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ORIGINAL CONTRIBUTION

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The sticking probability of colloidal particles in polymer-induced flocculation

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Abstract The interaction between colloidal particles in a solution containing polymer molecules is examined theoretically. In particular, the sticking probability of colloidal particles, which plays a significant role in the determination of the collision efficiency of an unstable dispersed system, is analyzed. We found that the sticking probability is extremely sensitive to the variation in the Hamaker constant of a colloidal particle. In the conventional analysis of the collision efficiency in polymer-induced flocculation, it is assumed that the adsorption of polymer is relatively fast than the collision of colloidal particles. Since the adsorption of polymer will significantly affect the properties of the surface of a colloidal particle, this assumption may lead to an appreciable deviation in the prediction of collision efficiency.

Key words Sticking probability – collision efficiency – Hamaker constant – flocculation – polymer adsorption

Introduction

The addition of polymer to a dispersed phase to accelerate the formation of flocs is one of the key steps in many wastewater treatment processes. The flocculation phenomenon comprises two steps in series: the adsorption of polymer molecules onto the surfaces of colloidal particles, followed by particle–particle collisions which result in the formation of molecular bridges. One of the measures often adopted to quantify the rate of flocculation is the fraction of the number of effective collisions between particles leading to agglomeration, or the collision efficiency. More often than not, the rate of adsorption of polymer molecules to colloidal surfaces is assumed to be much faster than the rate of flocculation [1–4]. In this case, the degree of coverage of a colloidal surface by polymer is treated as constant in the calculation of collision efficiency. As pointed out by Hsu and Lin [5], this assumption is unrealistic in practice, and the temporal behavior of the adsorption of polymer molecules needs to be considered. In the conventional analysis on the collision efficiency of a polymer-induced system the particle–particle and particle–polymer interactions are often oversimplified. Molski [4], for instance, assumes that three types of effective collision between two colloidal particles are possible: a) Two sites at the collision point are both bare. The probability of sticking between these particles is α. b) Two sites at the collision point are both occupied. The probability of sticking between these particles is β. c) One of the two sites at the collision point is bare and the other is occupied. The probability of sticking between these particles is unity. The values of α and β are assumed to be constant, and their dependence on the physical properties of the system is neglected.

The adsorption of polymer will affect the property of the surface of a colloidal particle. For instance, the surface charge will change if polymer molecules are charged. Also, the adsorbed polymer has the effect of pushing the shear plane towards the bulk liquid phase. This may lower the effective surface potential of a colloidal particle. Furthermore, the apparent Hamaker constant will be different from that of a polymer–free surface. Apparently, the collision efficiency is largely dependent on the surface property of a colloidal particle. Since this is almost always overlooked, the value of the collision efficiency estimated in the conventional analysis deserves a further investigation. In the present study, the interaction of two colloidal particles with adsorbed polymer molecules is examined, and the sticking probabilities due to various particle–particle interactions are estimated.

Analysis

The analysis is begun by a discussion of the collision efficiency, followed by the derivation of the sticking probabilities of various types of particle–particle interactions, and relating these probabilities to the physical properties of the system under consideration.

Collision efficiency

Intuitively, the collision efficiency E is a function of the fractional surface coverage of colloidal particles by polymer molecules θ. La Mer and Healy [1], for instance, proposed that E and θ are related by

$$E = \theta(1-\theta)\,. \tag{1}$$

This expression is based on the assumption that each particle has the same fractional surface coverage. Although Eq. (1) suggests that E has a maximum at $\theta = 1/2$, the experimental evidence reveals that the maximum rate of flocculation does not necessary occur at this value. Several attempts have been made to provide an explanation for the observed discrepancy. By taking the possibility of the reorientation of two colliding particles and the adsorbed polymer molecules into account, Hogg [2] obtained

$$E = 1 - \theta^{2n} - (1-\theta)^{2n}\,, \tag{2}$$

where n denotes the number of adsorption sites per particle. In the case $n = 1$, Eq. (2) reduces to

$$E = 2\theta(1-\theta)\,, \tag{3}$$

This is the correct formulation of the La Mer and Healy model if the statistics of collisions between a bare patch and an occupied surface patch are properly taken into account. The original La Mer and Healy model has also been modified by Moudgil et al. [3] through taking the heterogeneity of the colloidal surface into account. They considered two types of sites on the surface of a particle: active site and inactive site. An effective collision between two particles, which yields attachment, occurs only if a patch of adsorbed polymer finds a patch of free active sites on another particle, or vice versa. In this case, Eq. (1) becomes

