Effect of Cationic Electrolytes on the Deposition Rate of Brownian Particles

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Introduction

In their early work, Prieve and Ruckenstein (1974) calculated the rates of deposition of Brownian particles onto a spherical collector, as a function of Peclet number, aspect ratio and dimensionless van der Waals forces. This was accomplished with the aid of the convective-diffusive equation and without considering the double layer repulsion forces. Most importantly, the boundaries of regions where van der Waals forces or Brownian motion may be neglected were well established in terms of the above dimensionless groups. At a later time, in the presence of various shapes of interaction profiles, Rajagopalan and Kim (1981) provided an extensive analysis of deposition rates of particles for a wide range of Peclet numbers. [For details, see Hirtzel and Rajagopalan (1985) Adamczyk (1989).]

In a recent study, the author (1989a,b) examined the effect of multivalent electrolytes upon the electrostatic interaction force between a colloidal particle bearing with ionogenic groups and a collector surface with either constant potential or constant charge. This was based on the charge regulation models developed by Ninham and Parsegian (1971), and Prieve and Ruckenstein (1977, 1978). From the results of numerical computations, it was discovered that the presence of these cations in the suspension medium decreases the electrostatic repulsion force only when the separation distance between particle and collector surface is greater than a critical value. If the separation distance is smaller than this critical value, the repulsive force is greater than that if the cations are absent. This is interpreted as the requirement of continuous reequilibration of the ionogenic groups on the particle surface, and the screening out of those overloaded cations in the interaction region as the separation distance decreases (Chang, 1989a,b).

However, in the author's previous study, efforts were always made on the analysis of the effect of cations on the electrostatic repulsion force between particle and collector surface. Neither the van der Waals forces nor the hydrodynamic forces were considered. Also, there is a lack of a systematic analysis on the variation of deposition rate of particles in response to the changes of the concentration of cationic electrolytes in the suspension medium. Therefore, in this note we investigate the effect of the presence of cationic electrolytes in the suspension medium on the rates of deposition of Brownian particles onto a spherical collector. This is done with the aid of transport equations developed by Prieve and Ruckenstein (1974) and the charge regulation model.

Theoretical Formalism

Analogous to the model established by Prieve and Ruckenstein (1974), for the spherical collector system, the dimensionless particle deposition equations can be written as:

$$\frac{2R}{Pe} f_1(H) \frac{\partial^2 C}{\partial H^2} + \left\{ \frac{2R}{Pe} \left[\frac{df_1(H)}{dH} + \frac{2f_1(H)}{(R+H+1)} \right] - v \right\} \frac{\partial C}{\partial H} - \left[\frac{2}{(R+H+1)} \left(V + \frac{\partial U}{\partial \theta} \right) + \frac{\partial V}{\partial H} \right] C = \frac{U}{(R+H+1)} \frac{\partial C}{\partial \theta} \quad (1)$$

with

$$U = \left[\frac{3}{2} R^2 + (H+1) \left(\frac{9}{4} R + H + 1 \right) \right] \frac{(H+1) f_3(H) \sin\theta}{(R+H+1)^3} \quad (2a)$$

and

$$V = -(H+1)^2 \left(\frac{3}{2} R + H + 1 \right) \frac{f_1(H) f_2(H) \cos\theta}{(R+H+1)^3} - 2 \left(\frac{R}{Pe} \right) f_1(H) \frac{\partial \phi}{\partial H} \quad (2b)$$

The associated boundary conditions are:

$$C(H=0, \theta) = 0 \quad (3a)$$

$$C(H=\infty, \theta) = 1 \quad (3b)$$

and

$$\left. \frac{\partial C}{\partial \theta} \right|_{\theta=0} = 0 \quad (3c)$$

In Eq. 1, Pe is the Peclet number defined as the ratio of convective force to diffusion force, $f_1(H)$, $f_2(H)$ and $f_3(H)$ are the universal hydrodynamic correction factors, and they are given in tabulated forms by Brenner (1961), Goren and O'Neill (1971), and Goldman et al. (1967).

In the matter of neglecting the gravity force, the $\phi(H)$ in Eq. 2b is the dimensionless interaction potential exerted on the particles, and which is the sum of the van der Waals and electrostatic repulsion contributions:

$$\phi(H) = \phi_{vdw}(H) + \phi_{DL}(H) \tag{4}$$

where $\phi_{vdw}(H)$ is the unretarded van der Waals potential, which can be written as (Hamaker, 1937):

$$\phi_{vdw}(H) = \frac{Ad}{3}\left[\frac{1}{2}\ln\left(\frac{H+2}{H}\right) - \frac{(H+1)}{H(H+2)}\right] \tag{5}$$

with

$Ad = A/kT$, A is the Hamaker constant.

