

ARTICLES

Critical Coagulation Concentration of a Colloidal Suspension at High Particle Concentrations

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The critical coagulation concentration (CCC) of a spherical colloidal suspension is estimated. Here, the concentration of particles is high so that the classic DLVO theory, which is based on the interactions between two particles, can be inapplicable. A statistical mechanics approach based on the Ornstein-Zernike model and Percus-Yevick relation is adopted to estimate the total interaction energy. We show that, in general, the presence of the particles surrounding two interacting particles has the effect of reducing the total interaction energy between them and, therefore, of increasing the probability of coagulation. The effect of particle concentration on CCC is more significant under the following conditions: large Hamaker constant, high particle concentration, and low surface potential of the particle. The result predicted by the DLVO theory can be recovered as the limiting case of the present analysis in which the concentration of particles is low and the surface potential is high.

Introduction

The critical coagulation concentration (CCC) is one of the most important characteristics of a colloidal dispersion. The experimental observations reveal that the variation of CCC as a function of the valence of counterion follows roughly the inverse sixth power law, the well known Schulze–Hardy rule.¹ This was elaborated analytically by the DLVO theory, which considered two major forces between colloidal particles: the van der Waals attractive force and the electrical repulsive force.² The theoretical analysis was based on the interactions between two particles under the following conditions: (a) planar particle, (b) symmetric electrolyte, (c) high surface potential, and (d) two interacting particles separated far enough. Several attempts were made to consider a more general model which is closer to the conditions in practice. These include, for example, the model without assumptions c and d,³ spherical particles in asymmetric electrolytes,⁴ and spherical particles covered by an ion-penetrable membrane.⁵

A thorough review of literature reveals that previous discussions about CCC were mainly focused on the interactions between two isolated particles; the influence of the surrounding particles is neglected. This is equivalent to assuming that a solution is thin so that the probability of finding more than two particles in a finite domain is negligible. In general, if the concentration of particles is appreciable, a many-body problem needs to be considered. Typical example includes a dispersed system which is close to the point of phase transition. A concentrated wastewater is another example in practice. In these

cases the derivation of the governing equations involves a complicated formulation of the relations between particles. Apparently, solving these equations is nontrivial, even numerically. In the present study, an attempt is made through employing a statistical mechanics approach in which a many-body problem can be simulated through a two-body problem by considering the averaged behavior between paired bodies.

Analysis

Let us consider a suspension of spherical colloidal particles. The potential energy of mean force W can be evaluated by⁶

$$W = -k_B T \ln[g(r)] \quad (1)$$

where g is the radial distribution function, k_B the Boltzmann constant, and T the absolute temperature. The radial distribution function is related to the total correlation function $h(r)$ by

$$h(r) = g(r) - 1 \quad (2)$$

The total correlation function can be estimated by resorting to the Ornstein–Zernike model.⁷ It states that the total correlation function between particles i and j , $h(r_{ij})$, r_{ij} being the distance between these particles, consists of a direct correlation function, $c(r_{ij})$, and an indirect correlation function. The latter arises from an indirect influence of particle i on particle j through particle k , $k \neq j$. In mathematical expression, we have

$$h(\vec{r}_{ij}) = c(r_{ij}) + \rho \int c(\vec{r}_{ik}) h(\vec{r}_{jk}) d\vec{r}_k \quad (3)$$

where ρ is the number density of particles, and \vec{r}_k the position vector of particle k . The relation between $h(r)$ and $c(r)$ needs to be specified before the Ornstein–Zernike equation, (3), can