$$E = 2\theta\phi^2(1-\theta)\,, \tag{4}$$

where ϕ represents the fraction of active sites on the surface of a particle. In a recent study, Molski [4] points out that three types of effective collision between two colloidal particles are possible: a) Two sites at the collision point are both bare (coagulation). b) Two sites at the collision point are both occupied (weak flocculation). c) One of the two sites at the collision point is bare and the other is occupied (bridging). The probability of sticking associated with these collisions are respectively α, β, and unity. It can be shown that

$$E = 1 - (1-\alpha)(1-\theta)^2 - (1-\beta)\theta^2\,. \tag{5}$$

If $\alpha = 0$ (no coagulation), and $\beta = 0$ (no weak flocculation), this expression reduces to Eq. (3). Equation (5) is further modified by assuming that the probability of bridging is γ (not necessary unity), and the resultant expression is [6]

$$E = \alpha(1-\theta)^2 + \beta\theta^2 + 2\gamma\theta(1-\theta)\,. \tag{6}$$

If two colliding particles have different sizes, Eq. (6) becomes

$$E = \alpha(1-\theta)^2 + \beta\theta^2 + \gamma_1\theta(1-\theta) + \gamma_2\theta(1-\theta)\,. \tag{7}$$

For fixed values of α, β, γ_1, and γ_2, Eq. (7) predicts that the maximum value of E occurs at $\theta_{\max}$ [6],

$$\theta_{\max} = \frac{\gamma_1 + \gamma_2 - 2\alpha}{2(\gamma_1 + \gamma_2 - \alpha - \beta)}\,, \tag{8}$$

In the case where the repulsion due to the steric effect is significant between two polymer–covered surfaces, $\beta = 0$, Eq. (8) reduces to

$$\theta_{\max} = \frac{1}{2}\left\{1 - \frac{\alpha/(\gamma_1+\gamma_2)}{1 - [\alpha/(\gamma_1+\gamma_2)]}\right\}. \tag{9}$$

Equation (9) suggests that if polymer bridging is the dominant flocculation mechanism, the maximum collision efficiency is obtained for a surface coverage slightly less than 0.5. On the other hand, if polymer bridging is the only mechanism, i.e., $\alpha = \beta = 0$, the maximum collision efficiency occurs at $\theta = 0.5$. Equation (5) has also been extended to the case where the temporal variation in the adsorption of polymer is taken into account [5].

Sticking probability

The interactions between two colloidal particles include the electrostatic repulsion, steric repulsion, bridging attraction, and van der Waals attraction. If we exclude the steric repulsion and bridging attraction, and the electrostatic repulsion is suppressed by adding electrolytes until the energy barrier between two colloidal particles becomes zero, the phenomenon under consideration is called rapid coagulation. In this case, the maximum interaction potential between two colloidal particles $V\mathrm{max}$ is zero. It has been shown that the stability ratio W_{Fuchs} defined as (number of collisions between particles under $V\mathrm{max} = 0$)/(number of collisions between particles under $V\mathrm{max} \neq 0$), can be evaluated by [7]

$$W_{\mathrm{Fuchs}} = 2 \int_{2}^{\infty} \frac{\exp[V_T(R)/k_B T]}{R^2}\, dR \,, \tag{10}$$

where $R = r/a$, r and a being the center-to-center distance and the radius of a particle, respectively; k_B and T denote, respectively, the Boltzmann constant and temperature, and V_T denotes the total interaction potential between particles. In the derivation of Eq. (10), the effect of hydrodynamic interaction is excluded. Honing [8] suggests that if the hydrodynamic interaction is significant, the following function needs to be included in the integrand of Eq. (10):

$$F(R) = (6R^2 - 11R)/(6R^2 - 20R + 16)\,. \tag{11}$$

McGown and Parfitt [9] pointed out that for rapid coagulation near the primary minimum of the potential distribution between two colloidal particles, van der Waals attraction needs to be considered. This is because in the absence of van der Waals attraction coagulation is impossible. On the basis of the above discussion, we define the sticking probability SP as

$$SP = \frac{\int_{2}^{\infty} F(R) \frac{\exp[V_A(R)/k_B T]}{R^2}\, dR}{\int_{2}^{\infty} F(R) \frac{\exp[V_T(R)/k_B T]}{R^2}\, dR}\,, \tag{12}$$

where V_A is the van der Waals potential between two colloidal particles. According to Eq. (12), $SP \leqslant 1$, and it is a measure of the ratio (number of collisions between particles that result in flocculation)/(total number of collisions).

