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ORIGINAL CONTRIBUTION

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Theoretical approaches of stability ratio on concentrated colloidal dispersed system

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Abstract In the theory dealt with in this article, it is assumed that colloidal particles are smooth rigid spheres, their collisions are instantaneous, the probability of multiple encounter is negligible, and the increase of the probability of collisions depends on the radial distribution function in local equilibrium. A simple formula is obtained for the stability ratio in highly concentrated colloid. Good correspondence between theoretical predictions and experiments is shown.

Key words Stability ratio – stability monodisperse latex – coagulation

Introduction

Since the beginning of this century, the properties of electrostatically stabilized dilute colloidal dispersions have been thoroughly examined both experimentally and theoretically. In dilute dispersions, the kinetic of coagulation was first treated by Smoluchowski [1], who reasoned that the rate of coagulation of particles equals the rate of their collision due to Brownian motion. In the absence of a repulsive energy barrier, the rate constant for the second-order (K_f) is given by

$$K_f = 8kT/3\eta, \tag{1}$$

where k is Boltzmann's constant, T is temperature, and η is viscosity of the continuous medium. The coagulation rate constant in the presence of an energy barrier (K_s) is

$$K_s = K_f/W, \tag{2}$$

where the stability ratio, W, is given by Fuch [2] as:

$$W = 2a\int_{2a}^{\infty} \exp[U(r)/kT]r^{-2}dr. \tag{3}$$

Here, $U(r)$ is the potential energy of interaction between two particles of equal radius a whose centers are separated by a distance r.

The stability ratio is used extensively in the literature to characterize the stability of lyophobic colloid. It is also required in studies of the evolution of the particle size distribution, which are based on various forms of the population balance equation. Due to the complicated form of the function $\exp[U(r)/kT]$, many researchers resort to rough approximations of various types to estimate W. Recently, Qun Wang [3] commented on these approximated expressions.

In recent years, concentrated colloidal dispersions, for example, monodisperse latices, have been recommended as a model dispersion for study of a number of fundamental phenomena in the field of colloid science. In some cases, the particles form an ordered array and under certain conditions they show phase separation into an ordered (particle-rich) phase and a disordered (particle-dilute) phase [4–6]. The coagulation has been observed in these system at particle volume fractions significantly lower than the values characteristic of close packing [7, 8]. Several attempts have been made to account theoretically for these order/disorder transitions. One approach is to assume that the particles interact via DLVO potential; the properties of the system are then evaluated by the Monte Carlo technique or by solving for the radial distribution function obtained from OZ equation with PY closure, or by the hard sphere perturbution model [9–11]. Another approach is based on the double-layer interaction between the particles and current theories of first-order phase transitions, Lindemann's law [12, 13]. Barnes et al. and Beunen et al. [14, 15] suggested that the latex particle in a aqueous system may be regarded as an affective particle volume whose size is determined by the thickness of an electrical double layer on its surface. They elucidated the importance of such factors as the absence of an electrolyte reservoir and the effect of surface charge regulation on the phase diagram. All the above attempts to explain the properties of concentrated dispersions have been based on the equilibrium thermodynamics or statistical thermodynamics. Because the coagulation is a time-dependent process, Bensley and Huter (BH) [16] present a first attempt to explain quantitatively the coagulation behavior of concentrated dispersion by examining coagulation in term of the rate of diffusion of particles from potential energy minima, and they suggested that the coagulation time represents the boundary between stable and unstable dispersions.

The objective of this work is to perform a critical quantitative study of the kinetics of coagulation of concentrated colloidal dispersions. By analogy with the dilute sol, the stability of concentrated system would be anticipated in the form of the stability ratio. In this work, the theory of collision of gas is applied to suspension of charge-stabilized monodisperse colloidal particles suspended in electrolyte solutions. The particles are assumed as smooth rigid spheres, collisions of which are instantaneous, and probability of multiple encounter is negligible and the increase of the probability of collisions only depends on the radial distribution function in local equilibrium. Pair interactions bear some analogy to the square well potential. Thus, a simple formula is obtained for the stability ratio in highly concentrated colloid. A comparison of calculated results with experimental data is made.

