waals interaction energy is available, and the electrical interaction energy can be estimated by applying the Deryaguin's approximation. For $Z:Z$ symmetric electrolyte solution, it can be shown that

$$V = -\frac{A_{132}a}{12h} + \frac{a \cdot B'}{2}\exp(-\kappa h), \qquad [2]$$

where A_{132} is the Hamaker constant, a is the particle radius, h is the closest surface-to-surface distance between two particles, $(1/\kappa)$ is the Debye length defined as $\kappa^2 = 8\pi e^2 Z^2 C_\infty/\epsilon k_B T$, and B' is defined by

$$B' = 16\epsilon\left(\frac{k_B T}{Ze}\right)^2 \tanh^2\left(\frac{y_s}{4}\right) \qquad [2a]$$

with $y_s = Ze\psi_S/k_B T$. Here, $(1/\kappa)$ is a measure of the thickness of the electrical double layer surrounding a particle, y_s is the dimensionless electrical surface potential, ψ_s and ϵ are the electrical surface potential and the dielectric constant, respectively, k_B and T are the Boltzmann constant and the absolute temperature, respectively, and e and C_∞ are the elementary charge and the bulk concentration of electrolyte, respectively. If C_∞ reaches CCC, both the total interaction energy and its derivative with respect to h vanish; i.e.,

$$V_{h=h_m} = 0 \qquad [3a]$$

$$\left(\frac{dV}{dh}\right)_{h=h_m} = 0. \qquad [3b]$$

Substituting [2] into [3] and [3b] leads to

$$\kappa h_m = 1 \qquad [4a]$$

$$\kappa = \frac{6B'}{A_{132}\exp(1)}. \qquad [4b]$$

[4b] implies that

$$C_\infty = \frac{1152\epsilon^3 k_B^5 T^5 \tanh^4(y_s/4)}{\pi \exp^2(1) e^6 A_{132}^2 Z^6}. \qquad [4c]$$

This expression suggests that CCC is independent of particle size.

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Let us consider next that the thickness of an electrical double layer is not necessarily much smaller than the radius of a particle. The van der Waals potential energy for two identical spheres is (4)

$$V_{\mathrm{VDW}} = -\frac{A_{132}}{6}\left\{\frac{2a^2}{R^2-4a^2} + \frac{2a^2}{R^2} + \ln\left[\frac{R^2-4a^2}{R^2}\right]\right\}, \quad [5]$$

where R denotes the center-to-center distance between two particles. Sader *et al.* (5) derived the following approximate expression for the electrical interaction energy between two spheres for the case of large κa and moderate to high surface potentials

$$\begin{aligned} V_{\mathrm{DL}} &= \epsilon\left(\frac{k_{\mathrm{B}}T}{Ze}\right)^2 y^2(h)\,\frac{a^2}{R}\ln(1+\exp(-\kappa h)) \\ &= B\,\frac{a^2}{R}\ln(1+\exp(-\kappa h)), \quad [6] \end{aligned}$$

where

$$B = \epsilon\left(\frac{k_{\mathrm{B}}T}{Ze}\right)^2 y^2(h) \quad [6a]$$

$$y(h) = 4\exp\left(\frac{\kappa h}{2}\right)\tanh^{-1}\left[\exp\left(\frac{-\kappa h}{2}\right)\tanh\left(\frac{y_{\mathrm{s}}}{4}\right)\right]. \quad [6b]$$

[6] is valid for all κh. If κh is sufficiently large, [6b] becomes

$$y^2(h) \cong 16\tanh^2(y_{\mathrm{s}}/4). \quad [7]$$

In this case, B reduces to B'. Note that if an electrical double layer is thin, [3a], [3b], [5], and [6] yield

$$\kappa h_{\mathrm{m}}\exp(-\kappa h_{\mathrm{m}}) - [1+\exp(-\kappa h_{\mathrm{m}})]\ln[1+\exp(-\kappa h_{\mathrm{m}})] = 0. \quad [8]$$

Solving this expression for κh_{m} gives

$$\kappa h_{\mathrm{m}} \cong 8/7. \quad [9]$$

A comparison between [4a] and [9] shows that the deviation of DLVO theory is on the order of 15%, even the electrical double layer is thin. This deviation is due to the application of the superposition principle in the evaluation of the electrical interaction energy.

The value of κh_{m} can be calculated by considering [1], [3a], [3b], [5], and [6] simultaneously. This leads to two nonlinear algebraic equations, which need to be solved numerically. We suggest using the following approximate procedure. Substituting [5] and [6] into [1], and assuming that two particles are sufficiently close, and the double layer around a particle is thin, that is, $a > h > 1/\kappa$, we obtain

$$V = B\,\frac{a^2}{R}\exp(-\kappa h) - \frac{A_{132}a}{12h}\left(1 + \frac{3}{4}\frac{h}{a} + 2\,\frac{h}{a}\ln\left(\frac{h}{a}\right)\right). \quad [10]$$