Calculation of α, β, γ_1, and γ_2

A schematic representation of the system under consideration is illustrated in Fig. 1. In this figure, a_1 and a_2 are respectively the radius of particle 1 and that of particle 2, p_1 and p_2 denote the mean thickness of adsorbed polymer on the surfaces of particle 1 and particle 2, respectively, and d and r are respectively the surface to surface distance and center–to–center distance between two particles. The total interaction potential between particles 1 and 2, V_{Ti}, comprises the van der Waals potential, V_{Ai}, the electrical double layer potential, V_{Ri}, and the bridging potential V_{bdg}, $i = 1, 2, 3, 4$. The subscript i represents the following four types of interaction between surfaces: a) $i = 1$, both surfaces are bare, b) $i = 2$, both surfaces are covered by polymer, c) $i = 3$, the surface of particle 1 is covered by polymer and the surface of particle 2 is bare, and d) $i = 4$, the surface of particle 1 is bare and the surface of particle 2 is covered by polymer.

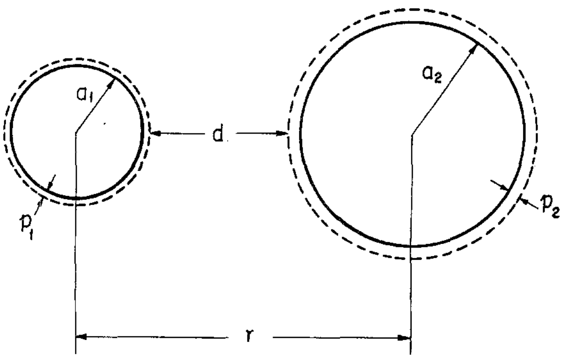


Fig. 1 A schematic representation of the linear dimensions used in the present study. The solid circles represent the surfaces of colloidal particles, and the dashed circles denote the outer region of the adsorbed polymer layer

van der Waals potential

The van der Waals potential is evaluated by [10, 11]

$$V_{Ai} = -A_i H_i/12\,, \tag{13}$$

$$H_i = \frac{y}{x^2 + xy + x} + \frac{y}{x^2 + xy + x + y} + 2\ln\left[\frac{x^2 + xy + x}{x^2 + xy + x + y}\right],\ i = 1, 2, 3, 4\,. \tag{14}$$

In this expressions,

$$A_1 = (A_{c1}^{1/2} - A_m^{1/2})(A_{c2}^{1/2} - A_m^{1/2}) \tag{14a}$$

$$A_2 = (A_{p1}^{1/2} - A_m^{1/2})(A_{p2}^{1/2} - A_m^{1/2}) \tag{14b}$$

$$A_3 = (A_{c2}^{1/2} - A_m^{1/2})(A_{p1}^{1/2} - A_m^{1/2}) \tag{14c}$$

$$A_4 = (A_{c1}^{1/2} - A_m^{1/2})(A_{p2}^{1/2} - A_m^{1/2}) \tag{14d}$$

$$x = d/2(a_1 + p_1) = [R - (1 + y_3 + y_1 + y_2)]/2(1 + y_1) \tag{14e}$$

$$y = (a_2 + p_2)/(a_1 + p_1) = (y_3 + y_2)/(1 + y_1) \tag{14f}$$

$$R = r/a_1 \tag{14g}$$

$$y_1 = p_1/a_1 \tag{14h}$$

$$y_2 = p_2/a_2 \tag{14i}$$

$$y_3 = a_2/a_1 , \tag{14j}$$

A_{c1}, A_{c2}, A_{p1}, A_{p2}, and A_m being the Hamaker constant of particle 1, particle 2, polymer on particle 1, polymer on particle 2, and liquid medium, respectively.

