

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231672202>

Effect of Particle Size on Collision Efficiency in the Deposition of Brownian Particles with Electrostatic Energy Barriers

ARTICLE *in* LANGMUIR · JUNE 1990

Impact Factor: 4.46 · DOI: 10.1021/la00096a023

CITATIONS

249

READS

119

2 AUTHORS, INCLUDING:



Menachem Elimelech

Yale University

394 PUBLICATIONS **32,538** CITATIONS

SEE PROFILE

Figure 8 shows the effect of temperature on the i_p/i_p^0 values of the $2C_{18}Si-SnO_2$ electrode in the presence of $C_{14}OH$ or $C_{18}OH$ alcohols. The presence of $C_{18}OH$ could block the penetration of ferrocyanide ions only in the solid state of the monolayer below the T_c , and the barrier effect of $C_{18}OH$ was reduced relatively in the fluid state of the monolayer above the T_c . Thus, $C_{18}OH$ can penetrate and eliminate defects in the solid-state monolayer compared with the fluid monolayer. In the presence of $C_{14}OH$, the i_p/i_p^0 value largely increased at temperatures above the T_c of the $2C_{18}Si$ monolayer compared with in the absence of $C_{14}OH$, although the i_p/i_p^0 value was nearly zero in the solid monolayer below the T_c . This means probably that the relatively short $C_{14}OH$ is removed easily from the fluid state of the monolayer above the T_c , although it can block the defects in the solid state monolayer.

Summary

The polymerized and covalently bonded $2C_{18}Si$ LB-type monolayer can cover the hydrophilic and rough surface of the SnO_2 electrode, and the electrochemical reaction can be controlled by the phase transition of the $2C_{18}Si$ monolayer. The pinhole defects of the $2C_{18}Si$ monolayer can be eliminated completely by the penetration of long-chain alcohols to the monolayer matrix on the electrode. This is an easy way to prepare the completely covered monolayer even on the rough surface of the substrate.

Registry No. $2C_{18}Si$, 105442-22-6; $C_{18}Si$, 121231-18-3; $3C_{18}Si$, 121231-20-7; $2C_{18}COOH$, 37519-63-4; C_6OH , 111-27-3; C_8OH , 111-87-5; $C_{10}OH$, 112-30-1; $C_{12}OH$, 112-53-8; $C_{14}OH$, 112-72-1; $C_{16}OH$, 36653-82-4; $C_{18}OH$, 112-92-5; SnO_2 , 18282-10-5; stearic acid, 57-11-4; barium stearate, 6865-35-6.

Effect of Particle Size on Collision Efficiency in the Deposition of Brownian Particles with Electrostatic Energy Barriers

Menachem Elimelech^{*,†} and Charles R. O'Melia[‡]

Civil Engineering Department, School of Engineering and Applied Science, University of California, Los Angeles, California 90024, and Department of Geography and Environmental Engineering, The Johns Hopkins University, Baltimore, Maryland 21218

Received June 14, 1989. In Final Form: January 3, 1990

The effect of particle size on the kinetics of deposition of polystyrene latex particles on spherical glass beads in porous media was investigated theoretically and experimentally. The latex particles cover a wide size range (46–753 nm) and have comparable surface properties. Experimental collision efficiencies were calculated from measured particle deposition rates. The results are presented as stability curves, i.e., the logarithm of the collision efficiency as a function of the logarithm of concentration of electrolyte (KCl). Experimental curves were compared to those calculated theoretically. It was found, in a marked contrast to theory, that the slopes of the stability curves are *insensitive* to particle size. Possible explanations for this discrepancy are discussed and evaluated.

Introduction

Deposition of Brownian particles onto surfaces from flowing suspensions is very important in many natural and industrial processes.^{1–3} It is also used as a means for investigating colloidal interactions.^{4–9} From the study

of the deposition of model colloids on well-defined solid surfaces, various theoretical aspects of colloid stability can be tested. Deposition involves two sequential steps: *transport* and *attachment*. The transport of suspended Brownian particles to a stationary surface is dominated by convection and diffusion, while the attachment of these particles is controlled by colloidal interaction forces which operate at short distances of separation. The sum of two of these colloidal interactions (the van der Waals and electrical double layer) yields the total interaction energy which forms the basis of the Derjaguin–Landau¹⁰ and Verwey–Overbeek¹¹ (DLVO) theory of colloid stability.

[†] University of California.

[‡] The Johns Hopkins University.

(1) Tien, C. *Granular Filtration of Aerosols and Hydrosols*; Butterworths Publishers: Stoneham, MA, 1989.

(2) Cookson, J. T. *Environ. Sci. Technol.* **1970**, *4*, 128.

(3) Tien, C.; Payatakes, A. C. *AIChE J.* **1979**, *25*, 737.

(4) Hull, M.; Kitchener, J. A. *Trans. Faraday Soc.* **1969**, *65*, 3093.

(5) Bowen, B. D.; Levine, S.; McCartney, L. N. *J. Colloid Interface Sci.* **1976**, *54*, 375.

(6) Bowen, B. D.; Epstein, M. J. *Colloid Interface Sci.* **1979**, *72*, 81.

(7) Gregory, J.; Wishart, A. *J. Colloids Surf.* **1980**, *1*, 313.

(8) Tobiasen, J. E. *Colloids Surf.* **1989**, *39*, 53.

