

## Electrostatic interaction between a charge-regulated particle and a solid surface in electrolyte solution: effect of cationic electrolytes

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**Abstract:** The effect of cations on the electrostatic interaction between a negative charge-regulated particle and a solid surface of constant negative potential in electrolyte solution is analyzed. Here, we assume that the rate of approach of a particle to a solid surface is faster than that of the dissociation of the ionogenic groups on the surface of particle. In other words, the effect of the time-dependent dissociation of ionogenic groups on the surface of a particle is taken into account. The result of the present study reveals that, although the solid surface is negatively charged, the presence of cations in the suspension medium has a negative effect on the rate of adhesion. The qualitative behaviors in the variation of the interaction force between a particle and a solid surface as a function of separation distance between them predicted by a kinetic model and the corresponding equilibrium model and constant charge density model are entirely different. The rate of approach of a particle to a solid surface is on the order (constant charge density model) > (kinetic model) > (equilibrium model).

**Key words:** Electrostatic interaction – charge-regulated particle – solid surface – electrolyte solution – cationic electrolytes

### Introduction

In the conventional analysis, the evaluation of the electrostatic force between two interacting surfaces is based on the DLVO theory. More often than not, it is assumed that the surfaces are fixed either at constant potential or at constant charge [1, 2]. For a surface bearing with ionizable groups (e.g., biological cells), however, it has been shown that neither the charge density nor the potential remains constant if the interacting surfaces are at ionic equilibrium with the surrounding medium [3–5]. This phenomenon is usually termed as charge regulation, and is interpreted thermodynamically in that the surfaces tend to minimize the total free energy of interaction [6]. On the basis of this charge regulation model, we recently examined the effect of cationic electrolytes on the electrostatic interaction between a particle under charge regulation and a solid surface with constant potential [7, 8]. The result

showed that, although both the solid surface and particle are negatively charged, the presence of cations in the suspension medium reduces the repulsive force between particle and solid surface only if the separation distance between them is greater than a critical value. If the separation distance is smaller than this value, the repulsive force is greater than that for the case when the cations are absent. The numerical calculation reveals that the presence of cationic electrolytes may increase the adhesion time. This is interpreted as the requirement for continuous reequilibration of the ionogenic groups on the surface of particle and the screening out of those overloaded cations in the interacting region between the particle and the solid surface, as the separation distance decreases.

One of the basic assumptions made in our previous analysis is that the rate of adhesion of a particle to a solid surface is sufficiently slow so that electrochemical equilibrium is maintained at

all times during the course of adhesion [7, 8]. This means that the rate of dissociation of the ionogenic groups on the surface of the particle is much faster than that of adhesion. In other words, the charge distribution on the surface of a particle is in a quasi-steady state during the course of adhesion. In a study of the stability of colloid, Overbeek [9] pointed out that the time for the charge adjustment through the double layer around a particle (about  $10^{-6}$  to  $10^{-4}$  s) can be longer than the time involved in Brownian coagulation (about  $10^{-5}$  to  $10^{-7}$  sec). In this case, since the rate of approaching of particle to solid surface is faster than that of the dissociation of the ionogenic groups on the surface of particle, assuming a quasi-steady state for the latter is unrealistic. Apparently, a more general treatment which takes the effect of the time-dependent dissociation of ionogenic groups on the surface of a particle into account is necessary.

In the present study, instead of using the equilibrium model as applied in our previous analysis, the kinetic behavior of the dissociation of ionogenic groups on the surface of a particle is incorporated in the equation governing the interaction force between the particle and the surface. In particular, the effect of cationic electrolytes on the electrostatic force and the adhesion time is examined.

## Analysis

Let us consider the adhesion of a charge-regulated particle onto a solid surface of constant negative potential. For simplicity, only the one-dimensional problem is examined. If there are multivalent cations present in the suspension medium, the distribution of the electrostatic potential  $\phi$  in the electrical double layer is described by the following Poisson-Boltzmann equation [3, 4]:

$$\frac{d^2\psi}{dH^2} = \frac{\tau^2}{2 + (q-1)\eta} [e^\psi - (1-\eta)e^{-\psi} - \eta e^{-q\psi}], \quad (1)$$