The $\phi_{DL}(H)$ in Eq. 4 is the repulsion energy between a particle with ionogenic groups on its surface and the collector. Applying with Derjaguin's approximation (Derjaguin, 1934), $\phi_{DL}(H)$ can be expressed as:

$$\phi_{DL}(H) = \frac{2\pi R a_p}{(1+R)}\int_H^\infty \int_\ell^\infty F(\ell')\, d\ell'\, d\ell \tag{6}$$

where $F(\ell')$ is the repulsive force per unit area exerted between two interacting surfaces separated by a distance ℓ'. Suppose that the approaching of particle to the surface of collector is sufficiently slow so that electrochemical equilibrium is always maintained during the whole deposition period, the $F(\ell')$ of Eq. 6 can be written as (Ninham and Parsegian, 1971):

$$F = -\left(\frac{\partial\psi}{\partial H}\right)^2 \frac{1}{\tau^2} + [(e^{\psi} - 1) + (1-\eta)(e^{-\psi} - 1) + \frac{\eta}{q}(e^{-q\psi} - 1)] \tag{7}$$

with

$$\tau = \kappa a_p$$

where ψ is the dimensionless regulated potential on the particle surface, η is the fraction of cationic electrolytes present in the suspension medium, and q is the valence for cations. Hence, the electrostatic repulsion force, F, acting between two approaching surfaces is composed of two contributions: the Maxwell stress (first term on the right hand side of Eq. 7) and the osmotic pressure (the remaining terms on the right hand side of Eq. 7) caused by the presence of cations in the suspension medium (Prieve and Ruckenstein, 1977).

Assume that the surface charge density of the particle (with N_s surface groups per unit area) is established by simultaneously considering the following dissociation equilibria (Healy et al., 1980):

$$AH_2^+ \rightleftarrows AH + H^+ \tag{8a}$$

$$AH \rightleftarrows A^- + H^+$$

which are characterized by the dissociation constants:

$$K_+ = \frac{[AH][H^+]_s}{[AH_2^+]} \text{ and } K_- = \frac{[A^-][H^+]_s}{[AH]} \tag{8b}$$

Then, the ψ shown in Eq. 7 can be described by the following nonlinear Poisson-Boltzmann equation as:

$$\frac{d^2\psi}{dH^2} = \frac{\tau^2}{2}[e^{\psi} - (1-\eta)\,e^{-\psi} - \eta e^{-q\psi}] \tag{9}$$

The boundary condition of ψ on the particle surface is:

$$\frac{d\psi}{dH} = \frac{\kappa\tau}{2n}\left[\frac{\frac{[H^+]_s}{K_+} - \frac{K_-}{[H^+]_s}}{1 + \frac{[H^+]_s}{K_+} + \frac{K_-}{[H^+]_s}}\right] N_s \tag{10}$$

with

$$[H^+]_s = [H^+]_r \exp(-\psi)$$

and the ψ value on the collector surface is assumed to keep at constant potential:

$$\psi|_{H=0} = -1 \tag{11}$$

Finally, the dimensionless deposition rate of particles onto the spherical collector can be expressed through the form of Sherwood number as (Prieve and Ruckenstein, 1974):

$$Sh = \frac{1}{2}\left[1 + \frac{(H+1)}{R}\right]^2 \int_0^\pi \left[2R\cdot f_1(H)\cdot\frac{\partial C}{\partial H} - Pe\cdot V\cdot C\right] \cdot \sin\theta\, d\theta \tag{12}$$

Inspection of the dimensionless deposition equations developed above reveals that four dimensionless groups—*Pe*, *Ad*, *R* and *F*—have the effects on the deposition rate of particles, and these effects will be discussed in the following numerical example. Numerical solutions of F in Eq. 7 and Sh in Eq. 12 can be obtained by using the Runge-Kutta-Gill technique and the Crank-Nicolson finite difference method, respectively, which were well described in the thesis of Prieve (1975).

Numerical Example

For illustration, the deposition behavior of TiO_2 particles onto the spherical collector is examined. The relevant physical parameters of TiO_2 reported were $a_p = 0.1$ μm, $N_s = 12.0 \times 10^{14}$/cm, p$K_- = 3.8$, p$K_+ = 7.8$, and $\kappa^{-1} = 30$ Å (Healy et al., 1980). In the numerical simulation, the value of q is assumed as 2 (divalent cations) and pH of the suspension medium is assumed at 7.0.