(9) Kallay, N.; Nelligan, J. D.; Matijević, E. *J. Chem. Soc., Faraday Trans. 1*, **1983**, *79*, 65.

(10) Derjaguin, B. V.; Landau, L. D. *Acta Physicochim.* **1941**, *14*, 633.

(11) Verwey, E. J. W.; Overbeek, J. Th. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.

The DLVO theory has enabled a large amount of experimental data to be explained in at least a semiquantitative manner. Early validations of the theory were based on coagulation studies of monodisperse suspensions. Predictions of the effect of counterion valence on the critical coagulation concentrations of indifferent electrolytes, while based on simplified assumptions, are in accord with many observations including the empirical Schulze-Hardy rule.^{11,12} However, predicted coagulation and deposition rates of colloidal particles when electrostatic energy barriers exist are orders of magnitude smaller than the observed values.^{1,4,7,8}

The DLVO theory predicts a marked increase of the total interaction energy with an increase in particle size and therefore a dramatic decrease in the rates of coagulation of colloidal particles.¹³ This predicted effect of particle size was not verified during coagulation studies;¹³⁻¹⁶ it was found that the experimental stability ratios ($W = \alpha^{-1}$, where W is the stability ratio and α is the collision efficiency commonly used in deposition) are insensitive to particle size. Among the explanations proposed for this anomalous particle size effect are coagulation in a secondary minimum¹⁶⁻¹⁹ and surface roughness of particles.¹³

Deposition of particles on surfaces from flowing suspensions is a unique process by which a variety of colloidal interaction phenomena can be investigated. Deposition and coagulation differ in several important aspects such as the nature of the interacting surfaces and the fluid flow field. Unlike coagulation of monodisperse suspensions, the surface charge and potential of surfaces and interacting particles are usually dissimilar. Furthermore, well-defined flow fields for deposition studies can be selected. As a result, phenomena such as deposition in secondary minima are less likely to occur.^{6-8,20} Coagulation in a secondary minimum, on the other hand, is supported by some experimental evidence^{21,22} and has been invoked to show that the apparent lack of sensitivity of slow coagulation rates to particle size is in accord with theory.¹⁶⁻¹⁹ It is also possible that interfacial dynamics of particle-particle interactions are different in coagulation and deposition. These depend on the surface properties and geometry of the interacting media and may have some influence on the relation between particle size and colloid stability.²³

Use of the deposition of colloidal particles on surfaces from flowing suspensions as a model system to investigate the role of particle size in colloid stability has not yet been reported. The objectives of this paper are (1) to develop a theoretical framework for the effect of particle size on the collision efficiency of Brownian particles in deposition and (2) to test the theoretical predictions by conducting deposition experiments with model particles and surfaces in a well-defined system. The research described in this paper is the first to investi-

gate the effect of particle size on the chemical aspects of the kinetics of particle deposition and to study the apparent disparity with respect to particle size in particle-particle interactions through deposition studies.

Theory

Colloidal Interaction Energies. The DLVO theory of colloid stability considers two interactions: (i) London-van der Waals (VDW) attraction and (ii) electrical double layer (EDL) repulsion. The sum of these two interactions gives the total energy of interaction ϕ_T :

$$\phi_T = \phi_V + \phi_E \quad (1)$$

where ϕ_V is the VDW interaction energy and ϕ_E is the EDL repulsion energy.

Theoretical expressions for EDL interactions are available in the literature for constant potential,²⁴ constant charge,¹⁷ and intermediate interactions.²⁵ The widely used expression for constant-potential interaction suggested by Hogg, Healy, and Fuerstenau²⁴ will be utilized in this work. This interaction energy between a sphere and a plane is given by (SI units)

$$\phi_E = \pi \epsilon_0 \epsilon_r a_p \left(2\psi_1 \psi_2 \ln \left(\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right) + (\psi_1^2 + \psi_2^2) \ln [1 - \exp(-2\kappa h)] \right) \quad (2)$$

where ϵ_r and ϵ_0 are the relative dielectric permittivity of water and permittivity under vacuum, respectively; a_p is the particle radius, ψ_1 and ψ_2 are the surface potentials of particles and collectors, respectively; κ is the Debye reciprocal length; and h is the separation distance (surface to surface) between the particle and the plane. The equation is valid for surface potentials less than about 60 mV and for 1:1 electrolytes.²⁴

For the VDW attraction, the Hamaker²⁶ expression should be corrected for the retardation effect. An approximate simple expression for the retarded VDW attraction energy was suggested by Gregory.²⁷ This expression is in good agreement with exact solutions at short separations (up to 20% of particle radius) and can be written for the sphere-plate case as

$$\phi_V = - \frac{A a_p}{6h(1 + 14h/\lambda)} \quad (3)$$

where A is the Hamaker constant for the interacting media and λ is the "characteristic wavelength" of the interaction, often assumed to be 100 nm. For larger separations, the exact expression for the retarded VDW interaction as derived by Czarnecki²⁸ will be used.