Electrical potential

The electrical double layer potential can be calculated by [12]

$$V_{Ri} = \frac{\varepsilon_r a_1 (1 + y_1)(y_3 + y_2)}{(1 + y_3 + y_1 + y_2)} (\psi_{1i}^2 + \psi_{2i}^2) \left\{ \frac{2\psi_{1i}\psi_{2i}}{(\psi_{1i}^2 + \psi_{2i}^2)} \ln\left[\frac{1 + \exp(-\kappa a_1 D^*)}{1 - \exp(-\kappa a_1 D^*)}\right] + \ln[1 - \exp(-2\kappa a_1 D^*)] \right\} , \tag{15}$$

$$i = 1, 2, 3, 4$$

$$\varepsilon_r = \pi \varepsilon_m \varepsilon_0 \tag{15a}$$

$$D^* = R - (1 + y_3 + y_1 + y_2) \tag{15b}$$

In these expressions, ε_m and ε_0 are, respectively, the dielectric constants of solution and vacuum, and ψ_{ij} is the surface potential, i denotes the identification of a particle (1 or 2), and j represents its status (whether it is covered by polymer).

Bridging potential

The bridging potential V_{bdg} plays the major role in the determination of the degree of attachment of a polymer molecule to a colloidal surface. Although relevant results about the adsorption of polymer to surfaces are ample in the literature, the exact form for V_{bdg} is still not well understood. The adsorption of polymer molecules onto the surfaces of colloidal particles correlates with the interaction energy among colloidal surface, polymer, and solvent. Since polymer dissolves in solvent, the interaction energy between polymer and solvent is greater than that of polymer and polymer. Similarly, the interaction energy between polymer and colloidal surface is greater than that of polymer and solvent so that adsorption occurs. Let E_s be the net interaction energy between polymer molecule and colloidal surface. The greater the E_s, the greater the fraction of colloidal surface covered by polymer. We assume that V_{bdg} is proportional to the product of E_s and the fraction of unadsorbed polymer η, i.e.,

$$V_{bdg} \propto E_s \eta \tag{16a}$$

Clearly, η is a function of E_s, the greater the E_s, the smaller the η. Suppose that

$$\eta \propto \exp(-E_s/k_B T) . \tag{16b}$$

Thus,

$$V_{bdg} = -C_1 E_s \exp(-E_s/k_B T), \tag{17}$$

where C_1 is constant.

We assume that the mean thickness of polymer on the surface of a colloidal particle is proportional to η. If we denote y^* as the ratio of the linear dimension of an unadsorbed polymer molecule with a_1, then

$$y_1 \text{ (or } y_2) = y^* \exp(-E_s/k_B T) . \tag{18}$$

Hydrodynamic interaction

The effect of hydrodynamic interaction is taken into account by considering the expression below [7]:

$$F_i = (6D^{*2} + 13D^* + 2)/(6D^{*2} + 4D^*) \tag{19}$$

For $i = 1$, $y_1 = y_2 = 0$; $i = 3$, $y_2 = 0$, $\psi_{13} = \psi_{12}$, $\psi_{23} = \psi_{21}$; $i = 4$, $y_1 = 0$, $\psi_{14} = \psi_{11}$, $\psi_{24} = \psi_{22}$.

We define α, β, γ_1, and γ_2 by [13, 14]

$$\alpha = \frac{\int_{1+y_3}^{\infty} [F_1 \exp(V_{A1}/k_B T)]/R^2 dR}{\int_{1+y_3}^{\infty} [F_1 \exp(V_{T1}/k_B T)]/R^2 dR} , \tag{20}$$

$$\beta = \frac{\int_{1+y_3+y_1+y_2}^{\infty} [F_2 \exp(V_{A2}/k_B T)]/R^2 dR}{\int_{1+y_3+y_1+y_2}^{\infty} [F_2 \exp(V_{T2}/k_B T)]/R^2 dR} , \tag{21}$$

$$\gamma_1 = \frac{C_2 y_1 \int_{1+y_3+y_1}^{\infty} [F_3 \exp(V_{A3}/k_B T)]/R^2 dR}{\int_{1+y_3+y_1}^{\infty} [F_3 \exp(V_{T3}/k_B T)]/R^2 dR} , \tag{22}$$