Results and Discussion

The variation of the electrostatic interaction force between particle and collector surface as a function of the separation distance is shown in Figure 1. Analogous to the author's previous work (Chang, 1989a,b), it is worth noting that the presence of cations in the suspension medium has the effect of decreasing the repulsion force if the separation distance is greater than a critical value at $H = 0.048$. However, if the separation distance is smaller than this critical value, the presence of cations in the suspension medium will increase the repulsive force between particle and collector surface.

The existence of this critical distance can be explained as

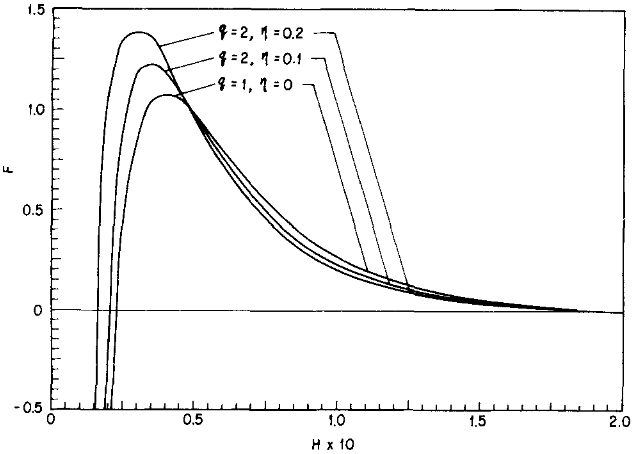

Figure 1. Dimensionless electrostatic interaction force between TiO_2 particle and spherical collector with constant potential.

It is a function of dimensionless separation distance.

follows: considering that there is a small amount of divalent cations present in the suspension medium, as the separation distance between two surfaces is decreased slowly enough to allow continuous reequilibration on the particle surface, the dissociation degree of acid sites on the particle surface is also decreased. Hence, the divalent cations in the interaction region of suspension medium will gradually become overloaded in neutralizing the negative charge on the particle surface. Finally, when the distance is smaller than the critical value shown in Figure 1, the osmotic pressure required to screen out these overloaded cations begins to raise the repulsion force from that of the case with no divalent cation present.

Corresponding to Figure 1, the total interaction energy curve vs. the separation distance is plotted in Figure 2 with Ad = 1.0 and R = 2,000, with the aid of Eqs. 4, 5 and 6. It can be found that the presence of divalent cation causes a higher primary maximum than in its absence. The height of primary maximum can be further increased if the concentration of divalent cation is increased from $\eta = 0.1$ to $\eta = 0.2$. Meanwhile, the energy curves shown in Figure 2 exhibit a large primary maximum and a negligible secondary minimum, which are similar to the type I curve in the article of Rajagopalan and Kim (1981). Under this condition, the deposition rate of particles is determined primarily by the height of the potential barrier, the magnitude of aspect ratio, and the strength of convective force (represented by the Peclet number).

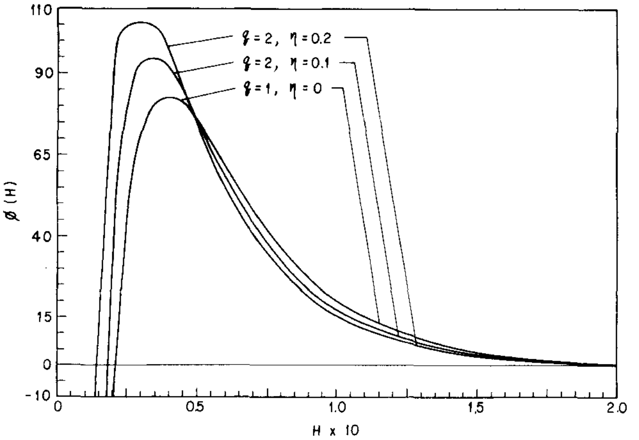

Figure 2. Dimensionless total interaction energy between TiO_2 particle and spherical collector with constant potential.

It is a function of dimensionless separation distance, at which Ad = 1.0 and R = 2,000.