Transport Equation for Brownian Particles. The concentration distribution of Brownian particles in a fluid flowing over a surface is described by the convective diffusion equation. For an incompressible fluid and in the presence of an external force field acting on the particles, the equation is given by²⁹

$$\frac{\partial N}{\partial t} + \vec{v} \cdot \nabla N = \nabla \cdot (D \nabla N - \frac{DN}{kT} \vec{F}) \quad (4)$$

where N is the particle concentration, t is the time, \vec{v} is

- (12) Overbeek, J. Th. G. *Pure Appl. Chem.* **1980**, *52*, 1151.
 (13) Reerink, H.; Overbeek, J. Th. G. *Discuss. Faraday Soc.* **1954**, *18*, 74.
 (14) Ottewill, R. H.; Shaw, J. N. *Discuss. Faraday Soc.* **1966**, *42*, 154.
 (15) Joseph-Petit, A. M.; Dumont, F.; Watillon, A. *J. Colloid Interface Sci.* **1973**, *43*, 649.
 (16) Penners, N. H. G.; Koopal, L. K. *Colloids Surf.* **1987**, *28*, 67.
 (17) Wiese, G. R.; Healy, T. W. *Trans. Faraday Soc.* **1970**, *66*, 490.
 (18) Hogg, R.; Yang, K. C. *J. Colloid Interface Sci.* **1976**, *56*, 573.
 (19) Marmur, A. *J. Colloid Interface Sci.* **1979**, *72*, 41.
 (20) Marshal, J. K.; Kitchener, J. A. *J. Colloid Interface Sci.* **1966**, *22*, 342.
 (21) Takamura, K.; Goldsmith, H. L.; Mason, S. G. *J. Colloid Interface Sci.* **1979**, *72*, 385.
 (22) Ludwig, P.; Peschel, G. *Prog. Colloid Polym. Sci.* **1988**, *77*, 146.
 (23) Lyklema, J.; van Leeuwen, H. P. *Adv. Colloid Interface Sci.* **1982**, *16*, 127.

- (24) Hogg, R.; Healy, T. W.; Fuerstenau, D. W. *Trans. Faraday Soc.* **1966**, *62*, 1638.
 (25) Gregory, J. *J. Colloid Interface Sci.* **1975**, *61*, 44.
 (26) Hamaker, H. C. *Physica* **1937**, *4*, 1058.
 (27) Gregory, J. *J. Colloid Interface Sci.* **1981**, *83*, 138.
 (28) Czarnecki, J. *J. Colloid Interface Sci.* **1979**, *72*, 361.
 (29) Spielman, L. A.; Friedlander, S. K. *J. Colloid Interface Sci.* **1974**, *46*, 22.

the fluid velocity vector, D is the position-dependent diffusion coefficient of the particles, \vec{F} is an external force field, k is Boltzmann's constant, and T is the absolute temperature. The external force field acting on the particles can be derived from the total interaction energy so that

$$\vec{F} = -\nabla \phi_T \quad (5)$$

When several spherical solid collectors are in close proximity in a flow field such as in a packed bed, the effect of the neighboring spheres on the flow field should be included. Several theoretical models to account for this effect have been suggested.³⁰⁻³² Happel's^{31,33,34} cell model is widely used. For very thin concentration boundary layers, as applied to Brownian particles, the stream function close to the spherical collector may be approximated by³⁵

$$\Psi = -\frac{3}{4}A_s U y^2 \sin^2 \theta \quad (6)$$

where U is the approach (superficial) velocity, A_s is a porosity-dependent parameter of Happel's model ($A_s \approx 38$ for a porosity of 0.4), θ is a tangential coordinate, and y is a boundary layer coordinate perpendicular to the surface ($y = r - a_c$, where a_c is the radius of the spherical collector and r is a radial coordinate). The fluid velocity field can be derived from the stream function Ψ . The convective diffusion equation with the external force field and the fluid velocity field as described earlier has no analytical solution. It can be solved numerically for the concentration distribution around the sphere and for the rate of deposition of particles onto the spherical collector.

Approximate Analytical Solution for the Transport Equation. Spielman and Friedlander²⁹ and Ruckenstein and Prieve³⁶ suggested that the effect of colloidal interaction forces on the rate of deposition of Brownian particles can be incorporated into a boundary condition of the usual convective diffusion equation (without the external force term). This boundary condition has the form of an irreversible pseudo-first-order chemical reaction on the surface of the collector. The principal assumption is that the interaction forces act over distances which are short compared to the diffusion boundary layer. A necessary condition to use this approximation is that EDL repulsion is sufficiently strong.³⁷

A useful approach in studying rate of particle deposition on collector surfaces is to introduce the concept of a dimensionless single collector efficiency, η , defined as³⁸

$$\eta = \frac{\text{rate of particle removal by a collector}}{\text{rate of particle flux toward the collector}} \quad (7)$$

For an isolated single spherical collector, the denominator is equal to $\pi a_c^2 U N_0$, where N_0 is the upstream concentration of the suspended particles.