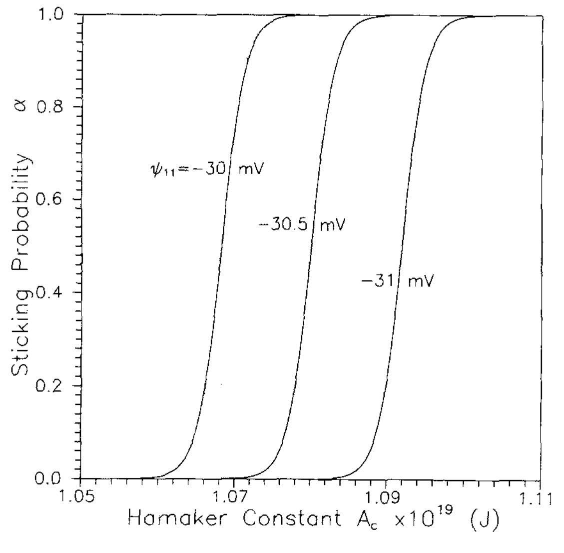
$$\gamma_2 = \frac{C_2 y_2 \int_{1+y_3+y_2}^{\infty} [F_4 \exp(V_{A4}/k_B T)]/R^2 dR}{\int_{1+y_3+y_2}^{\infty} [F_4 \exp(V_{T4}/k_B T)]/R^2 dR} , \tag{23}$$

where C_2 is constant, $V_{Ti} = V_{Ai} + V_{Ri}$. $i = 1, 2$, and $V_{Ti} = V_{Ai} + V_{Ri} + V_{bdg}$, $i = 3, 4$. Equations (22) and (23) are based on the assumption that the sticking probabilities γ_1 and γ_2 are proportional to the extended length of adsorbed polymer.

Results and discussion

The variation of sticking probabilities α, β, γ_1, and γ_2 as functions of the relevant parameters are examined through numerical simulation. For convenience, we assume $a_1 = a_2$ and $\gamma_1 = \gamma_2 = \gamma$. Figure 2 shows the variation of sticking probability as a function of the Hamaker constant of a colloidal particle A_c at different values of the surface potential of a particle; the variation of α as a function of A_c at different values of the reciprocal Debye length is illustrated in Fig. 3. These figures reveal that α is extremely sensitive to the variation in the Hamaker constant of colloidal particle. This is expected since the attraction of particles is due to van der Waals force, and it is proportional to Hamaker constant. Figure 2 suggests that decreases with the increase in the absolute value of the surface potential of colloidal particle. According to DLVO theory, the greater the surface potential, the higher the energy barrier that prevents two particles from becoming closer, and, therefore, the lower the value of α. As can be seen from Fig. 3, α increases with the increase in κ. This is because the greater the value of κ, the thinner the double layer, and the lower the energy barrier. The qualitative behavior of the variation of sticking probability as functions of Hamaker constant and the reciprocal Debye length is consistent with those observed by Valioulis and List [17].

Fig. 2 Variation of sticking probability α as a function of the Hamaker constant of a colloidal particle at different values of the surface potential of particle ψ_{11} for the case $\kappa = 10^8$/m. Key: $a_1 = a_2 = 1\,\mu m$, $y_3 = 1$, $k_B = 1.38062 \times 10^{-23}\ J/°K$, $T = 298.15\,°K$, $\varepsilon_0 = 8.854 \times 10^{-12}\ N/m$, $\varepsilon_m = 78.54$, $A_m = 4.8 \times 10^{-20}\ J$



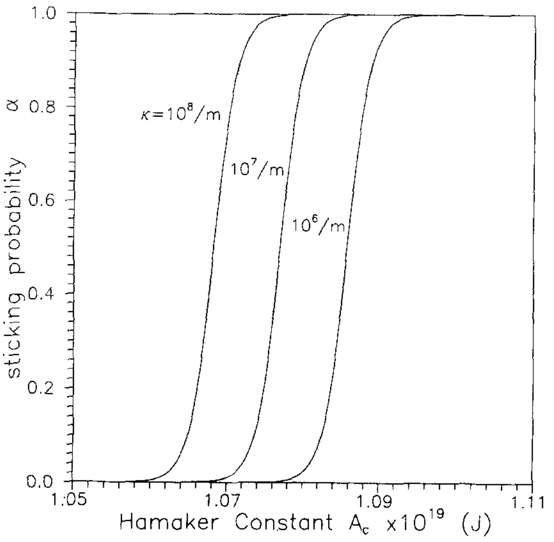


Fig. 3 Variation of sticking probability α as a function of the Hamaker constant of a colloidal particle at different values of the reciprocal Debye length for the case $\psi_{11} = \psi_{21} = -30$ mV. Key: same as Fig. 2