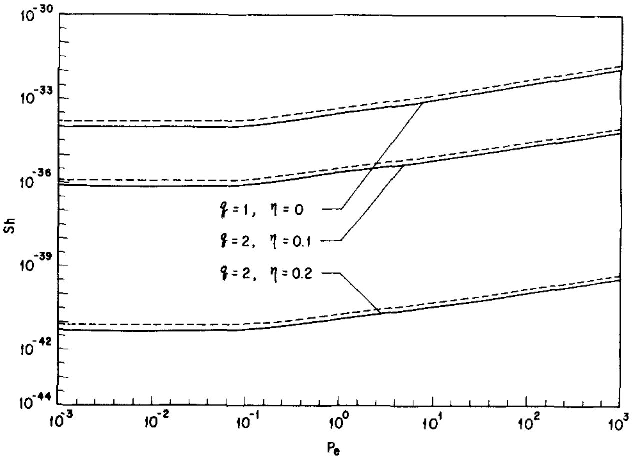

Figure 3. Effect of changes in concentration of divalent cations on deposition rates of TiO_2 particles for different Peclet numbers at Ad = 1.0.

———, at R = 2,000; - - -, at R = 1,000.

An example of investigating the effect of Peclet number on the deposition rate of particles at Ad = 1.0 and R = 2,000 is shown by the solid lines in Figure 3. For the situation where there is no divalent cation present in the suspension medium (q = 1 and η = 0.0 in Figure 3), because of the repulsive force existing between two interacting surfaces, the values of computed Sherwood numbers are quite lower than that of Levich-Lighthill equation $Sh = 0.995\,(Pe)^{1/3}$ (Levich, 1962, Lighthill, 1950). The increase in the Peclet number within the range $10^{-3} - 10^{-1}$ does not affect the computed Sh values. This means that the determining step of particle deposition is the diffusion of particles against the repulsive energy barrier. For $Pe > 0.1$, the hydrodynamic forces, which the fluid imports on the particles, become increasingly important and causes the deposition rates of particles to increase. When there is a small amount of divalent cation present in the suspension medium (q = 2 and η = 0.1 in Figure 3), the deposition rate of particles is reduced in comparison with the situation where there is no divalent cation present. A similar result is observed in Figure 3 if the concentration of divalent cations is increased from η = 0.10 to η = 0.20. This reduction of particle deposition rate can be explained by the effect of the increased height of primary maximum caused by the presence of divalent cations as shown in Figure 2. Considering the effect of aspect ratio, because of the value of $\phi_{DL}(H)$ in Eq. 6 increases with increase of R, Figure 3 reveals that the deposition rate of particles increases with the decrease of the magnitude of aspect ratio.

Similar results are observed at Figure 4, at which the computed Sherwood number is plotted vs. the Ad parameter at Pe = 100. The greater the concentration of cations, the smaller the deposition rate of particles. Also, the deposition rate increases with the decrease of the magnitude of aspect ratio. Figure 4 shows that the deposition rate of particles is extremely

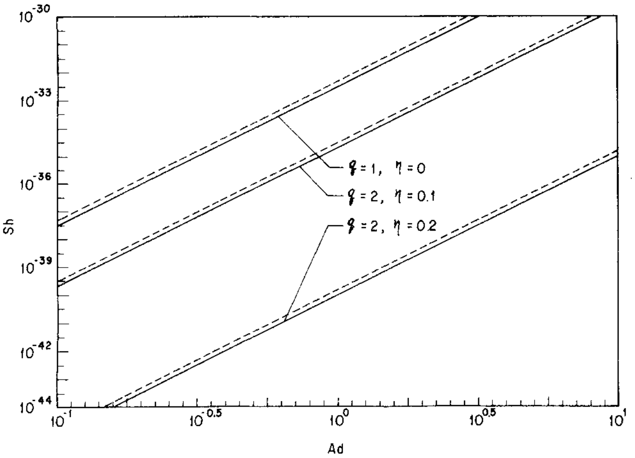

Figure 4. Effect of changes in concentration of divalent cations on deposition rates of TiO_2 particles for different *Ad* parameters at *Pe* = 100.

———, at $R = 2{,}000$; - - -, at $R = 1{,}000$.

sensitive to the values of *Ad* parameter. Small increases in the value of *Ad* produce large increases in the value of *Sh*.

Acknowledgement

The authors greatly appreciate the financial support received from the National Science Council of the Republic of China, Research Grants No. NSC-78-0421-E029-02Z.