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be solved. Several approximate relations have been proposed in the literature.⁸ Here, the Percus–Yevick relation⁹ expressed below is adopted:

$$c(r) = [1 + h(r)] \left[1 - \exp\left(\frac{U(r)}{k_B T}\right) \right] \quad (4)$$

where $U(r)$ is the interaction potential energy between two particles. According to the DLVO theory, $U(r)$ comprises the van der Waals interaction energy U_{VDW} and the electrical interaction energy U_{DL} .² We have

$$U(r) = U_{VDW}(r) + U_{DL}(r) \quad (5)$$

For the case of spherical particles, U_{VDW} can be calculated by¹

$$U_{VDW} = -\frac{A_{132}}{12} \left[\frac{1}{x^2 - 1} + \frac{1}{x^2} + 2 \ln\left(1 - \frac{1}{x^2}\right) \right] \quad (6)$$

where A_{132} denotes the Hamaker constant, and $x = R/D$, R and D being, respectively, the center-to-center distance between two particles and the diameter of particle. For the case the ratio (particle radius/Debye length) is sufficiently large, the following approximate expression for the electrical interaction energy between two particles is available:¹⁰

$$U_{DL} = B \frac{Y^2}{x} \ln[1 + \exp[-\kappa D(x - 1)]] \quad (7)$$

where

$$B = \frac{\epsilon D}{4} \left(\frac{k_B T}{Ze} \right)^2 \quad (7a)$$

$$Y = 4 \exp\left[\frac{\kappa D(x - 1)}{2}\right] \tanh^{-1} \left[\exp\left[-\frac{\kappa D(x - 1)}{2}\right] \tanh\left(\frac{y_s}{4}\right) \right] \quad (7b)$$

In these expressions,

$$y_s = Ze\psi_s/k_B T \quad (7c)$$

$$\kappa^2 = 8\pi e^2 I / \epsilon k_B T \quad (7d)$$

Here, ψ_s is the electrical potential on particle surface, ϵ and Z the dielectric constant and the valence of electrolyte, respectively, κ the reciprocal Debye length, and e and I the elementary charge and the ionic strength, respectively. Equation 3 needs to be solved with the relations (4)–(7). This can be nontrivial, even numerically. Several possible approaches have been proposed for the resolution of (3).^{11,12} It was shown that the performances of these approaches are essentially the same, unless the critical region is approached at which the computing time necessary to obtain a satisfactory result may be quite long.¹³ Here, we propose a new iterative procedure. If we denote $\hat{h}(s)$ and $\hat{c}(s)$ as the Fourier transforms of $h(r)$ and $c(r)$, respectively, then (3) leads to

$$\hat{h}(s) = \frac{\hat{c}(s)}{1 - \rho \hat{c}(s)} \quad (8)$$

At the critical coagulation concentration (CCC), both the interaction energy and its derivative with respect to the position variable vanish, i.e.,

$$W_{x=x_m} = 0 \quad (9a)$$

$$\left(\frac{dW}{dx} \right)_{x=x_m} = 0 \quad (9b)$$

where x_m denotes the scaled center-to-center distance between two particles. Equations 4 and 8 are solved through an iterative procedure. Since $g(r) \rightarrow 1$ as $r \rightarrow \infty$, and it fluctuates around unity, (2) and (4) suggest that an initial guess for $c(r)$ and $c_0(r)$, is

$$c_0(r) = \exp\left[\frac{U(r)}{k_B T}\right] f(r) \quad (10)$$

where

$$f(r) = \exp\left[-\frac{U(r)}{k_B T}\right] - 1 \quad (10a)$$

Taking the Fourier transform on $c_0(r)$, we obtain $\hat{c}_0(s)$. Substituting $\hat{c}_0(s)$ into (8) gives the first-order approximation of $\hat{h}(s)$ and $\hat{h}_1(s)$, which can be transformed to $h_1(r)$. Substituting $h_1(r)$ into (4) yields the first-order approximation of $c(r)$ and $c_1(r)$, which can be transformed to $\hat{c}_1(s)$. Substituting $\hat{c}_1(s)$ into (8) leads to the second-order approximation of $\hat{h}(s)$. This is continued until $h(r)$ converges. Equations 9a and 9b are then employed to calculate CCC.