The analytical expression for the single-collector efficiency when considering colloidal interaction forces and the effect of neighboring collectors on the flow field is²⁹

$$\eta = 4.0 A_s^{1/3} P e^{-2/3} \left(\frac{\beta}{1 + \beta} \right) S(\beta) \quad (8)$$

$$\beta = (1/3) 2^{1/3} \Gamma(1/3) A_s^{-1/3} \left(\frac{D_\infty}{U a_c} \right)^{1/3} \left(\frac{K_F a_c}{D_\infty} \right) \quad (9)$$

where $S(\beta)$ is a slowly varying function of β with tabulated values given by Spielman and Friedlander, Pe is the Peclet number defined as $2a_c U/D_\infty$, D_∞ is the particle diffusion coefficient far away from the collector, and K_F is the pseudo-first-order rate constant given by^{29,39}

$$K_F = D_\infty \left(\int_0^\infty [f(h, a_p) \exp(\phi_T/kT) - 1] dh \right)^{-1} \quad (10)$$

Here $f(h, a_p)$ is a hydrodynamic function which accounts for the reduced mobility of the particles at close separation due to hydrodynamic interactions. An approximate expression for this function as suggested by Dahneke³⁹ will be used:

$$f(h, a_p) = 1 + a_p/h \quad (11)$$

The collision efficiency α is defined as the ratio of the single-collector efficiency (η) in the presence of EDL repulsive forces to the single-collector efficiency when no such repulsive forces exist (η_0). When eq 8-11 are solved for the single-collector efficiency when EDL repulsive forces are not included (η_0), the definite integral in eq 10 slowly diverges as the upper limit of the integration is increased so that η_0 can not be calculated accurately. This phenomenon was also reported by others.³⁷ It is widely accepted that the approximate analytical solution for the rate of deposition, presented in this section, is valid only in the presence of repulsive forces, that is, when an energy barrier exists.^{29,36,37}

A different approach to evaluate the theoretical collision efficiency was employed in this work. An analytical expression for the single collector efficiency, when colloidal and hydrodynamic interactions are not included, was used for η_0 . The latter can be derived from the classical collection by a spherical collector^{40,41} and is given by

$$\eta_0 = 4.0 A_s^{1/3} P e^{-2/3} \quad (12)$$

In the derivation of this expression, it is assumed that EDL forces are negligible and that hydrodynamic resistance and VDW attraction counterbalance each other. Thus, the collision efficiency is obtained by dividing eq 8 by eq 12:

$$\alpha = \left(\frac{\beta}{1 + \beta} \right) S(\beta) \quad (13)$$

Since the expression for η_0 (eq 12) is not completely corrected for hydrodynamic interactions, the theoretical collision efficiency (α) contains some hydrodynamic effects.

The Role of Particle Size. The dependence of VDW and EDL forces on particle size is a result of the necessity to account for the radius of curvature in the force calculations. In order to illustrate better the effect of particle size, it is convenient to write the total interaction energy as a product of two functions as follows:

$$\phi_T = F(a) G(\psi_1, \psi_2, A, \kappa, h) \quad (14)$$

where $F(a)$ is a geometric factor given by $(a_1 a_2)/(a_1 + a_2)$ for the interaction of two particles of radii a_1, a_2 and by a_p for particles of radius a_p interacting with a plate.

(39) Dahneke, B. J. *Colloid Interface Sci.* 1974, 48, 520.

(40) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice Hall: NJ, 1962.

(41) Yao, K. M.; Habibian, M. T.; O'Melia, C. R. *Environ. Sci. Technol.* 1971, 5, 1105.

(30) Brinkam, H. C. *Appl. Sci. Res.* 1947, A1, 27.

(31) Happel, J. *AIChE J.* 1958, 4, 197.

(32) Kuwabara, S. J. *Phys. Soc. Jpn.* 1959, 14, 527.

(33) Payatakes, A. C.; Rajagopalan, R.; Tien, C. J. *Colloid Interface Sci.* 1974, 49, 321.

(34) Pfeffer, R.; Happel, J. *AIChE J.* 1964, 10, 611.

(35) Pfeffer, R. *Ind. Eng. Chem. Fundam.* 1964, 3, 380.

(36) Ruckenstein, E.; Prieve, D. C. *J. Chem. Soc., Faraday Trans. 2* 1973, 69, 1522.

(37) Prieve, D. C.; Ruckenstein, E. *J. Colloid Interface Sci.* 1976, 57, 547.

(38) Friedlander, S. K. *Ind. Eng. Chem.* 1958, 50, 1161.

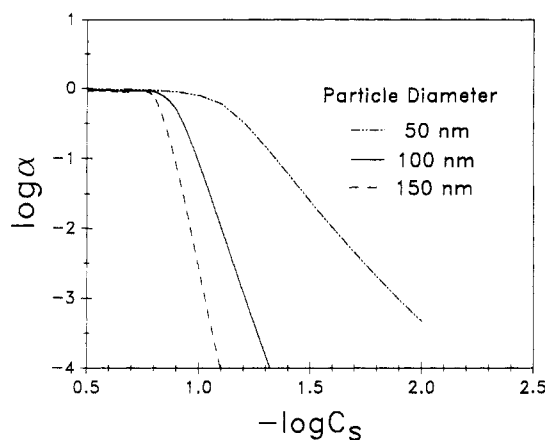


Figure 1. Theoretical stability curves for particles of different size and similar surface potentials and Hamaker constant in the presence of 1:1 electrolyte (C_s in M). Surface potentials of particles and collectors = -40 and -20 mV, respectively, collector diameter = 0.2 mm, approach velocity = 0.136 cm/s, porosity = 0.4 , and temperature = 24 °C.

The function G is independent of particle size and is highly sensitive to the chemistry of the solution.