Notation

a = radius of collector, cm
a_p = radius of particle, cm
A = Hamaker constant, erg
Ad = A/kT
c = local concentration of particles, particles/cm^3
c_∞ = concentration of particles far from the collector, particles/cm^3
C = c/c_∞
F = dimensionless interaction force acting between particle and collector per nkT
f_1 = correction factor for effect of wall proximity on radial particle mobilities
f_2, f_3 = universal functions used to relate particle and fluid velocities
h = minimum separation distance between particle and collector surface, cm
H = h/a_p
$[H^+]_r$ = hydrogen ion concentration in the suspending medium, mol/dm^3
$[H^+]_s$ = hydrogen ion concentration on the particle surface, mol/dm^3
k = Boltzmann's constant, erg/K
K_+, K_- = dissociation constants for the amphoteric surface of TiO_2 defined in Eq. 8
n = ionic strength in the suspending medium, ions/cm^3
N_s = ionogenic groups on the particle surface, groups/cm^2
Pe = Peclet number
q = valence of cationic electrolytes
R = aspect ratio, $R = a/a_p$
Sh = Sherwood number
T = absolute temperature, K
U = dimensionless angular particle velocity
V = dimensionless radial particle velocity

Greek letters

η = fraction of cationic electrolytes in the suspending medium, $0 \leq \eta \leq 1$
θ = angular position of particle center
κ = reciprocal of Debye length, cm^{-1}
τ = κa_p
ℓ = distance between two plate surfaces in Derjaguin's model
ϕ = dimensionless total interaction energy between particle and collector surface
ϕ_{vdw} = dimensionless unretarded van der Waals potential between particle and collector surface
ϕ_{DL} = dimensionless double-layer interaction potential between particle and collector surface
ψ = dimensionless electrostatic potential between particle and collector surface

Literature Cited

Adamczyk, Z., "Particle Deposition from Flowing Suspensions," *Colloids and Surfaces*, **39**, 1 (1989).

Brenner, H., "The Slow Motion of a Sphere through a Viscous Fluid Towards a Plane Surface," *Chem. Eng. Sci.*, **16**, 242 (1961).

Chang, Y. I., "Divalent Cations Can Increase Cell-Substrate Repulsion at Small Distances," *Colloids and Surfaces*, **41**, 245 (1989a).

Chang, Y. I., "The Effect of Cationic Electrolytes on the Electrostatic Behavior of Cellular Surfaces with Ionizable Groups," *J. Theor. Biol.*, **139**, 561 (1989b).

Derjaguin, B. V., "Untersuchungen uber die Reibung und Adhusion," *Kolloid Z.*, **69**, 155 (1934).

Goldman, A. J., R. G. Cox, and H. Brenner, "Slow Viscous Motion of a Sphere Parallel to a Plane Wall: I. Motion through a Quiescent Fluid," *Chem. Eng. Sci.*, **22**, 637 (1967).

Goren, S. L., and M. E. O'Neill, "On the Hydrodynamic Resistance to a Particle of a Dilute Suspension When in the Neighborhood of a Large Obstacle," *Chem. Eng. Sci.*, **26**, 325 (1971).

Hamaker, H. C., "The London-van der Waals Attraction between Spherical Particles," *Physica*, **4**, 1058 (1937).

Healy, T. W., D. Chan, and L. R. White, "Colloidal Behavior of Materials with Ionizable Group Surfaces," *Pure Appl. Chem.*, **52**, 1207 (1980).

Hirtzel, C. S., and R. Rajagopalan, *Colloidal Phenomena: Advanced Topics*, Noyes Pub., Park Ridge, NJ (1985).

Levich, V. G., *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, NJ (1962).

Lighthill, M. J., "Contributions to the Theory of Heat Transfer Through a Laminar Boundary Layer," *Proc. Royal Soc.*, **A202**, 359 (1950).

Ninham, B. W., and V. A. Parsegian, "Electrostatic Potential between Surfaces Bearing Ionizable Groups in Ionic Equilibrium with Physiologic Saline Solution," *J. Theor. Biol.*, **31**, 405 (1971).

Prieve, D. C., "Rate of Deposition of Brownian Particles under the Action of London and Double-Layer Forces," PhD. Diss., Univ. of Delaware (1975).

Prieve, D. C., and E. Ruckenstein, "Effect of London Forces upon the Rate of Deposition of Brownian Particles," *AIChE J.*, **20**, 1178 (1974).

Prieve, D. C., and E. Ruckenstein, "Role of Surface Chemistry in Particle Deposition," *J. Colloid Interf. Sci.*, **60**, 337 (1977).

Prieve, D. C., and E. Ruckenstein, "The Double Layer Interaction between Dissimilar Ionizable Surfaces and Its Effect on the Rate of Deposition," *J. Colloid Interf. Sci.*, **63**, 317 (1978).

Rajagopalan, R., and J. S. Kim, "Adsorption of Brownian Particles in the Presence of Potential Barriers: Effect of Double-Layer Interaction," *J. Colloid Interf. Sci.*, **83**, 428 (1981).

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Manuscript received Aug. 15, 1990, and revision received Mar. 25, 1991.