where

$$\psi = e\phi/kT \quad (1a)$$

$$H = r/a_c \quad (1b)$$

$$\tau = \kappa a_c \quad (1c)$$

$$\kappa^2 = e^2 \sum Z_i^2 n_i^0 / \epsilon kT \quad (1d)$$

$$\eta = qn_q^0/n \quad (1e)$$

$$n = \sum |Z_i| n_i^0 / 2. \quad (1f)$$

In these expressions,  $e$  is the charge of electron,  $r$  is the separation distance between the particle and the surface,  $a_c$  is the radius of the particle,  $k$  is the Boltzmann constant,  $\epsilon$  and  $T$  are the dielectric constant of solution and the absolute temperature, respectively,  $\eta$  and  $q$  are the fraction of cationic electrolyte in the suspension medium, and the valence of cation, respectively,  $Z_i$  denotes the valence of ion  $i$ ,  $n_i^0$  is the number concentration of ion  $i$  in the bulk liquid phase,  $n$  is the total charge number, and  $\kappa$  is the reciprocal Debye length. Since the solid surface remains at constant potential, the boundary condition associated with Eq. (1) on the solid surface is

$$\psi|_{H=0} = -1. \quad (2)$$

On the particle side, we assume that the surface possesses some acidic groups and some basic groups, and they undergo the dissociation reactions below:



where  $AH$  and  $BH^+$  denote, respectively, the acidic groups and the conjugated acid of the basic groups. If these reactions are at equilibrium during the course of adhesion, the boundary condition on the surface of particle is

$$\left( \frac{d\psi}{dH} \right)_{\text{particle surface}} = \frac{\kappa\tau}{n[2 + (q-1)\eta]} \left[ \frac{[H^+]_s}{K_b + [H^+]_s} S_b^{-1} - \frac{K_a}{K_a + [H^+]_s} S_a^{-1} \right], \quad (5)$$

with

$$[H^+]_s = [H^+]_r \exp(-\psi). \quad (5a)$$

In these expressions,  $[H^+]_s$  and  $[H^+]_r$  denote the acid concentration on the particle surface and that in the bulk liquid phase, respectively,  $K_a$  and  $K_b$  are the dissociation equilibrium constants for Eqs. (3) and (4), respectively,  $S_a^{-1}$  and  $S_b^{-1}$  are the densities of acidic groups and that of basic groups on particle surface, respectively.

On the other hand, if the kinetic behavior of Eqs. (3) and (4) needs to be considered, we assume

$$d[AH]/dt = k_2[A^-][H^+] - k_1[AH] \quad (6)$$

$$d[B]/dt = k_3[BH^+] - k_4[B][H^+]. \quad (7)$$

Here,  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are rate constants, and a symbol with square brackets denotes concentration. If we define the conversions  $X_A$  and  $X_B$  as

$$X_A = 1 - [AH]/[AH]_0 \quad (8)$$

$$X_B = 1 - [BH^+]/[BH^+]_0, \quad (9)$$

where  $[AH]_0$  and  $[BH^+]_0$  are the initial concentrations of  $AH$  and  $BH^+$ , respectively. Equations (6) and (7) can be recast as

$$dX_A/dt = a + bX_A + cX_A^2 \quad (10)$$

$$dX_B/dt = a' + b'X_B + c'X_B^2. \quad (11)$$

In these equations,

$$a = k_1[1 - M_A M_H(1 - X_{Ae})/u] \quad (11a)$$

$$b = -k_1[1 + (M_A + M_H)(1 - X_{Ae})/u] \quad (11b)$$

$$c = -k_1(1 - X_{Ae})/u \quad (11c)$$

$$M_A = [A^-]_0/[AH]_0 \quad (11d)$$

$$M_H = [H^+]_0/[AH]_0 \quad (11e)$$

$$X_{Ae} = 1 - [AH]_e/[AH]_0 \quad (11f)$$

$$a' = k_3[1 - (M_B M'_H(1 - X_{Be})/v)] \quad (11g)$$

$$b' = -k_3[1 + (M_B + M'_H)(1 - X_{Be})/v] \quad (11h)$$

$$c' = -k_3(1 - X_{Be})/v \quad (11i)$$

$$M_B = [B]_0/[BH^+]_0 \quad (11j)$$

$$M'_H = [H^+]_0/[BH^+]_0 \quad (11k)$$

$$X_{Be} = 1 - [BH^+]_0/[BH^+]_0 \quad (11l)$$

$$u = (M_A + X_{Ae})(M_H + X_{Ae}) \quad (11m)$$

$$v = (M_B + X_{Be})(M'_H + X_{Be}), \quad (11n)$$

where  $X_{Ae}$  and  $X_{Be}$  are the equilibrium conversions of  $AH$  and  $BH^+$ , respectively; subscript 0 and  $e$  represent the initial value and the equilibrium value, respectively. Solving Eqs. (10) and (11)