Theory

The stability ratio W is treated here as the ratio between the total number of collisions and the number of successful ones. The effect of hydrodynamic interaction is neglected, and the collisions between colloidal particles are treated as in the collisions between gas molecules. This work refers to the colloidal particles that are smooth rigid spheres. In this case the motions of particles affect each other only at collisions.

Consider collisions occurring between pairs of particles at rest in a uniform steady state. The number of collisions per unit volume and per unit time, with the velocities of the colliding particles lying in the range C_1, dC_1, and C_2, dC_2, is

$$f_1 f_2 g\, \sigma_{12}^2 \cos\theta \sin\theta\, d\theta\, d\varphi\, dC_1\, dC_2, \tag{4}$$

where σ_{12} is the mean diameter of particle 1 and particle 2, viz $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, m_1 and m_2 are their masses, f is the velocity distribution function, g is the relative particle velocity which makes an angle of θ with the line of centers $(0 \le \theta \le \pi/2)$, the plane through relative particle velocity before collision and relative particle velocity after collosion makes an angle φ with the initial plane $(0 \le \varphi \le 2\pi)$

The total number of collsions in the absence of any repulsive energy barrier is

$$N_{12} = n_1 n_{12}\, \sigma_{12}^2 (2\pi)^{1/2} (\mu/kT)^{3/2} \int_0^\infty \exp(-\mu g^2/2kT) g^3\, dg; \tag{5}$$

μ is the reduced mass, n_1 and n_2 are the number densities of the two particles.

$$N_{12} = 2n_1 n_2\, \sigma_{12}^2 (2\pi kT/\mu)^{1/2}. \tag{6}$$

If the particles have identical diameter, we get

$$N_{11} = 2n_1^2\, \sigma_1^2 (\pi kT/m_1)^{1/2}. \tag{7}$$

For rapid coagulation, the probability of multiple encounters is negligible, and it will be assumed that both sets

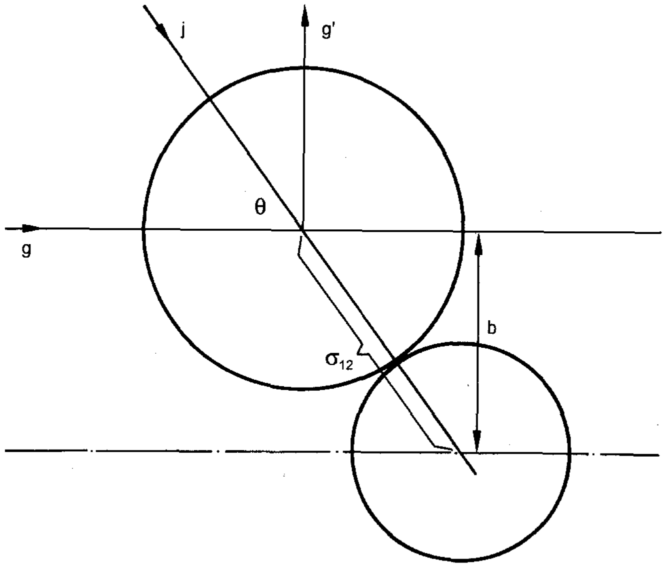


Fig. 1 Schematic diagram of the collision between two particles

of particles are distributed at random, and without any correlation between their velocities and positions; in other words, the assumption of particle chaos is valid. We have assumed the particles to be the rigid spheres; the advantage of this assumptions that collisions are instantaneous encounters in which more than two particles take part which are negligible in number and effect, compared to binary encounters. Even if the dispersions are concentrated, this assumption is still valid.