An approximate analytical expression for $c(r)$ can also be obtained. Substituting (4) into (3) yields

$$g(r_{12}) = \exp\left[-\frac{U(r_{12})}{k_B T}\right] [1 + \rho \int f(r_{13}) f(r_{23}) dr_3 + \dots] \quad (11)$$

Since the product κa (=particle radius/Debye length) is usually very small at CCC, the pair potential energy in (10a) can be approximated by the hard sphere model. Substituting (11) into (1) yields

$$W \cong U - k_B T \ln(g_{HS}) \quad (12)$$

where g_{HS} represents the radial distribution function of a hard sphere. The range of the position variable we are interested is $1 \leq x < 2$, and x close to 1. In this case, g_{HS} can be expanded by^{14,15}

$$g_{HS} = \frac{1}{x} \sum_{i=0}^2 a_i \exp[t_i(x - 1)] \quad (13)$$

where

$$a_i = \frac{\left(1 + \frac{\Phi}{2}\right) t_i^2 + (1 + 2\Phi) t_i}{3(1 - \Phi)^2 t_i^2 + 12\Phi(1 - \Phi) t_i + 18\Phi^2}, \quad i = 0, 1, 2 \quad (13)$$

Φ being the volume fraction of particles. Here, t_i ($i = 0, 1$, and 2) are the roots of the equation

$$(1 - \Phi)^2 t^3 + 6\Phi(1 - \Phi) t^2 + 18\Phi^2 t - 12\Phi(1 + 2\Phi) = 0 \quad (14)$$

We suggest using the following expression to minimize the round-off error at low particle concentrations:

$$t_i = \frac{-2\Phi + (2\Phi f)^{1/3} (y_+ j^i + y_- j^{-i})}{1 - \Phi} \quad (15)$$

where

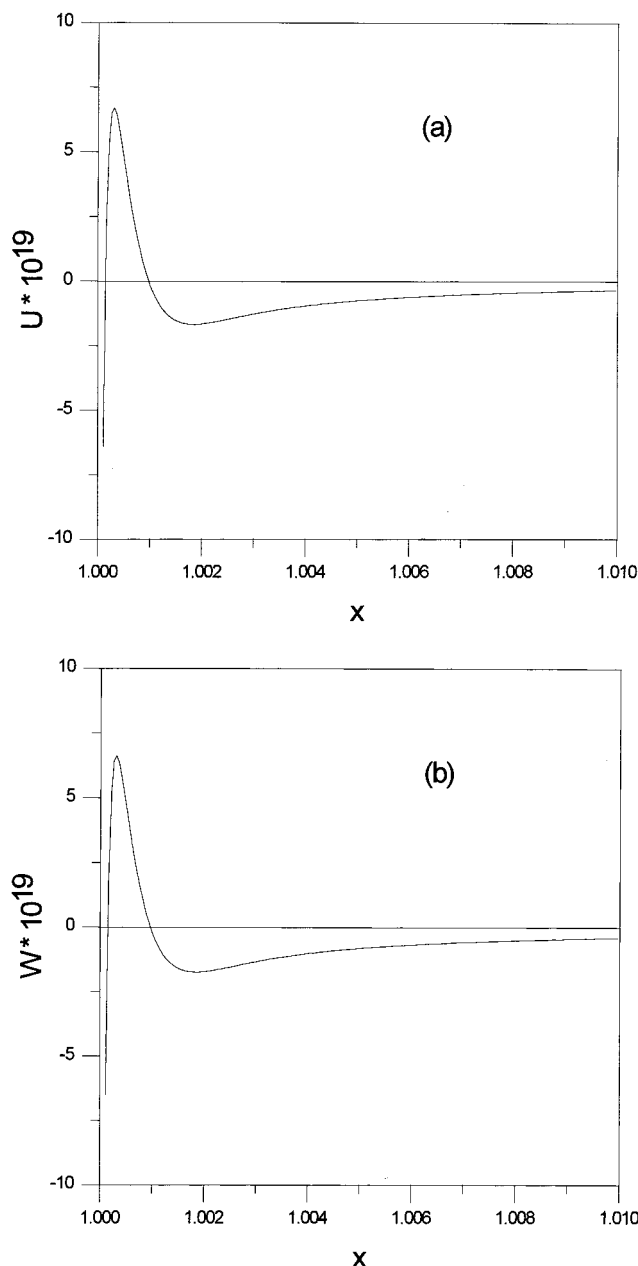


Figure 1. Variation in the interaction energy as a function of x . (a): pair potential energy U . (b): the total energy of mean force W . Parameters used are $y_s = 2$, $T = 298$ K, $D = 10^{-6}$ m, $\Phi = 0.5$, $A_{132} = 10^{-20}$ J, $\kappa = 2.5 \times 10^9$ m $^{-1}$, and $Z = 1$.