simultaneously, we obtain

$$X_A = \left\{ \sqrt{q_A} \tanh \left[ \left( t - \frac{2}{\sqrt{q_A}} \tanh^{-1} \right. \right. \right. \\ \left. \left. \times \left( \frac{b}{\sqrt{q_A}} \right) \right) - \frac{\sqrt{q_A}}{2} \right] - b \right\} / 2c \quad (12)$$

$$X_B = \left\{ \sqrt{q_B} \tanh \left[ \left( t - \frac{2}{\sqrt{q_B}} \tanh^{-1} \right. \right. \right. \\ \left. \left. \times \left( \frac{b'}{\sqrt{q_B}} \right) \right) - \frac{\sqrt{q_B}}{2} \right] - b' \right\} / 2c' \quad (13)$$

where  $q_A = b^2 - 4ac$  and  $q_B = b'^2 - 4a'c'$ . Note that since both  $a$  and  $a'$  are positive, and  $b$ ,  $b'$ ,  $c$ , and  $c'$  are negative,  $q_A$  and  $q_B$  are both positive. The surface charge density  $\sigma_0$  is

$$\sigma_0 = N_s e(\theta^+ - \theta^-), \quad (14)$$

where

$$\theta^+ = \frac{[BH^+]}{[AH] + [A^-] + [BH^+] + [B]} \\ = \frac{[BH^+]}{N_s} \quad (14a)$$

$$\theta^- = \frac{[A^-]}{[AH] + [A^-] + [BH^+] + [B]} \\ = \frac{[A^-]}{N_s}. \quad (14b)$$

Since  $\theta^+$  and  $\theta^-$  are functions of  $X_A$  and  $X_B$ , respectively, Eq. (14) can be rewritten as

$$\sigma_0 = e[BH^+]_0[(1 - X_B) \\ - M(M_A + X_A)], \quad (15)$$

where  $M = [AH]_0/[BH^+]_0 = M'_H/M_H$ . Therefore, the temporal variation in the surface charge density is described by substituting Eqs. (12) and (13) into Eq. (15). The boundary condition on the particle surface is then

$$\left( \frac{d\psi}{dH} \right)_{\text{particle surface}} = \frac{\kappa\tau[BH^+]_0}{n[2 + (q - 1)\eta]} \\ \times [1 - X_B - M(M_A + X_A)]. \quad (16)$$

In summary, if the rate of dissociation of the ionogenic groups on the surface of a particle is

much faster than that of adhesion, Eq. (1) needs to be solved subject to the boundary conditions Eqs. (2) and (5). On the other hand, if the rate of dissociation of the ionogenic groups on the surface of the particle is much slower than that of adhesion, Eq. (1) needs to be solved subject to the boundary conditions Eqs. (2) and (16). Here, we assume that the time scale for the migration of charges on the surface of a particle is much greater than that for the relaxation of the ions in the electrical double layer. In other words, the electrolytes in the double layer reaches Boltzmann distribution much faster than the distribution of charges on the particle surface to reach equilibrium. This assumption is realistic for conditions often encountered in practical applications (Appendix A).

The temporal variation in the distance between the particle and the solid surface is governed by Newton's second law of motion. The interaction electrostatic force between the particle and the solid surface,  $F$ , is described by

$$\begin{aligned} \frac{F}{nkT} = & (e^\psi - 1) + (1 - \eta)(e^{-\psi} - 1) \\ & + \frac{n}{q}(e^{-q\psi} - 1) \\ & - \left(\frac{d\psi}{dH}\right)^2 \left[ \frac{1 + (q-1)\eta/2}{\tau^2} \right]. \end{aligned} \quad (17)$$

The electrostatic potential  $\phi_{DL}$  can be evaluated by

$$\phi_{DL} = 2\pi a_c^3 \int_H^\infty \int_1^\infty \frac{F(l')}{kT} dl' dl. \quad (18)$$

The van der Waals potential between the particle and the solid surface  $\phi_{VDW}$  is evaluated by

$$\phi_{VDW} = \frac{A_{132}}{3kT} \left[ \frac{1}{2} \ln \left( \frac{H+2}{H} \right) - \frac{(H+1)}{H(H+2)} \right], \quad (19)$$

where  $A_{132}$  is the Hamaker constant for the system under consideration. If the effect of hydrodynamic retardation is neglected, the total interaction potential between the particle and the solid surface,  $\phi_{TOT}$ , is

$$\phi_{TOT} = \phi_{DL} + \phi_{VDW}. \quad (20)$$

Applying Newton's second law of motion yields

$$\frac{d\phi_{TOT}}{dH} = \frac{4\pi a_c^5 \rho}{3kT} \frac{d^2 H}{dt^2}, \quad (21)$$

where  $\rho$  is the density of particle. The algorithm for the solution of Eqs. (1) and (21) is summarized in Appendix B.