An approach similar to that developed by Reerink and Overbeek¹³ for coagulation will be employed. By use of this approach, the slope of the logarithm of the collision efficiency α against the logarithm of the electrolyte concentration C_s should be proportional to the particle size. Their approximate analytical expression for the slope of the stability curves was derived under several simplifying assumptions, among them that the surface potentials of the interacting particles are constant over the entire salt concentration range. If electrokinetic (ζ) potential is considered as a substitute for the surface potential in the theoretical calculations of the collision efficiency (this will be discussed in Results and Discussion), then the experimental observation of the increase of ζ potentials with decreasing salt concentration should be considered. This will result in an increase of the slopes of the stability curves with decreasing salt concentration. The variation of the slopes with salt concentration implies that the slopes of stability curves of particles of different size should be compared at a given salt concentration.

It is not possible to derive an analytical expression for the $\log \alpha$ - $\log C_s$ relationship in deposition. Numerical calculations based on eq 13 are possible. The numerical solution for the slope of the stability curves, at a given salt concentration, is of the general form

$$\frac{d(\log \alpha)}{d(\log C_s)} = -B(\psi_1, \psi_2, z)a_p \quad (15)$$

in which B is a function of the surface potentials of particles and collectors and the counterion valence z .

Results of numerical calculations of theoretical $\log \alpha$ - $\log C_s$ curves for particles of different size in 1:1 electrolyte, assuming that the surface potentials are constant over that salt concentration range, are presented in Figure 1. The integral of the pseudo-first-order rate constant in eq 10 was evaluated numerically. The upper limit of the integral, when an energy barrier in the total interaction energy profile was present, has been taken arbitrarily as 100 nm. Larger values of the upper limit did not change the value of the integral. At high salt concentrations and low surface potentials, when an energy barrier in the total interaction profile is absent, the integral slowly diverges as the upper limit of the integration is increased. This results in theoretical α values which are slightly smaller than unity at large values of the upper limit of the inte-

gral, especially with large particles (the hydrodynamic interaction function, eq 11, depends on particle size). As a result, a value of 50 nm for the upper limit was chosen for cases where the energy barrier was absent. The theoretical α values were close to unity when this procedure was employed. The diffusion coefficient of the particles, D_∞ , was calculated by using the Stokes-Einstein equation ($D_\infty = kT/(6\pi\mu a_p)$), where μ is the viscosity of the fluid). It is clearly demonstrated, from the results presented in Figure 1, that the slopes of the stability curves and the critical deposition concentration increase with particle size.

Experimental Section

Materials. All inorganic chemicals were analytical reagent grade. Inorganic salt solutions were filtered through 0.2 - μ m membrane filters after preparation. Solutions and suspensions were prepared with distilled, deionized, and 0.2 - μ m filtered water (Milli-Q system, Millipore Corp., Bedford, MA).

Four different sizes (46 , 121 , 378 , and 753 nm) of surfactant-free polystyrene latex particles were used as model colloids (supplied by Interfacial Dynamics Corp., Portland, OR). Particles were extensively dialyzed by the manufacturer to remove impurities. The latices were prepared with potassium persulfate as an initiator and, as a result, carry sulfate functional groups. The density of the particles, as reported by the manufacturer, is 1.055 g/cm³.

Two sizes of spherical glass beads (Ferro Corp., Jackson, MS) with average diameters of 0.2 and 0.4 mm were utilized as model surface collectors for deposition studies. The glass beads are manufactured from crushed fragments of soda-lime glass. The beads were thoroughly cleaned by soaking for 30 min in an ultrasonic bath with distilled deionized water and 1 M HNO_3 successively; they were then rinsed several times with distilled deionized water and dried in an oven at 60 °C. Scanning electron micrographs were taken to estimate the degree of surface roughness.

Potentiometric and Conductometric Titrations. Latex particles were ion exchanged into the H^+ form before titrations following the procedure described by van den Hul and Vanderhoff.⁴² Analytical grade ion-exchange resins (Bio Rad, Richmond, CA) were used. Titrations were conducted at 25.0 °C in CO_2 -free suspensions by bubbling purified nitrogen gas into the titration vessel. A YSI Model 31A (YSI Co. Inc., Yellow Springs, OH) conductance bridge with platinum-iridium electrodes was used for conductivity measurements. Potentiometric titrations were carried out by using research grade combination pH electrodes (Orion Model 91-03) with an internal Ag/AgCl reference system.

Electrokinetic Measurements. Electrophoretic mobility studies were carried out at 25.0 °C by use of a Mark II microelectrophoresis apparatus (Rank Brothers, Cambridge, UK). A thin-walled cylindrical cell with a four-electrode arrangement was employed for measuring the mobility of the latex particles. A 3 -m W laser was used on some occasions for the illumination of the particles. The mobility of latex D (121 nm) was measured by a System 3000 electrokinetics analyzer (Pen Kem Inc., Bedford Hills, NY). Latex concentrations for mobility studies were in the range 1 - 3 ppm. In order to determine the electrokinetic potential of the glass bead collectors, smaller glass beads (about 5 μ m) were utilized (Ferro Corp., Jackson, MS). These microspheres are made of the same raw glass and are produced by the same process as those used as collectors in deposition studies. A flat cell with platinum electrodes was employed to measure the mobility of these microspheres. For each sample of latex particles or glass microspheres, the reported mobility represents an average of 20 individual particles in both directions.

Deposition Experiments. The glass bead collectors were packed in a cylindrical Plexiglas column. For a selected height of media, the amount of glass beads was adjusted to give a poros-

(42) van den Hul, H. J.; Vanderhoff, J. W. *J. Electroanal. Chem.* 1972, 37, 161.