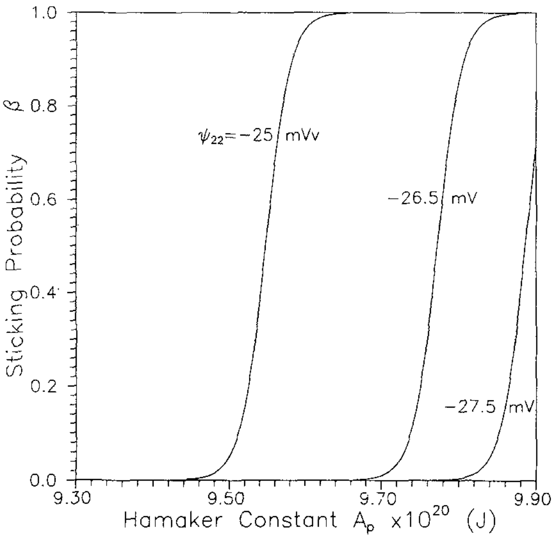


Fig. 4 Variation of sticking probability β as a function of the Hamaker constant of polymer at different values of the surface potential of polymer for the case $\kappa = 10^8$/m and $y_1 = y_2 = 0.03$. Key: same as Fig. 2

Figure 4 shows the variation of sticking probability β as a function of the Hamaker constant of polymer A_p at different values of the surface potential of polymer ψ_{22}; the variation of β as a function of A_p at different values of the reciprocal Debye length is shown in Fig. 5. The qualitative behavior of the variation in β is similar to that of α shown in Figs. 2 and 3. It is worth noting that the adsorption of polymer will affect the properties of the surface of a colloidal particle. If the sign of the surface charge is the same as that of polymer, the adsorption of polymer has the effect

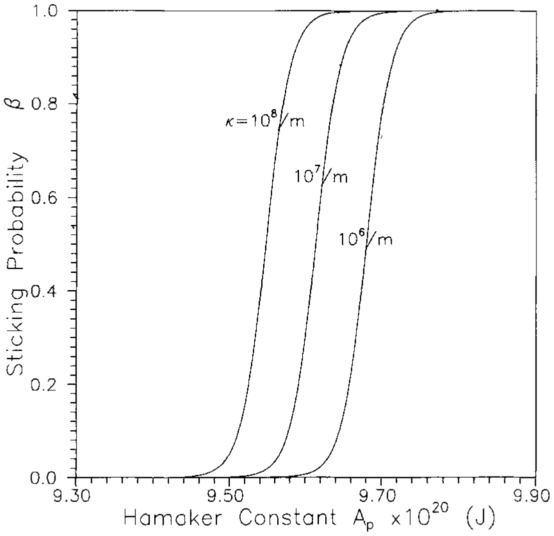


Fig. 5 Variation of sticking probability β as a function of the Hamaker constant of polymer at different values of the reciprocal Debye length for the case $\psi_{12} = \psi_{22} = -25\,\mathrm{mV}$ and $y_1 = y_2 = 0.03$. Key: same as Fig. 2

of increasing the apparent surface charge. On the other hand, if the sign of the surface charge is different from that of polymer, the adsorption of polymer will lower the apparent surface charge. The adsorption of uncharged polymer has the effect of pushing the shear plane towards the bulk liquid phase, and this may lower the effective surface potential. Also, the apparent Hamaker constant is different from that of a polymer–free surface.

Figure 6(a) shows the variation of sticking probability as a function of E_s at different values of the reciprocal Debye length. This figure reveals that for a fixed κ, γ increases first with the increase in E_s, passes through a maximum, and then decreases with a further increase in E_s. The bridging attraction [15] and the thickness of adsorbed polymer layer [16] are two major factors affecting the magnitude of γ. Apparently, the greater the bridging attraction and/or the thicker the adsorbed polymer layer, the easier a bridge between two colloidal particles can be formed. On the other hand, the thicker the adsorption layer, the greater the double layer repulsion force, and the harder it is to form a bridge between two colloidal particles. By referring to Eqs. (17) and (18), both the bridging attraction and the thickness of adsorbed polymer layer vary with E_s, as illustrated in Fig. 6(b). This figure shows that the thickness of adsorbed polymer layer decreases monotonically with the increase in E_s. The bridging attraction increases first with the increase in E_s, passes through a maximum, and then decreases with a further increase in E_s. Thus, there exists an optimal E_s such that the bridging attraction–thickness of adsorbed polymer layer combination is the most appropriate to the formation of a bridge between two colloidal particles.