## Result and discussion

Figure 1 shows the temporal variation in the distance between a particle and a solid surface for the case when the ionic strength of the system is low. The corresponding variation in the interaction force per unit area between the particle and the surface is illustrated in Fig. 2. Figure 1 reveals that the presence of cations in the suspending medium has the effect of increasing the adhesion time. The greater the concentration of cations, the greater the adhesion time. The same conclusion is drawn for the equilibrium model [7, 8].

Figure 2 suggests that the presence of cations in the suspending medium has the effect of reducing the electrostatic repulsive force if the separation distance is greater than a critical value (about  $H = 1.6 \times 10^{-2}$ ). However, if the separation distance is less than this critical value, the presence of cations in the suspending medium will increase the repulsive force between particle and surface. This has a negative effect on the adhesion of the particle. One plausible interpretation for this behavior is the screening out of those overloaded cations in the interaction region between particle and solid surface as the separation distance decreases [5, 7, 8]. The existence of a critical distance can be explained as follows. Suppose that there exists a small amount of cations in the suspension medium. The electrical neutrality requires that the degree of dissociation of the acid sites on the cellular surface decreases with the separation distance between two surfaces. As this distance decreases with time, the divalent cations in the interaction region gradually become overloaded for the neutralization of the negative charges on the cellular surface. If the separation distance is less than a critical value, the osmotic pressure required to screen out those overloaded cations will be greater than that for the case when the cations are absent. As can be seen from Fig. 2,

increasing the concentration of cations in the suspending medium has the effect of shifting the curve upwards and to the left. This means that the maximum repulsive force experienced by a particle in a suspending medium with lower

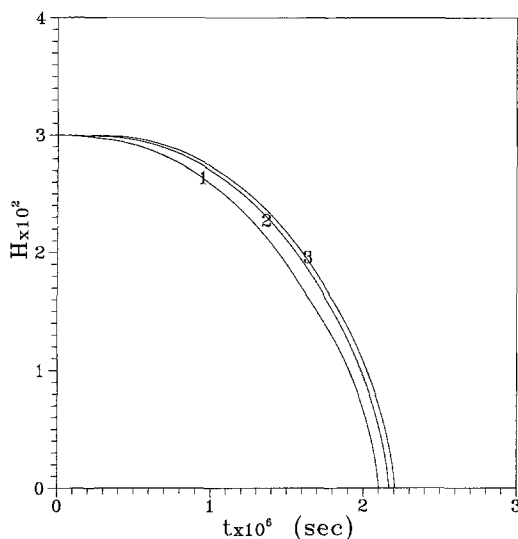


Fig. 1. Temporal variation in the distance between a particle and a solid surface. Key:  $a_c = 4 \times 10^{-7}$  m,  $A_{132} = 5 \times 10^{-21}$  J,  $\rho = 1$  g/cm<sup>3</sup>,  $\epsilon_r = 78$ ,  $T = 298^\circ\text{K}$ ,  $n = 6.02 \times 10^{23}$  charge/m<sup>3</sup>,  $k_1 = k_3 = 1.5 \times 10^4$  s<sup>-1</sup>,  $S_a^{-1} = S_b^{-1} = 6 \times 10^6$  groups/m<sup>2</sup>,  $X_{Ac} = 0.25$ ,  $[BH^+]_0 = 3 \times 10^{16}$  groups/m<sup>2</sup>,  $X_{Be} = 0.5$ ,  $M'_H = 1$  ( $M = 1$ ),  $M_A = M_B = M_H = 1$ . Curve 1:  $\eta = 0$ ; curve 2:  $\eta = 1/2$ ,  $q = 2$ ; curve 3:  $\eta = 2/3$ ,  $q = 2$ .