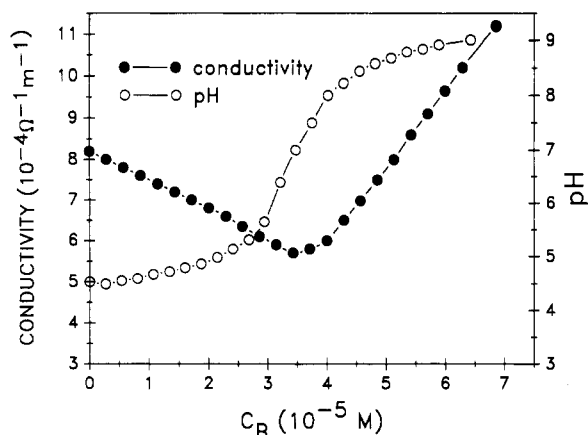


Figure 2. Potentiometric and conductometric titration curves of latex C. The measured conductivity and pH values are presented as a function of base concentration (C_B) after addition of NaOH to the titration vessel (particle concentration in the titrations was 8.4 g/L).

Table I. Surface Charge and Site Densities of Latex Particles Used in This Research As Determined by Conductometric Titrations

latex	diameter, nm	charge, $\mu\text{C}/\text{cm}^2$	area per site, nm^2
A	46	3.90	4.11
B	378	4.25	3.77
C	753	5.64	2.85
D	121	0.78	20.55

ity of 0.4. The majority of the experiments were conducted with 0.2-mm glass beads as collectors. At high salt concentrations where removal of particles is high, 0.4-mm glass beads were used. A dilute suspension of latex particles (0.5, 1.0, 2.0, and 4.0 ppm for the particles of 46, 121, 378, and 753 nm in size, respectively), with a desired solution chemistry and flow rate, was pumped through the packed bed. The pH of the suspension was adjusted to 6.7 by adding 5×10^{-5} M NaHCO_3 . Samples of effluent were taken at short time intervals for particle concentration measurements. The particle concentration was determined by light scattering on a Perkin Elmer (Model Lambda 3) spectrophotometer. Wavelengths of 220, 225, 247, and 354 nm were used for the particles with diameters of 46, 121, 378, and 753 nm, respectively.

Results and Discussion

Surface Charge of Latex Particles. Conductometric and potentiometric titrations were carried out in order to determine the surface charge density of the particles and the nature of the surface functional groups. Typical titration results are shown in Figure 2. As shown, the end points of the conductometric and potentiometric titrations are similar. The charge and site densities of the latex particles, as determined in this work, are given in Table I. The shape of the conductometric titration curve indicates that the surface functional groups are strong acids.⁴³ These are sulfate groups (OSO_3^-) with a pK_a in the range 1–2.⁴⁴ The functional groups are fully dissociated at pH values larger than 3. Electrophoretic mobility measurements conducted in this research demonstrated that electrokinetic potentials at a given ionic strength are constant at pH values of 3.5–10, in agreement with the charge density studies.

In order to investigate the effect of particle size on the collision efficiency, it is necessary that the surface charges

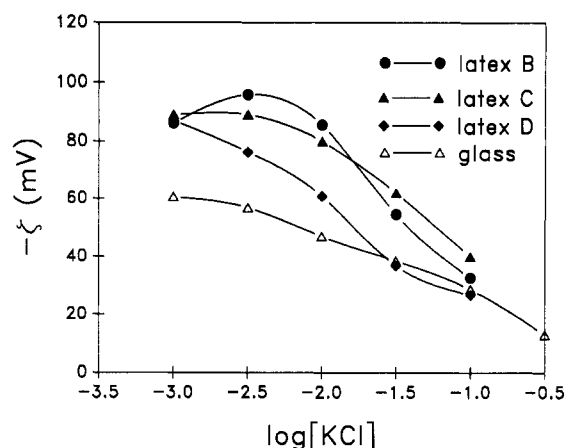


Figure 3. ζ potentials of latices B–D and glass beads as a function of molar KCl concentration, calculated from the measured electrophoretic mobilities (measurements were carried out at pH values between 6.7 and 7).

and potentials of the particles be comparable. As shown in Table I, the surface charges of latices A–C are comparable. These particles also cover a wide size range and therefore can be used as model colloids in this research. Latex D, on the other hand, has a lower surface charge density and as a result is expected to have lower stability.

ζ Potentials. Mean electrophoretic mobilities were converted to ζ potentials by using the tabulated numerical calculations of Ottewill and Shaw,⁴⁵ which include correction for the relaxation and retardation effects. The ζ potentials of latices B–D as a function of KCl concentration are presented in Figure 3. It is shown that the ζ potentials of latices B and C are comparable, in accord with the charge density studies described previously. Latex D has smaller values of ζ potential, probably due to its lower surface charge density.

Due to the small size of latex A (46 nm) and the low refractive index of polystyrene, it is not possible to measure its mobility by microelectrophoresis. It is therefore assumed in this research that the ζ potentials of suspensions A and B are similar. This is a reasonable assumption since the charge density and the surface properties of these particles are comparable.

The maximum in the ζ potential–KCl curve, as observed in Figure 3, is a common feature of surfactant-free polystyrene latices with strong acid groups.^{46–48} At concentrations larger than $10^{-2.5}$ M KCl, the ζ potential curves behave normally, i.e., a continuous decrease of the ζ potential with an increase of KCl concentration. The investigation of the effect of particle size on the collision efficiency is confined to this salt concentration range.