Coagulation in the presence of an energy barrier will be referred to as successful collisions. We assume that the potential energy profile function is similar to the square well potential

$$U(r) = \begin{cases} -\infty & r < \sigma \\ V_{\max} & r = \sigma \\ -E_{\min} & \sigma < r \leqslant \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases} \qquad (8)$$

$V_{\max}$ represents height of energy barrier of the particles, $-E_{\min}$ represents the secondary minimum of the potential energy profile function. Particles adhere if the sum of their relative kinetic energies is greater than the potential barrier $\Delta V_{\max} = V_{\max} + E_{\min}$. Particles are trapped at the secondary minimum if the sum of their relative kinetic energies is smaller than $-E_{\min}$. The interactions between the particles at $r = \sigma$ and $r = \lambda$ are not equal to zero, therefore, the collisions occur merely at $r = \sigma$ and $r = \lambda\,\sigma$. Thus, the assumption of particle chaos ought to be corrected to fit needs of concentrated dispersions. The assumption of particle chaos is concerned with the particle velocity chaos, and not the particle position chaos.

From Eq. (4), we found the probability per unit time and per unit volume. This expression requires correction when the system is concentrated. First, since the center of the first particle is at the position vector $\boldsymbol{r}$, that of the second one is at $(\boldsymbol{r} - \sigma\boldsymbol{j})$, where $\boldsymbol{j}$ is the unit vector of the direction of the line of centers, so that f_2 in eq. (4) must be replaced by $f_2(\boldsymbol{r} - \sigma\boldsymbol{j})$. Secondly, in a concentrated dispersion the volume of the particles is comparable to the volume occupied by the system. Its effect is to reduce the volume in which the center of any one particle can lie, and so to increase the probability of collision. In other words, Eq. (4) should be multiplied by a factor which is a function of position, not a function of velocity. This factor is the radial distribution function in local equilibrium, $g(r)$, which represents ratio of local density to average density; $g(r)$ must be evaluated at the point $(\boldsymbol{r} - \sigma\boldsymbol{j}/2)$ at which the spheres actually collide. According to the given model of potential Eq. (8), collision points are located at $r = \sigma$ and $r = \lambda\,\sigma$. Therefore, we need the value of radial distribution function at $r = \sigma$ and $r = \lambda\,\sigma$; such values are denoted by $g(\sigma^+)$ and $g(\lambda\,\sigma^+)$.

Now, Eq (4) reads at the point of $r = \sigma$

$$g(\sigma^+) f_1 f_2(\boldsymbol{r} - \sigma\boldsymbol{j})\, g^2 \sigma^2 \cos\theta \sin\theta\, d\theta\, d\varphi\, dC_1 dC_2 \qquad (9)$$

at $r = \lambda\,\sigma$,

$$g(\lambda\,\sigma^+) f_1 f_2(\boldsymbol{r} - \sigma\boldsymbol{j}) g^2 (\lambda\,\sigma)^2 \cos\theta \sin\theta\, d\,\theta\, d\,\varphi\, dC_1 dC_2. \qquad (10)$$

here, f_1 and f_2 are the velocity distribution function. When the system is located in a uniform steady state, the distribution of particle velocities is given by Maxwell–Boltzmann distribution. This is the case in Eq. (5). When the density, mean velocity, and temperature of a uniform system are assigned, there is only one possible permanent mode of distribution of the particle velocities (and that actual mode, e.g., concentrated dispersion, is different from a uniform steady state) so that probably the velocity of one particle is related to the velocities of other neighboring particles. Therefore,

$$f = f_{(0)} + f_{(1)} + f_{(2)} + \ldots \qquad (11)$$

f can be determined by successive approximation to any desired degree of accuracy; the first, second, third, $^+$ approximation are $f_{(0)}, f_{(0)} + f_{(1)}, f_{(0)} + f_{(1)} + f_{(2)}, \cdots$. Here, we have assumed "particle velocity chaos," and, for simplicity, the first approximation is taken as the velocity distribution function of particles. The first approximation, $f_{(0)}$, is identical with Maxwell-Boltzmann's distribution, and the actual velocity distribution function will tend to approach Maxwell–Boltzmann's distribution.