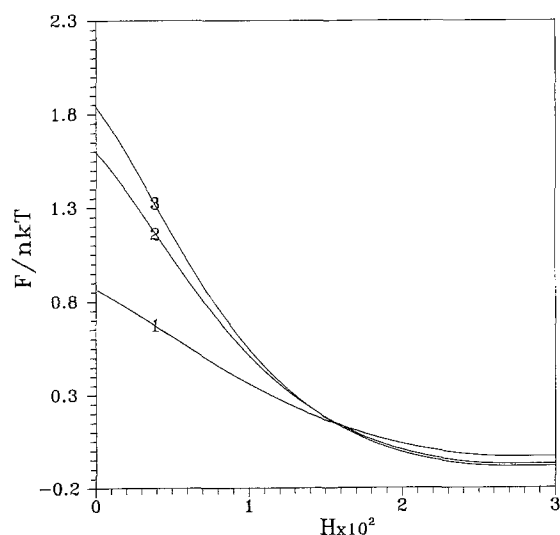


Fig. 2. Variation in the interaction force per unit area between the particle and the solid surface for the case of Fig. 1.

concentration of cations is smaller than that experienced by the particle in a suspending medium with higher concentration of cations. Also, the higher the concentration of cations, the less the repulsive force if the separation distance is greater than the critical value, and the greater the repulsive force if the separation distance is smaller than the critical value.

A comparison between the present kinetic model and the corresponding equilibrium model and constant charge density model in the temporal variation of the distance between a particle and a solid surface is presented in Fig. 3. The corresponding comparison in the interaction force per unit area between the particle and the surface is illustrated in Fig. 4. In the case of constant charge density model, the surface charge density is chosen as the arithmetic mean of the initial and the equilibrium charge densities of the kinetic model. Figure 3 indicates that the rate of approaching of a particle to a solid surface is in the order (constant charge density model) > (kinetic model) > (equilibrium model). Figure 4

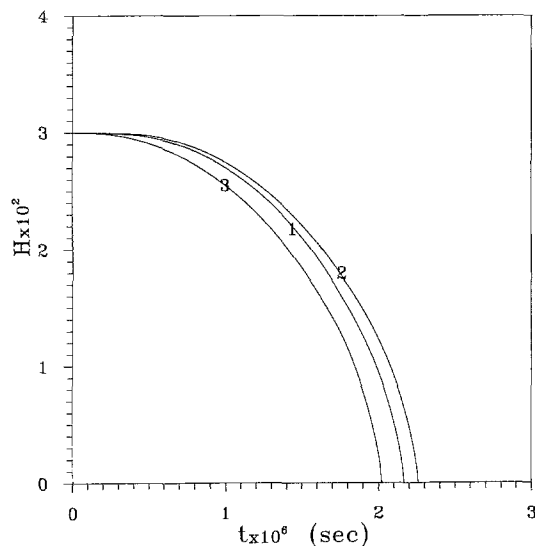


Fig. 3. A comparison between the present kinetic model and the corresponding equilibrium model and constant surface charge density model in the temporal variation in the distance between a particle and a solid surface for the case  $[H^+]_r = 10^{-7}$  M. Key: same as that of Fig. 1. Curve 1 (kinetic model) is the same as curve 2 of Fig. 1. In curve 2 (equilibrium model),  $pKa = 4$ ,  $pKb = 16$ ,  $\eta = 1/2$ ,  $q = 2$ . In the case of constant charge density model (curve 3)  $\eta = 1/2$ ,  $q = 2$ ,  $(d\psi/dH) = -1.7756$  at particle surface.

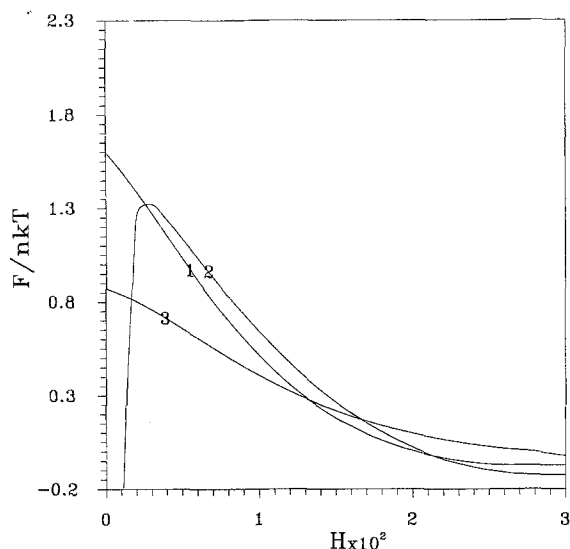


Fig. 4. A comparison between the present kinetic model and the corresponding equilibrium model in the variation of the interaction force per unit area between the particle and the solid surface for the case of Fig. 3. Key: same as that of Fig. 1. Curve 1 (kinetic model) is the same as curve 2 of Fig. 2. In curve 2 (equilibrium model),  $pKa = 4$ ,  $pKb = 16$ ,  $\eta = 1/2$ ,  $q = 2$ .