The ζ potentials of the glass beads as calculated from the mobility measurements are also presented in Figure 3. The absolute values of these potentials are smaller than those of the latex particles under similar chemical conditions. The results are comparable to values of ζ potential of glass surfaces measured by the streaming potential technique.^{49,50}

Deposition Studies. Particle deposition experiments were conducted at pH 6.7 and a temperature

(45) Ottewill, R. H.; Shaw, J. N. *J. Electroanal. Chem.* **1972**, *37*, 133.

(46) Kamel, A. A.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Dispersion Sci. Technol.* **1981**, *2*, 183.

(47) Elimelech, M.; O'Melia, C. R. *Colloids Surf.*, in press.

(48) Zukoski, C. F.; Saville, D. A. *J. Colloid Interface Sci.* **1986**, *114*, 45.

(49) Li, H. C.; de Bruin, P. L. *Surf. Sci.* **1966**, *5*, 203.

(50) FitzPatrick, J. A. *Ph.D. Dissertation*; Harvard University, 1972.

(43) Stone-Masui, J.; Watillon, A. *J. Colloid Interface Sci.* **1975**, *52*, 479.

(44) James, R. O. In *Polymer Colloids*; Buscall, R., Corner, T., Stageman, J. F., Eds.; Elsevier: Amsterdam, 1985.

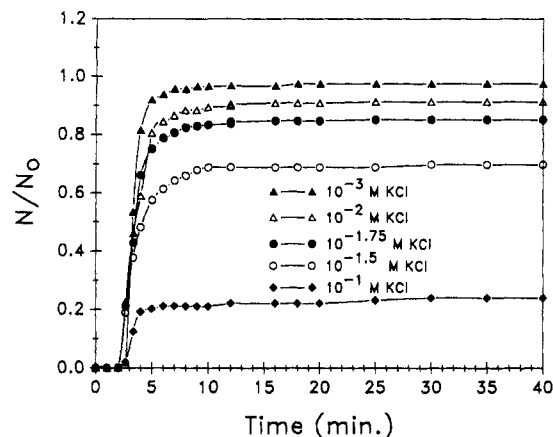


Figure 4. Particle breakthrough curves of latex C at different KCl concentrations. The fraction of residual concentration of particles is plotted as a function of time. Bed depth = 20 cm, collector diameter = 0.2 mm, porosity = 0.4, approach velocity = 0.136 cm/s, temperature = 24 °C, and pH = 6.7.

between 23 and 25 °C under similar chemical conditions utilized in the electrophoretic mobility measurements. The results are presented as breakthrough curves; that is, the effluent concentration of particles, N , as a function of time is given as a fraction of the influent concentration N_0 . Typical breakthrough curves at various KCl concentrations are presented in Figure 4. The results are in qualitative agreement with theory; deposition rates increase (N/N_0 decreases) with increasing KCl concentrations. This is often ascribed to reduced EDL repulsion forces caused by compression of the diffuse double layer. The removal by clean collectors or the initial removal efficiency can be determined from the particle breakthrough curves. This removal efficiency corresponds to the initial stage of deposition, where the degree of deposition is determined by the colloidal interactions between the bare collector surfaces and the approaching latex particles. The initial removal was taken as the value of N/N_0 at the time when the suspension being studied has displaced the initial contents of the bed. This point was estimated from breakthrough curves of an inert tracer. Tracer studies showed that a complete breakthrough was obtained after three to four mean residence times of the packed bed (e.g., 12 min for the deposition experiments presented in Figure 4).

Performing a mass balance of particles over a differential packed bed length and then integrating over the entire bed depth allow an expression for the experimental collision efficiency, α_{exp} , to be derived:⁵¹

$$\alpha_{\text{exp}} = -\frac{4a_c}{3(1-f)\eta_0 L} \ln((N/N_0)_0) \quad (16)$$

where f is the porosity of the packed bed, L is the media depth, and $(N/N_0)_0$ is the initial removal efficiency as discussed earlier. This expression is a ratio of the experimental single-collector efficiency as calculated from the measured initial removal rate, $(N/N_0)_0$, to the theoretical single-collector efficiency when repulsive forces are not included (η_0).

A summary of the experimental deposition runs using latices A–C is found in Table II. Included are the physical and chemical conditions of the experiments, observed initial removals $(N/N_0)_0$, and calculated α_{exp} values. The comparable values of α_{exp} obtained for different bed depths