$$y_{\pm} = \left[1 \pm \sqrt{1 + 2 \left(\frac{\Phi^2}{\nu} \right)^{2/3}} \right]^{1/3} \quad (15a)$$

$$j = \exp\left(\frac{2}{3}\pi\sqrt{-1}\right) \quad (15b)$$

$$\nu = 3 + 3\Phi - \Phi^2 \quad (15c)$$

Substituting (12) into (9a) and (9b) yields two nonlinear equations, which need to be solved numerically.

Discussion

It should be pointed out that the Percus–Yevick closure is mainly for a hard sphere system.¹⁶ In our case, since the electrical double layer is thin, a charged particle can be approximated reasonably by a hard sphere. In other words, other closures that are suitable for charged entities such as the

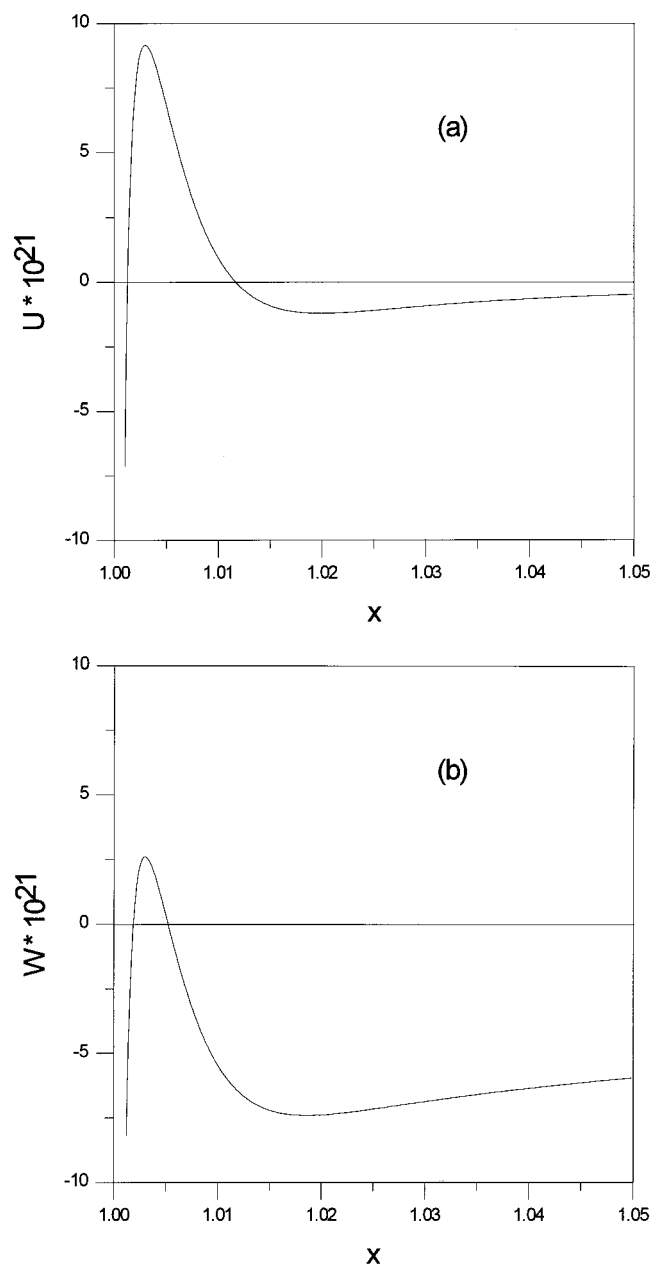


Figure 2. Variation in the interaction energy as a function of x . (a): pair potential energy U . (b): the total energy of mean force W . Parameters used are $y_s = 0.2$, $T = 298$ K, $D = 10^{-6}$ m, $\Phi = 0.5$, $A_{132} = 10^{-21}$ J, $\kappa = 2.5 \times 10^8$ m $^{-1}$, and $Z = 1$.

hypernetted chain approximation and the mean spherical approximation may not be adequate for the present problem. Note that the effect on the interaction between two particles due to the presence of the charges on a particle has been taken into account by the U_{DL} expressed in (7). To calculate U_{DL} , the Poisson–Boltzmann equation governing the electrical potential distribution needs to be solved.