reveals that if the dimensionless separation distance between a particle and a solid surface is smaller than  $3 \times 10^{-3}$  or greater than  $2.1 \times 10^{-2}$ , the repulsive force obtained by the kinetic model is greater than that obtained by the corresponding equilibrium model. If the dimensionless separation distance is in the range  $3 \times 10^{-3}$  to  $2.1 \times 10^{-2}$ , the repulsive force obtained by the kinetic approach is smaller than that obtained by the corresponding equilibrium model. This may be due to that at a separation distance in this range, the degree of dissociation of the acid sites on the particle surface for the case of curve 1 is smaller than that for the case of curve 2. Therefore, the neutralization capacity for the divalent cations for the case of curve 1 is smaller than that for the case of curve 2. In this case, the osmotic pressure required to screen out those overloaded cations for the case of curve 1 becomes smaller than that for the case of curve 2. Note that the equilibrium model predicts that the electrostatic repulsive force increases with the decrease of the separation distance, passes through a maximum, and then decreases rapidly. If the dimensionless separation distance is less than about  $3 \times 10^{-3}$ , the inter-

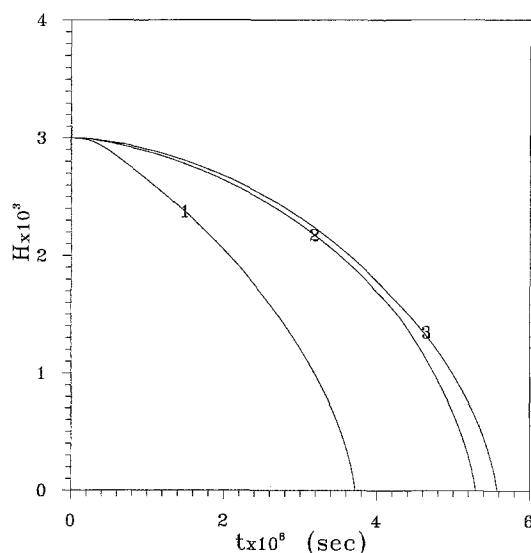


Fig. 5. Temporal variation in the distance between a particle and a solid surface. Key:  $a_c = 4 \times 10^{-7}$  m,  $A_{132} = 5 \times 10^{-21}$  J,  $\rho = 1$  g/cm<sup>3</sup>,  $\epsilon_r = 78$ ,  $T = 298^\circ\text{K}$ ,  $n = 6.02 \times 10^{26}$  charge/m<sup>3</sup>,  $k_1 = k_3 = 2 \times 10^4$  s<sup>-1</sup>,  $S_a^{-1} = 8 \times 10^{16}$  groups/m<sup>2</sup>,  $S_b^{-1} = 1 \times 10^{12}$  groups/m<sup>2</sup>,  $X_{Ae} = 0.2$ ,  $[BH^+]_0 = 5 \times 10^{11}$  groups/m<sup>2</sup>,  $X_{Be} = 0.4$ ,  $M'_H = 8 \times 10^4$  ( $M = 8 \times 10^4$ ),  $M_A = M_B = M_H = 1$ . Curve 1:  $\eta = 0$ ; curve 2:  $\eta = 1/2$ ,  $q = 2$ ; curve 3:  $\eta = 2/3$ ,  $q = 2$ .

action force changes from repulsive to attractive. This means that if a particle is close enough to a surface, it will experience an attractive force, and this leads to an irreversible adhesion. Similar behavior is not observed for the kinetic model. The reversal in the sign of the interaction force in the equilibrium model is due to that, if the separation distance is smaller than  $3 \times 10^{-3}$ , the first term on the righthand side of Eq. (5) is greater than the second term, and the differential surface potential becomes positive. This will induce an attractive force. On the other hand, the kinetic model does not predict this regulation behavior. A comparison between curves 1 and 3 reveals that if the dimensionless separation distance is smaller than  $1.3 \times 10^{-2}$ , the repulsive force obtained by the kinetic model is greater than that obtained by the corresponding constant charge density model. On the other hand, if the dimensionless separation distance is greater than  $1.3 \times 10^{-2}$ , the repulsive force obtained by the kinetic approach is smaller than that obtained by the corresponding constant charge density model.