Substituting this expression into [3a] and [3b] gives

$$B\,\frac{a^2}{R}\exp(-\kappa h_{\mathrm{m}}) - \frac{A_{132}a}{12h_{\mathrm{m}}} - \frac{A_{132}}{16} - \frac{A_{132}}{6}\ln\left(\frac{h_{\mathrm{m}}}{a}\right) = 0 \quad [11a]$$

$$-B\,\frac{a^2}{R}\exp(-\kappa h_{\mathrm{m}})\left(\frac{1}{R}+\kappa\right) + \frac{A_{132}a}{12h_{\mathrm{m}}^2} - \frac{A_{132}}{6h_{\mathrm{m}}} = 0. \quad [11b]$$

In the derivation of these expressions, we assume that $y(h)$ is a weak function of h (5), and, therefore, κh_{m} is approximated by (8/7) in [6b], and [6a] becomes

$$B = \epsilon\left(\frac{k_{\mathrm{B}}T}{Ze}\right)^2\left\{4\exp\left(\frac{8}{14}\right)\tanh^{-1}\left[\exp\left(\frac{-8}{14}\right)\tanh\left(\frac{y_{\mathrm{s}}}{4}\right)\right]\right\}^2. \quad [11c]$$

Solving [11a] and [11b] simultaneously yields

$$\kappa h_{\mathrm{m}} = \frac{8 - 12(h_{\mathrm{m}}/a) - 8(h_{\mathrm{m}}/a)^2}{(4 + 3(h_{\mathrm{m}}/a) + 8(h_{\mathrm{m}}/a)\ln(h_{\mathrm{m}}/a))(2 + (h_{\mathrm{m}}/a))} - \frac{(h_{\mathrm{m}}/a)}{2 + (h_{\mathrm{m}}/a)}. \quad [12]$$

As a first approximation, we let $\ln(h_{\mathrm{m}}/a) = \lambda$. Substituting this expression into [12] and expanding the resultant expression in terms of (h_{m}/a), we obtain

$$\kappa h_{\mathrm{m}} \cong 1 - \left(\frac{13}{4} + 2\lambda\right)\frac{h_{\mathrm{m}}}{a}. \quad [13]$$

Note that if $h_{\mathrm{m}} \ll a$, this reduces to that predicted by the DLVO theory. As shown in [9], a factor of (8/7) is needed to correct the deviation that arises from adopting the superposition principle. Multiplying both sides of [13] by (8/7), we have

$$\kappa \cong \frac{8}{7h_{\mathrm{m}}} - \frac{26 + 16\lambda}{7a}. \quad [14]$$

Expanding the term $\exp(-\kappa h_{\mathrm{m}})$ in [11a] at $\kappa h_{\mathrm{m}} = 8/7$ gives

$$\frac{1}{h_{\mathrm{m}}} = Q'\,\frac{1 + [(13/4) + 2\lambda](h_{\mathrm{m}}/a)}{1 + (h_{\mathrm{m}}/2a)} - \frac{3 + 8\lambda}{4a}. \quad [15]$$

Expanding [15] into its Taylor series yields

$$\frac{1}{h_{\mathrm{m}}} \cong Q'\left[1 + \left(\frac{11}{4} + 2\lambda\right)\frac{h_{\mathrm{m}}}{a}\right] - \frac{(3 + 8\lambda)}{4a}, \quad [16]$$

where

$$Q' = \frac{6B}{A_{132}}\exp\left(-\frac{8}{7}\right). \quad [16a]$$

Solving [14] and [16] simultaneously, we obtain

$$\kappa = \frac{4}{7}Q' - \frac{29 + 24\lambda}{7a} + \sqrt{\frac{16}{49}Q'^2 + \frac{152 + 64\lambda}{49a}Q' + \frac{9 + 48\lambda + 64\lambda^2}{49a^2}}. \quad [17]$$

Note that, if a is large, this expression leads to $8Q'/7$. A comparison with the result for planar surfaces suggests that Q' should be replaced by Q defined

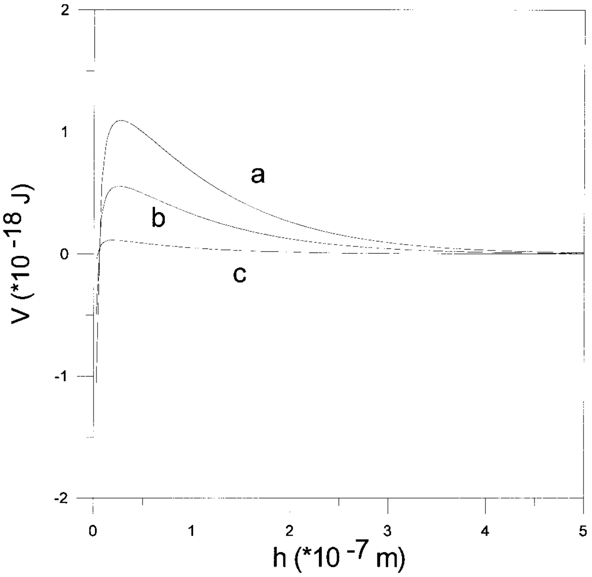

FIG. 1. Variation in the total interaction energy V as a function of the closest surface-to-surface distance between two particles h for three different particle sizes at a fixed electrolyte concentration for the case $T = 298$ K, $y_s = 1$, $A_{132} = 10^{-19}$ J, and $\kappa = 0.1/\mu$m. (a) $a = 1$ μm, (b) $a = 0.5$ μm, (c) $a = 0.1$ μm.