$$f = n\left(\frac{m}{2\,\pi\,kT}\right)^{3/2} \cdot \exp\left(-\frac{m\,c^2}{2\,kT}\right) \qquad (12)$$

The number of successful collisions at $r = \sigma$ is

$$N_1 = g(\sigma^+).2n^2\,\sigma^2(\pi/m)^{1/2}(kT)^{-3/2} \int_{\Delta V_{\max}}^{\infty} \exp(-V/kT)\,V\,dV\,, \qquad (13)$$

where V is relative kinetic energy, $\Delta V_{\max} = V_{\max} + E_{\min}$.

$$N_1 = g(\sigma^+).2n^2\,\sigma^2(\pi\,kT/m)^{1/2}(1 + \Delta V_{\max}/kT) \exp(-\Delta V_{\max}/kT) \qquad (14)$$

at $r = \lambda\,\sigma$

$$N_2 = 2g(\lambda\,\sigma^+)^2 n^2(\lambda\,\sigma)^2(\pi/m)^{1/2}(kT)^{-3/2} \int_{-E_{\min}}^{0} \exp(-V/kT)\,V\,\mathrm{d}V$$

$$= 2g(\lambda\,\sigma^+)^2 n^2(\lambda\,\sigma)^2(\pi\,kT/m)^{1/2}[1 - (1 - E_{\min}/kT) \exp(E_{\min}/kT)]. \qquad (15)$$

The total number of successful collisions is

$$N = N_1 + N_2$$
$$= 2n^2 \sigma^2 (\pi kT/m)^{1/2} \{ g(\sigma^+)(1 + \Delta V_{\max}/kT)$$
$$\exp(-\Delta V_{\max}/kT)$$
$$+ \lambda^2 g(\lambda \sigma^+)[1 - (1 - E_{\min}/kT)\exp(E_{\min}/kT)]\}. \quad (16)$$

Obviously,

$$W^{-1} = g(\sigma^+)(1 + \Delta V_{\max}/kT)\exp(-\Delta V_{\max}/kT)$$
$$+ \lambda^2 g(\lambda \sigma^+)[1 - (1 - E_{\min}/kT)\exp E_{\min}/kT)]. \quad (17)$$

The primary stability ratio W_p^{-1} is

$$W_p^{-1} = g(\sigma^+)(1 + \Delta V_{\max}/kT)\exp(-\Delta V_{\max}/kT). \quad (18)$$

The secondary stability ratio W_s^{-1} is

$$W_s^{-1} = \lambda^2 g(\lambda \sigma^+)[1 - (1 - E_{\min}/kT)\exp(E_{\min}/kT)]. \quad (19)$$

The values of $g(\sigma^+)$ and $g(\lambda \sigma^+)$ should be equal to unity for an extremely dilute dispersion; then, Eqs (18) and (19) reduce to the formula developed by Qun Wang [3]. The functions $g(\sigma^+)$ and $g(\lambda \sigma^+)$ become infinite as the system approaches the state in which the particles are packed so closely together that motion is impossible. This means the system behaves as a solid.

Results and discussion

To calculate the stability ratio of concentrated dispersion the height of the energy barrier $\Delta V_{\max}$ must be evaluated. This in turn requires a model for interaction between particles in concentrated dispersion. The stability of dilute electrostatically stabilized colloidal dispersions has been successfully described by DLVO theory. DLVO theory assumes that stability of a dispersion can be correctly determined by examining the energy of interaction between two particles in th absence of all others. Clearly, this assumption must be modified if dispersions of high particle volume fraction are to be considered. Bensley and Huter (BH) [16] have derived a multiparticle interaction model, where total potential energy of interaction between two particles is assumed to be the sum of the direct interaction between the pair and the interaction between the pair and the surrounding particles. Also, the average center–center interparticles separation is assumed to be equal to that in a regular 12-coordinated lattice of the same particles at the same particle volume fraction Φ. That is,