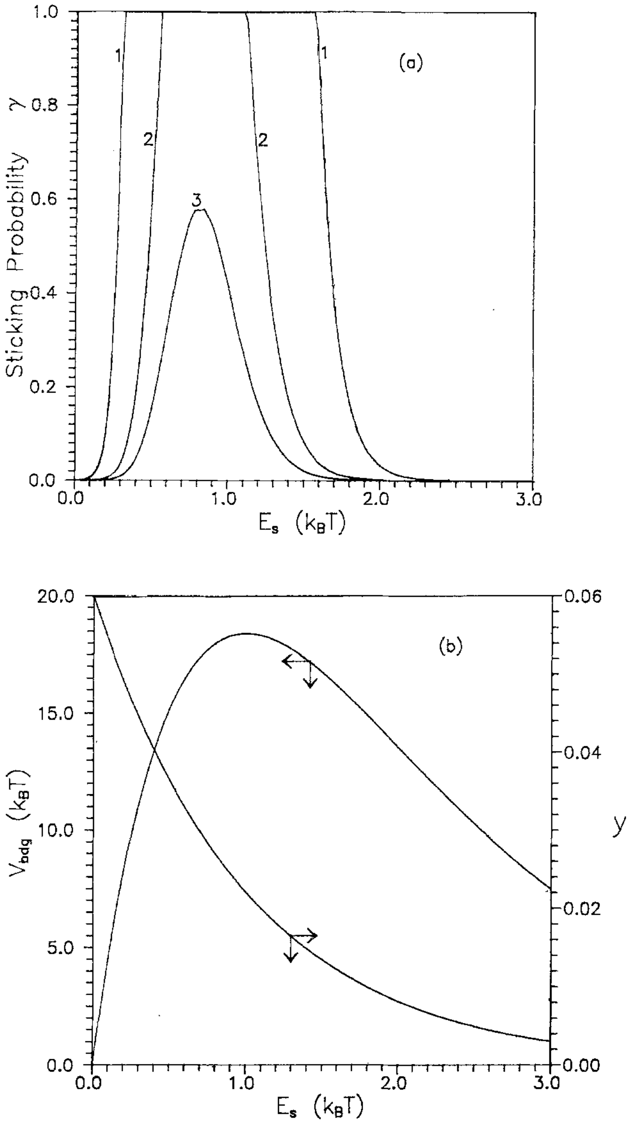


Fig. 6 a) Variation of sticking probability γ as a function of net interaction energy E_s at different reciprocal Debye lengths for the case $A_{c1} = A_{c2} = 1.05 \times 10^{-19}\,J$, $A_{p1} = A_{p2} = 8.8 \times 10^{-20}\,J$, $\psi_{11} = \psi_{21} = -30\,\mathrm{mV}$, $\psi_{12} = \psi_{22} = -23\,\mathrm{mV}$, $C_1 = 50$, $C_2 = 3$, and $y^* = 0.06$. Curve 1: $\kappa = 10^7$/m; 2: $\kappa = 2 \times 10^6$/m; 3: $\kappa = 10^6$/m. Key: same as Fig. 2. b) Variation of bridging potential and the thickness of adsorbed polymer layer as functions of E_s

Figure 7 illustrates a typical variation in the collision efficiency as a function of the fractional surface coverage of colloidal particles by polymer. This figure shows that the collision efficiency increases with the increase of θ, passes through a maximum, and then decreases with a further increase of θ. Here, θ is defined as the fractional coverage of the active sites on the colloidal surface. The maximal