According to (12), the presence of the particles surrounding two interacting particles has the effect of reducing the total interaction energy between them. This leads to a higher probability of coagulation between the interacting particles. Table 1 shows the variation in the ratio $[CCC/CCC(\Phi \rightarrow 0)]$ as a function of the volume fraction of colloidal particles Φ and of the scaled surface potential of particles y_s for the case $A_{132} = 10^{-19}$ J. That for the case of a lower A_{132} is illustrated in Table 2. Here, $CCC(\Phi \rightarrow 0)$ denotes the CCC at which the volume fraction of particles is infinitely small, i.e., the CCC

TABLE 1: Variation of CCC/CCC($\Phi \rightarrow 0$) as a Function of the Volume Fraction of Particles Φ and of the Scaled Surface Potential y_s for the case $A_{132} = 10^{-19}$ J

Φ	y_s				
	0.2	0.5	1	2	4
0.1	0.9439	0.9900	0.9972	0.9994	0.9998
0.2	0.8955	0.9792	0.9944	0.9986	0.9996
0.3	0.8553	0.9678	0.9912	0.9978	0.9993
0.4	0.8334	0.9556	0.9876	0.9969	0.9990

TABLE 2: Variation of CCC/CCC($\Phi \rightarrow 0$) as a Function of the Volume Fraction of Particles Φ and of the Scaled Surface Potential y_s for the Case $A_{132} = 10^{-21}$ J

Φ	y_s				
	0.2	0.5	1	2	4
0.1	0.9376	0.9851	0.9972	0.9985	0.9998
0.2	0.8717	0.9772	0.9943	0.9978	0.9995
0.3	0.8032	0.9657	0.9910	0.9969	0.9993
0.4	0.7315	0.9516	0.9874	0.9960	0.9990

predicted by the DLVO theory. As can be seen from Tables 1 and 2, the effect of particle concentration on CCC is more significant for the case of low y_s , high Φ , and small A_{132} . These tables also show that, $[CCC/CCC(\Phi \rightarrow 0)] \rightarrow 1$ as $\Phi \rightarrow 0$ and $y_s \rightarrow \infty$. In other words, the result predicted by the DLVO theory can be recovered as the limiting case of the present analysis in which the concentration of particles is low and the surface potential is high.

Figure 1 shows the variation in the total interaction energy as a function of the scaled center-to-center distance between two particles x for the case $A_{132} = 10^{-20}$ J. Both the result based on the present analysis W and that on the classic DLVO theory U are illustrated. That for the case of a smaller Hamaker constant is illustrated in Figure 2. As can be seen from Figure 1, the distributions of the total interaction energy based on two different approaches are very close. In this case, the effect of particle concentration on CCC is inappreciable at the conditions assumed. The result of Kaldasch et al.¹⁷ provides some indirect evidence for this conclusion. For the case of low surface potential, high particle density, and small Hamaker constant,

the difference in the distribution of total interaction energy based on the present method and that on the classic DLVO theory can be significant, as suggested by Figure 2. This leads to an appreciable difference in CCC, as shown in Table 2.

In summary, the effect of particle concentration on the critical coagulation concentration of a spherical colloidal suspension is examined through a statistical mechanics approach. We show that the presence of the particles surrounding two interacting particles has the effect of reducing the total interaction energy between them. This has the effect of increasing the probability of coagulation between the interacting particles. The concentration of particles needs to be taken into account at the conditions of small Hamaker constant, high particle concentration, and low surface potential of the particle.

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