$$D = [8\pi/3\sqrt{2}]^{1/3} a/\Phi^{1/3}. \quad (20)$$

If the particles are assumed to approach each other by equal displacement, q, from the position of minimum energy, total potential energy has the form

$$\Delta V(R) = U(D - 2q) - U(D)$$
$$+ 12 \int_\delta^\pi [U(r) - U(D)] \sin\alpha \, d\alpha, \quad (21)$$

where

$$\delta = \cos^{-1}(2/3)^{1/2}$$
$$r = (D^2 + q^2 - 2Dq\cos\alpha)^{1/2};$$

$U(r)$ is the pair potential energy between two particles whose center–center separation is r.

The pairwise interaction energy at center–center separation, R, was assumed to be given by

$$U_T = U_R + U_A, \quad (22)$$

with U_R as the potential energy is electrostatic repulsion and U_A as the potential energy of van der Waals attraction. For the condition $\kappa a < 5$ and constant surface potential during interaction U_R was taken to have the form [17]

$$U_R = \beta 4\pi \varepsilon_r \varepsilon_0 a^2 \psi_0^2 \exp[-\kappa(R - 2a)]/R, \quad (23)$$

and for the condition $\kappa a > 5$

$$U_R = 2\pi \varepsilon_r \varepsilon_0 a^2 \psi_0^2 Ln\{1 + \exp[-\kappa(R - 2a)]\}, \quad (24)$$

where ε_r is the relative permitivity of medium, ε_0 is the permitivity of free space, ψ_0 is the surface potential of the particles, κ is the Debye-Hückel reciprocal double layer thickness, which for 1:1 electrolytes is given by

$$\kappa^2 = 2e^2 N_A C * 10^3/\varepsilon_r \varepsilon_0 kT, \quad (25)$$

where e is the fundamental charge on the electron, C is the electrolyte concentration in mol/dm^3, and N_A is Avogadro's constant.

β in Eq. (23) is the complex function of κa and R, and is defined in Verwey and Overbeek's book; numerical values are always between. 0.60 and 1.00 for the interaction of particles of equal radius and potential [17].

The attractive term in Eq. (22) for two spheres of equal size is given by

$$U_A = -A/6 * \{2a^2/R^2 + 2a^2/(R^2 - 4a^2)$$
$$+ Ln[(R^2 - 4a^2)/R^2]\}, \quad (26)$$

where A is Hamaker's constant.

To judge the stability of concentrated dispersion some criterion must be advanced to separate stable from unstable dispersion. Because the coagulation is a time-dependent process, we first examine the time of coagulation. The time of rapidly coagulating sol is given by Smoluchowski's theory

$$t = 3\eta/4kTN_0, \quad (27)$$

which, for water as dispersion medium and $T = 298\text{K}$, is equal to $t \sim 1.6 \times 10^{17}/N_0$, and is seen to depend (at given temperature and for a given dispersion medium) solely on the concentration of particles N_0. In other words, the time of coagulation or stability ratio is the function of the volume fractions.

A colliod may be termed stable when it does not coagulate in a week or a month, which means that the time of coagulation should be longer than 10^6 s, but the shortest time of rapid coagulation is of the order of 10^{-3} s. Consequently, the stability ratio between rapid and slow coagulation will have to surpass 10^5 for dilute and 10^9 for concentrated dispersions. If radius of particles approximately equals 100 nm, the ratio W is roughly 10^9 at the volume fraction $\Phi < 0.1$; and 10^{10} at $\Phi > 0.1$. In the following, we will apply the criterion for examining the stability of concentrated dispersions.