Figure 5 shows the temporal variation in the distance between a particle and the solid surface

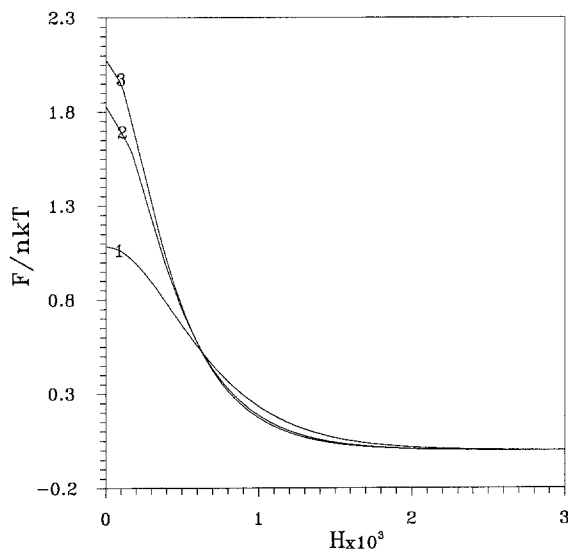


Fig. 6. Variation in the interaction force per unit area between the particle and the solid surface for the case of Fig. 5.

for the case when the ionic strength of the system is high. The corresponding variation in the interaction force per unit area between the particle and the solid surface is illustrated in Fig. 6. A comparison between the kinetic model and the corresponding equilibrium model and constant charge density model in the temporal variation of the distance between a particle and a solid surface is presented in Fig. 7. The corresponding comparison in the interaction force per unit area between the particle and the solid surface is illustrated in Fig. 8. Similar conclusions to those drawn from Figs. 1 through 4 can be obtained from Figs. 5 through 8.

## Conclusion

The dynamic behavior of the adhesion of a charge-regulated particle to a solid surface of constant potential is investigated. The kinetic behavior of the dissociation of ionogenic groups on the surface of a particle is incorporated in the equation governing the interaction force between the particle and the surface. The numerical analysis leads to the following results: a) For a fixed ionic strength, the adhesion time increases with the increase in the concentration of multivalent cations in the suspending medium. b) The

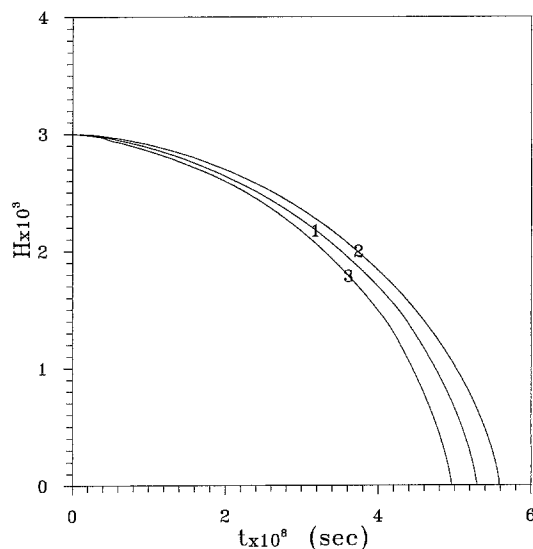


Fig. 7. A comparison between the present kinetic model and the corresponding equilibrium model and constant charge density model in the temporal variation of the distance between a particle and a solid surface for the case  $[H^+]_r = 10^{-7}$  M. Key: same as that of Fig. 5. Curve 1 (kinetic model) is the same as curve 2 of Fig. 5. In curve 2 (equilibrium model),  $pKa = 3$ ,  $pKb = 12$ ,  $\eta = 1/2$ ,  $q = 2$ . In the case of constant charge density model (curve 3)  $\eta = 1/2$ ,  $q = 2$ ,  $(d\psi/dH) = -0.4836$  at particle surface.

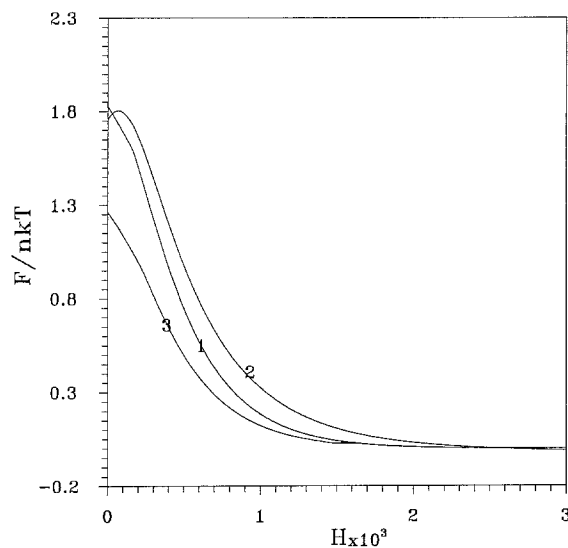


Fig. 8. A comparison between the present kinetic model and the corresponding equilibrium model in the variation of the interaction force per unit area between the particle and the solid surface for the case of Fig. 7. Key: same as that of Fig. 5. Curve 1 (kinetic model) is the same as curve 2 of Fig. 6. In curve 2 (equilibrium model),  $pKa = 3$ ,  $pKb = 12$ ,  $\eta = 1/2$ ,  $q = 2$ .