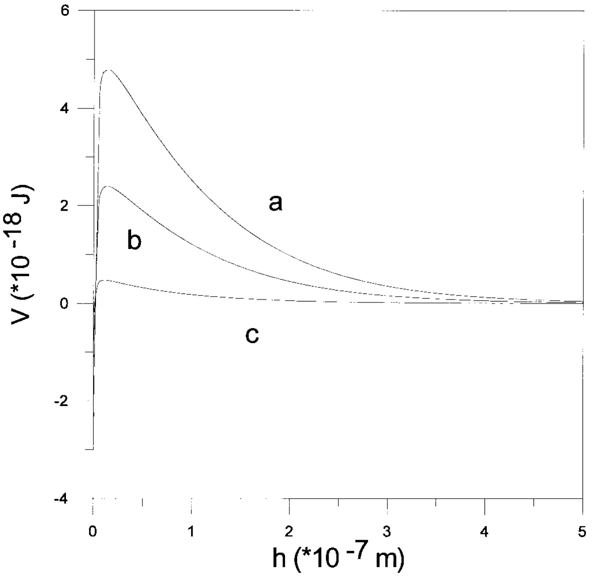

FIG. 2. Variation in the total interaction energy V as a function of the closest surface-to-surface distance between two particles h for the case of Fig. 1, except that $y_s = 2$.

$$Q = \frac{6B}{A_{132}} \ln\left[1 + \exp\left(-\frac{8}{7}\right)\right]. \qquad [18]$$

Neglecting the last term in the square root sign on the right-hand side of [17] for large a, and expanding the last term on the right-hand side of [17] into its Taylor series in terms of $(1/a)$, we obtain

$$\kappa \cong \frac{8}{7} Q - \frac{80 + 128\lambda}{56a}. \qquad [19]$$

The simulated variations in the total interaction energy, V, as a function of the closest surface-to-surface distance between two particles, h, at three different particle sizes are shown in Figs. 1 and 2. These results are obtained by solving [5] and [6] numerically. Figures 1 and 2 reveal that, for a fixed electrolyte concentration (constant κ), V varies with particle size. Note that the larger the particle, the greater the energy barrier. This means that, if the concentration of electrolyte is fixed, larger particles are less probable to coagulate than smaller ones. A comparison between Figs. 1 and 2 shows that the higher the surface potential, the greater the repulsion energy between two particles, as expected.

The variation in the inverse Debye length, κ, as a function of particle radius, a, at CCC is presented in Fig. 3. The calculations are based on the approximate expression [19]. Calculations based on the exact numerical solution of [1], [5], and [6], and those predicted by the DLVO theory are also shown in this figure. The value of the parameter λ in [19] is estimated through a least squares procedure. As can be seen from Fig. 3, the performance of the approximate expression, [19], is satisfactory. Since $\kappa \propto C_\infty^{1/2}$, Fig. 3 indicates that the smaller the particle, the higher the CCC. This agrees with the experimental observations (3). Note that if a is larger than 1 μm, κ, and, therefore, CCC, approaches to a constant value. In other words, if the size of a particle is sufficiently large, CCC is independent of particle size. As can be seen from Fig. 3, if a is large, DLVO theory will overestimate CCC, and underestimate CCC if a is small. Also, the higher the surface potential, the more appreciable the deviation.

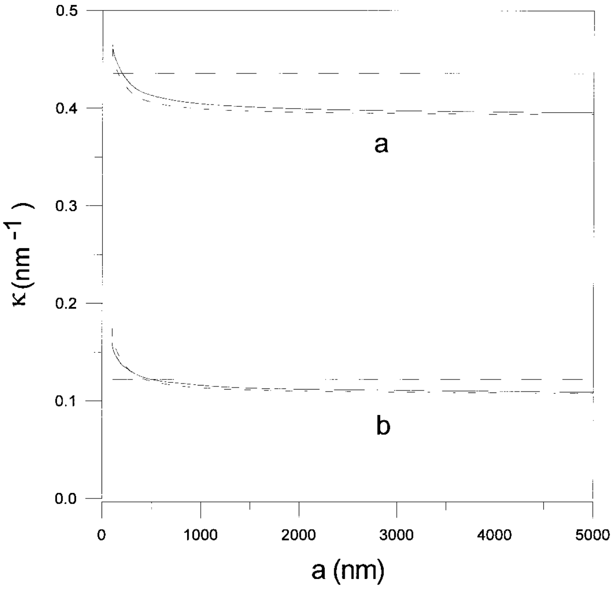

FIG. 3. Variation in the inverse Debye length κ at CCC as a function of particle radius a at two levels of surface potential for the case $T = 298$ K, and $A_{132} = 10^{-19}$ J. (a) $y_s = 2$, (b) $y_s = 1$, (solid line) exact numerical result based on [5] and [6], (---) approximate solution based on [15] with $\lambda = -3.6$, (– –) DLVO theory.

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