Here, we accept the model for multiparticle interaction developed by BH to calculate the height of the energy barrier preventing coagulation. For the values of radial distribution function at $r = \sigma$, we employ exact PY result [18]:

$$g(\sigma^+) = (1 + 0.5\Phi)/(1 - \Phi)^2; \tag{28}$$

for $g(\lambda\,\sigma^+)$ there is no simple analytical expression and we use the values from Monte Carlo simulation [19, 20]. The comparison with the experimental data of Goodwin et al. [21] is given in Table 1; they directly determined the excess osmotic pressure of aqueous dispersions of polystyrene latices combining with the optical diffraction. Number average particle radius of their polystyrene latex, RB31, is 91 nm, the deviation of the mean radius is mall (< 2.5%), a potential of 50 mV in 10^{-5}, 10^{-4}, 10^{-3} mol/dm^3 NaCl solution Hamaker's constant was taken as $9.09{*}10^{-21}$ J.

The results obtained for latex in 10^{-3} and 10^{-4} mol/dm^3 show that the agreement between calculation and experiment is fairly good. It can be noted that for the result in 10^{-5} NaCl a large discrepancy is found. The sources of this discrepancy are numerous. First, the BH model of multiparticle interaction was based on the pairwise DLVO interaction energies was employed. Serious discrepancies might be caused by the loss of pairwise interaction. BH also indicated that serious discrepancies caused by the loss of pairwise additivity should only occur for $\kappa\,a \leq 5$; recently, Reiner et al [22] found that the pair approximation is valid only when typical interparticle spacings are greater than the Debye length. This condition is insufficient for low electrolyte concentrations, for example, in 10^{-5} NaCl $\kappa\,a = 0.94$. Second, in a concentration dispersion the concentration of potential determining ions from the dissociation of surface groups can make a significant contribution to the counter-ion concentration in the dispersion medium. Consequently, the screening parameter, κ, for double-layer interaction will no longer be simply related to the concentration of added electrolyte, as it is in the dilute system [14, 23]. Obviously, Eq. (25) is inappropriate to the double-layer repulsion. In fact, experimental osmotic pressure rises quite steeply even at low volume fraction; it is about $\Phi = 0.2$. The system in 10^{-5} mol/dm^3 salt appeared to be highly ordered at volume fraction ca 0.2, and a sharp peak was observed in the intensity curves. However, only the higher volume fraction, for example $\Phi = 0.592$, seemed to give good agreement with f.c.c. lattice [21]. If $\Phi = 0.2$ is taken as experimental transition point, calculated results can be fitted to the experimental data.

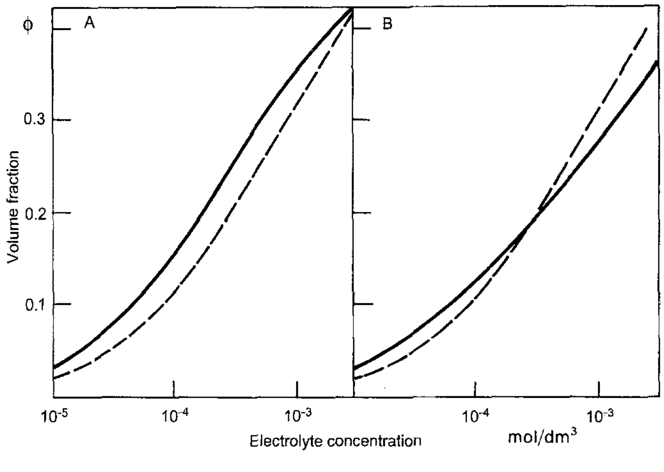
Table 1. Comparison of present calculated results with experimental data [21]

Concentration of NaCl (mol/dm^3)	Transition point of order/coexistence (Φ)	
	Experiment	Calculation
10^{-3}	0.56	0.635
10^{-4}	0.54	0.50
10^{-5}	0.58 (0.2)	0.25

Figures 2 and 3 show the calculated results obtained with latices of particles radius 50 nm and 85 nm, and potential of 30 mV and 25 mV, $KT = 4.11{*}10^{-21}$ J, Hamaker's constant was taken as $1{*}10^{-20}$ J, W was taken as 10^9 in Figs. 2a and 3a. W was taken as 10^9, during $\Phi < 0.1$; 10^{10}, $\Phi > 0.1$ in Figs. 2b and 3b.