presence of cations in the suspending medium has the effect of reducing the electrostatic repulsive force only if the separation distance is greater than a critical value. The reverse is true if the separation distance is less than this critical value. c) The rate of approaching of a particle to a solid surface is on the order (constant charge density model)  $>$  (kinetic model)  $>$  (equilibrium model). d) No general rule is obtained for the relative magnitudes of the repulsive force between a particle and a surface calculated by a kinetic model and the corresponding equilibrium model and constant charge density model.

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#### Appendix A

In a study of the rate of ionic equilibrium in the electrical double layer and that of Brownian coagulation, Overbeek (9) suggests that the relaxation time of ions in double layer,  $t_{\text{relax}}$ , can be estimated by

$$t_{\text{relax}} = \frac{(1/\kappa)^2}{2D_i}, \quad (\text{A1})$$

where  $D_i$  denotes the diffusivity of ions. For a 1:1, 5 mM electrolyte solution,  $t_{\text{relax}}$  is about  $10^{-8}$  s (9). The time scale for the migration of charges on a colloidal surface,  $t_{\text{migrat}}$ , can be estimated by the ratio of surface charge density,  $\sigma$ , and charge exchange current density,  $i_0$ , i.e.,

$$t_{\text{migrat}} = \sigma/i_0. \quad (\text{A2})$$

For a typical colloidal particle,  $i_0$  is in the range  $10^{-10}$  to  $1 \text{ A.cm}^{-2}$ . Since for a biological cell the resistance for the distribution of charges on its surface is usually greater than that for a colloidal particle, the value of  $i_0$  is even smaller. The current density on cell surface is in the range  $10^{-10}$  to  $10^{-2} \text{ A.cm}^{-2}$ .

Based upon the above discussion, the ratio ( $t_{\text{migrat}}/t_{\text{relax}}$ ) is in the range  $2 \times 10^3$  to  $2 \times 10^{11}$  for an electrolyte concentration of  $10^{-3} \text{ M}$ , and is in

the range  $2 \times 10^6$  to  $2 \times 10^{14}$  for an electrolyte concentration of  $1 \text{ M}$ .

#### Appendix B

The temporal variation in the distance of a particle and the variation of the interaction force between the particle and the solid surface are calculated through the numerical procedure below:

**Step 1:** At a specific time  $t_k$ , the differential boundary condition on the particle surface,  $\psi'_p$ , is calculated by Eq. (16).

**Step 2:** Equation (1) is solved numerically subject to the boundary condition described by Eq. (2) and an estimated differential potential on the solid surface,  $\psi'_{0g}$ .

**Step 3:** The position at which the estimated differential surface potential,  $\psi'_c$ , and  $\psi'_p$  are close enough is defined as  $x_1$ . If such an  $x_1$  does not exist, return to step (2) with a newly estimated  $\psi'_{0g}$ .

**Step 4:** The interaction electrostatic force between the particle and the solid surface is calculated by Eq. (17), and the result is substituted into Eq. (18) to evaluate  $\phi_{\text{DL}}$ . Add  $\phi_{\text{DL}}$  and the van der Waals potential between the particle and the solid surface at  $x_1$ ,  $\phi_{\text{VDW}}$  to obtain the total interaction potential.

**Step 5.** Solving Eq. (21!) subject to the initial conditions  $H = H_{k-1}$  and  $v = v_{k-1}$  at  $t = t_{k-1}$ , we obtain the distance  $H = x_2$  at  $t = t_k$ . Here, we assume that  $H_0 = \delta$  and  $v_0 = 0$  at  $t_0 = 0$ ,  $\delta$  being the position of the secondary minimum of the total interaction potential between the particle and the solid surface, and  $v_i$  is the velocity of particle. If  $x_1$  and  $x_2$  are inconsistent, return to step (2) with a newly estimated  $\psi'_{0g}$ . The procedure is repeated until the difference between  $x_1$  and  $x_2$  is smaller than a prespecified value.

**Step 6:** The time is advanced by  $t_{k+1} = t_k + \Delta t$ ,  $\Delta t$  being a prespecified time interval, and the procedure is repeated by returning to step (1).

The numerical procedure for the case when the dissociation of the ionogenic groups on the surface of a particle is at equilibrium is similar to that described above except that Eq. (16) is replaced by Eq. (5).

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