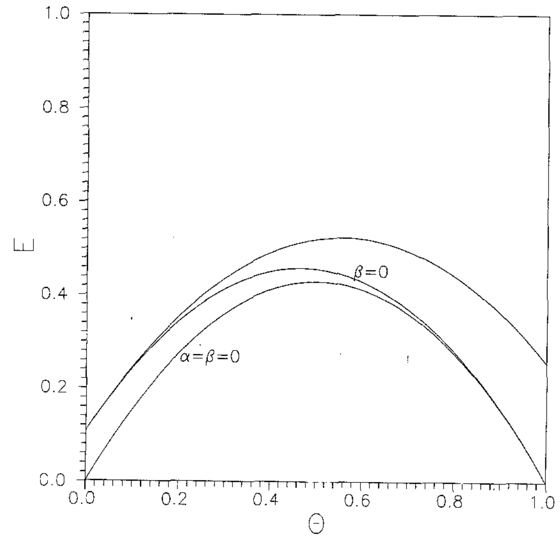


Fig. 7 Variation in the collision efficiency as a function of fractional surface coverage of colloidal particles for the case $A_c = 1.065 \times 10^{-19}$ J, $\psi_{11} = -30\,\mathrm{mV}$, $\psi_{22} = -25\,\mathrm{mV}$, $\kappa = 10^8/\mathrm{m}$, $y_1 = 0.02$, $V_{bdg} = 4k_BT$, $A_p = 9.53 \times 10^{-20} J$, and $C_2 = 3$

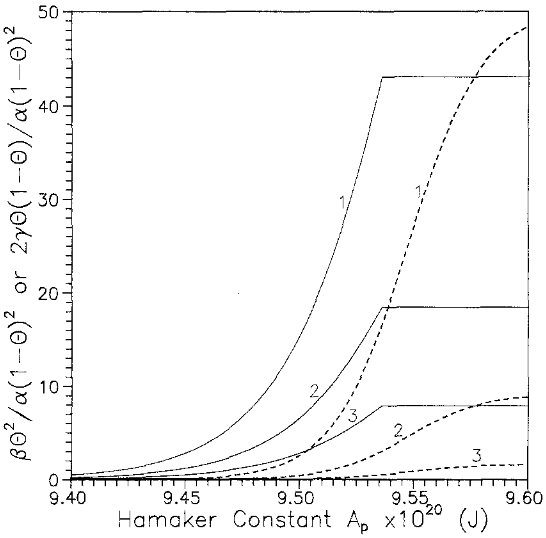


Fig. 8 Variation in the relative significance of (weak flocculation/coagulation), dashed lines, and (bridging flocculation/coagulation), solid lines, as a function of the Hamaker constant of polymer A_p at various degrees of surface coverage of colloidal particles by polymer for the case $A_c = 1.065 \times 10^{-19} J$, $\psi_{11} = -30\,\mathrm{mV}$, $\psi_{22} = -25\,\mathrm{mV}$, $V_{bdg} = 4k_BT$, $C_2 = 3$, $y_1 = 0.02$, and $\kappa = 10^8/\mathrm{m}$. Curve 1: $\theta = 0.7$; 2: $\theta = 0.5$; 3: $\theta = 0.3$

value of θ depends on the values of α, β, and γ, which in turn are determined by the properties of colloidal particles, solution, and polymer used. We found that, in general, the maximal value of collision efficiency is slightly greater than 0.5. However, if $\beta = 0$, this value is slightly less than 0.5; it equals 0.5 only if $\alpha = \beta = 0$.

Figure 8 shows the variation in the ratios $\beta\theta^2/\alpha(1-\theta)^2$ and $2\gamma\theta(1-\theta)/\alpha(1-\theta)^2$ as a function of the Hamaker constant of polymer A_p at various degrees of surface coverage of colloidal particles by polymer. The former is a measure of the relative significance of weak flocculation (flocculation due to the collision at which two sites at the collision point are both occupied by polymer) and coagulation (flocculation due to the collision at which two sites at the collision point are both bare), and the latter is a measure of the relative significance of the bridging flocculation (flocculation due to the collision in which one site at the collision point is occupied by polymer and the other is bare) and coagulation. Figure 8 reveals that a fixed surface potential of colloidal particles, both ratios increase with the increase of A_p. At a fixed A_p, both ratios increase with the degree of surface coverage of colloidal particles by polymer.

Conclusion

In summary, the interactions between two colloidal particles in a solution containing polymer molecules are calculated. These interactions play a significant role in the estimation of the collision efficiency of an unstable dispersed system. We find that the sticking probability is extremely sensitive to the variation in the Hamaker constant of a colloidal particle. Since the adsorption of polymer will affect the properties of the surface of a colloidal particle, we conclude that the kinetic behavior of polymer induced flocculation needs to be considered in the evaluation of collision efficiency.

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