The calculated results show that the general dependencies be expected to be correct. The phase diagram for aqueous monodisperse polystyrene latex of particle radius 85 nm has been mapped out by Hachisu et al. [4]. Barnes

Fig. 2 Volume fraction-electrolyte concentration curves for latex with the particle radius of 50 nm, $\psi_0 = 30$ mV, $A = 1 \times 10^{-20}$ J. Full curves: theoretical results. Dash-dotted curves: Eq. (29). A) W is taken to be 10^9. B) W is taken to be 10^9 during $\Phi < 0.1$; if $\Phi > 0.1$, W is 10^{10}



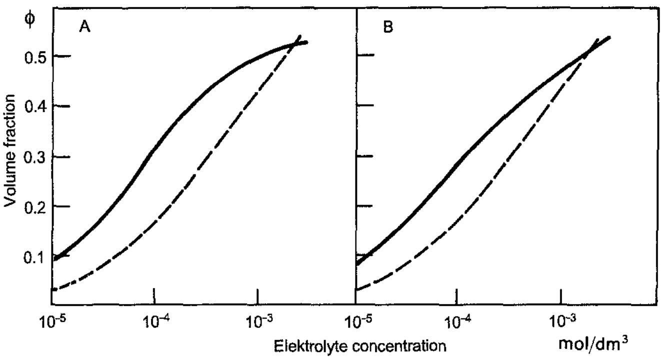


Fig. 3 Volume fraction-electrolyte concentration curves for latex with the particle radius of 85 nm, $\psi_0 = 25$ mV, $A = 1{*}10^{20}$ J. Full curves: theoretical results. Dashed curves: Eq (29). A) W is taken to be 10^9. B) W is taken to be 10^9 during $\Phi < 0.1$; inf $\Phi < 0.1$; if $\Phi > 0.1$, W is 10^{10}

et al. [14] referenced the experimental data of Hachisu et al, based on the concept "effective spheres" to obtain the expression of the order/coexistence phase boundary, namely,

$$\Phi_0 = 0.74/[1 + \lambda(a)/\kappa\, a]^3, \qquad (29)$$

where $\lambda(a) = 1.9 + \mathrm{Ln}(a/85\ \mathrm{nm})$.

The dashed curves in Figs. 2 and 3 are obtained using Eq. (29). When the particle radius equals 85 nm, Eq. (29) is precise in the range from $\Phi = 0.05$ to 0.4. The theoretical curves seemed to have agreement with experimental data, but large discrepancy is found. The effect of particle surface potential and particle size on the onset of instability is as expected. Any change which causes the magnitude of interaction energy to increase, either by an increase in the surface potential or by an increase in the particle size, will shift the onset of coagulation to higher particle volume fractions. This effect is apparent in Figs. 2 and 3.

In the case of electrostatically stabilized dispersions, a homogeneous disordered phase is observed at low volume fraction and high electrolyte concentration. At high volume fractions and low electrolyte concentrations an ordered structure has been found. Between these extreme there is an intermediate range of volume fractions and electrolyte concentrations for which the ordered and disordered phases coexist. The reason why a coexistence region occurs is not yet clear. One possibility is that coexistence suggests that there should be secondary minimum at different volume fractions; these would be quite shallow to allow easy transition between the two states. For the colloidal system, this would probably need a depth on the order of ca. 0.1 kT [21]. However, we make use of the BH model to calculate multiparticle interaction. No secondary minimum is apparent on the potential energy curves calculated, and it is certain that the present model is able to predict such a subtle effect.

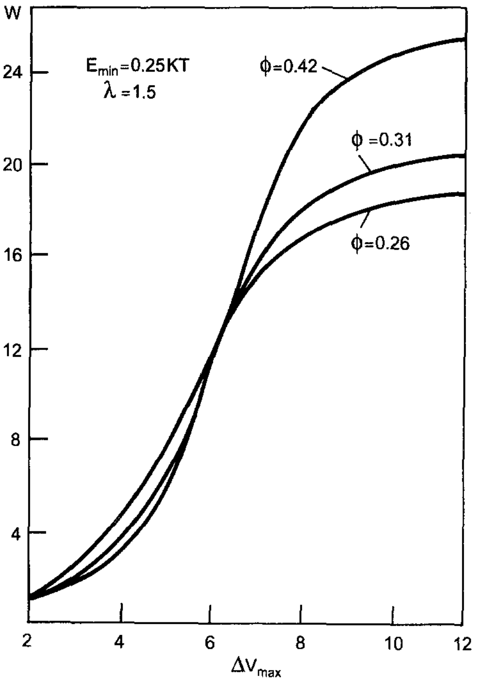


Fig. 4 The dependence of the overall stability ratio on $\Delta V_{\max}$

Figure 4 presents the predicted effect of secondary minimum coagulation on the overall stability ratio W (primary and secondary combined). It can be seen that the present model predicts W to be quite sensitive to the coexistence of a secondary minimum. A system is considered to be more stable, the higher its volume fraction when the height of the energy barrier of preventing coagulation is above a certain value (in Fig. 4 ca. $7kT$). If, on the contrary, the height of the energy barrier is below a certain value (ca. $7kT$), the lower volume fraction, the system is more stable. When $\Delta V_{\max}$ is above a certain value (in Fig. 4 ca. $14kT$) the stability ratio W remains essentially constant. This situation would be meaningful for predicting the phase boundary of disorder/coexistence; it shows why the phase coexistence firstly occurs in lower volume fraction. The phase coexistence will occur in the range where the height of energy barrier is greater than that of ca. $7kT$. When the electrolyte concentration and volume fraction were increased to a certain value, so that the height of energy barrier is below ca. $7kT$, the system of higher volume fraction will then change to a face-centered cubic arrangement; this is the boundary of order/coexistence. This fact challenges us to develop a new calculated model, and the criterion of stability ratio W must be elucidated.

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References

1. von Smoluchowski M (1916) Z Physik 17:557, 585
2. Fuch N (1934) Z Physik 89:736
3. Qun Wang (1991) J Colloid Interface Sci 145:99
4. Hachisu S, Kobayashi Y, Kose A (1973) J Colloid Interface Sci 42:342
5. Furusawa K, Yamashita S (1982) J Colloid Interface Sci 89:574
6. Monovoukas Y, Gast AP (1989) J Colloid Interface Sci 128:533
7. Homola A, Rubertson AA (1972) J Colloid Interface Sci 54:286
8. Bensley CN, Huter RJ (1983) J Colloid Interface Sci 92:448
9. Snook I, van Megan W (1976) J Chem Soc Faraday II 72:216
10. Keavey KM, Richmond P (1976) J Chem Soc Faraday II 72:773
11. Voegtli LP, Zukoshi CF (1991) J Colloid Interface Sci 141:79
12. Marcelja S, Mitchell DJ, Ninham BW (1976) Chem Phys Lett 43:353
13. Ohtsuki T, Kishimoto A, Mitaku S, Okano K (1981) Jap J Appl Phys 20:509
14. Barnes CJ, Chan DYC, Evert DH, Yeates DE (1978) J Chem Soc Faraday II 78:136
15. Beunen JA, White LR (1981) Colloid & Surface 3:371
16. Bensley CN, Huter RJ (1983) J Colloid Interface Sci 92:436
17. Verwey EJ, Overbeek J Th G (1948) "Theory of the Stability of Lyophobic Colloids". Elsevier Amsterdam
18. Thiele E (1963) J Chem Phys 39:474
19. Henderson D, Madden WG, Fitts DD (1976) J Chem Phys 64:5026
20. Henderson D, Scalise OH, Smith WR (1980) J Chem Phys 72:2431
21. Goodwin JW, Ottewiu RH, Parentich A (1990) Colloid Polym Sci 263:1131
22. Reiner ES, Radke CJ (1991) AIChE J 37:805
23. Chen CS, Levine S (1972) J Chem Soc Faradey II 68:197