Table II. Summary of Deposition Experiments with Latices A–C^a

run	log [KCl] ^b	depth, cm	size, mm	$(N/N_0)_0$	log α_{exp}
A1	-2.5	20	0.2	0.94	-2.35
A2	-2.0	20	0.2	0.68	-1.56
A3	-2.0	20	0.2	0.81	-1.82
A4	-1.75	20	0.2	0.47	-1.26
A5	-1.5	20	0.4	0.62	-0.96
A6	-1.5	20	0.4	0.64	-0.99
A7	-1.25	20	0.4	0.35	-0.62
A8	-1.0	15	0.4	0.27	-0.40
A9	-1.0	15	0.4	0.23	-0.35
A10	-0.5	15	0.4	0.35	-0.49
A11	-0.5	15	0.4	0.34	-0.48
B1	-2.5	40	0.2	0.93	-1.99
B2	-2.5	20	0.2	0.96	-1.94
B3	-2.0	20	0.2	0.92	-1.63
B4	-2.0	20	0.2	0.91	-1.58
B5	-1.75	20	0.2	0.84	-1.31
B6	-1.5	20	0.2	0.72	-1.03
B7	-1.5	20	0.2	0.70	-1.00
B8	-1.25	20	0.2	0.48	-0.68
B9	-1.0	20	0.4	0.68	-0.45
B10	-1.0	20	0.2	0.20	-0.35
B11	-0.5	20	0.4	0.58	-0.30
C1	-2.5	20	0.2	0.95	-1.71
C2	-2.5	20	0.2	0.97	-1.93
C3	-2.0	20	0.2	0.90	-1.39
C4	-2.0	20	0.2	0.92	-1.49
C5	-1.75	20	0.2	0.84	-1.17
C6	-1.5	20	0.4	0.89	-0.80
C7	-1.5	20	0.2	0.69	-0.85
C8	-1.25	20	0.2	0.44	-0.50
C9	-1.0	20	0.2	0.22	-0.24
C10	-1.0	20	0.4	0.72	-0.35
C11	-0.5	20	0.4	0.62	-0.19

^a The approach velocity in all experiments was 0.136 cm/s (latex A, runs A1–A11; latex B, runs B1–B11; latex C, runs C1–C11). ^b [KCl] in M.

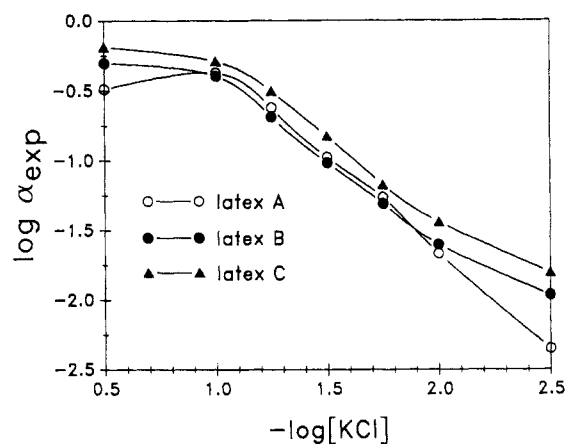


Figure 5. Experimental stability curves of latices A–C (KCl concentration in M). Approach velocity = 0.136 cm/s, porosity = 0.4, and temperature = 24 °C. The appropriate bed depths and collector sizes are given in Table II.

and media sizes at a given KCl concentration (e.g., runs B1, B2 and C6, C7) confirm the validity of eq 16 and the precision of the experiments. Stability curves of these latices are presented in Figure 5 in the form of $\log \alpha_{\text{exp}}$ versus $\log C_s$, where C_s is the molar concentration of KCl. Average values of α_{exp} are used when more than one experiment at a given KCl concentration was performed. The variation of the slope with particle size as predicted from theory was not observed. The slopes of all the curves are remarkably similar, despite the fact that the particle diameters varied by more than 1 order of magnitude. Also, the observed critical deposition concentrations were insen-

(51) Yao, K. M. *Ph.D. Dissertation*; University of North Carolina at Chapel Hill, 1968.

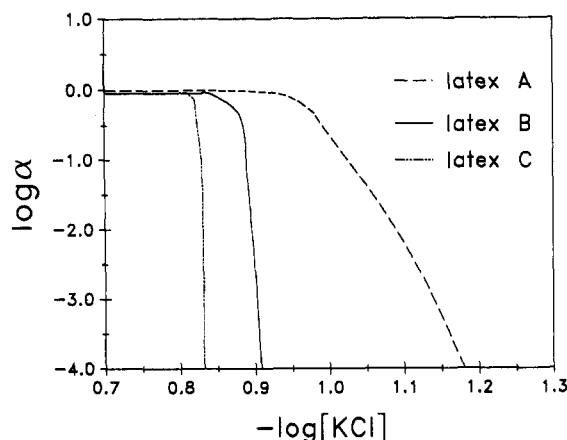


Figure 6. Theoretical stability curves of latices A-C (KCl concentration in M). Surface potentials of particles and collectors were replaced by the measured mean ζ potentials, approach velocity = 0.136 cm/s, porosity = 0.4, collector diameter = 0.2 mm, and temperature = 24 °C.

sitive to particle size (about 0.1 M for all particles), in contrast to theoretical predictions.

In order to calculate EDL repulsion, proper values for the surface potentials are required. Since EDL interaction arises from the overlapping of diffuse double layers, the surface potentials can be represented by the potential at the boundary between the Stern and diffuse layer (the so called "Stern potential" or "diffuse layer potential"). This potential cannot be measured directly, and the electrokinetic (ζ) potential is usually considered as a good first approximation.⁷ Since the ζ potential is located at a plane at some distance from the true surface, an effective separation distance should be used. Thus, EDL repulsion acts over a distance $h - 2\Delta$ rather than h , where Δ is the distance from the true surface and the location of the ζ potential. It has been suggested^{7,52} that Δ can be taken as the thickness of the Stern layer, so 2Δ is about 0.5 nm.

Calculations of EDL repulsion (eq 2), using $h - 2\Delta$ instead of h , showed that a higher EDL repulsion is obtained. If these repulsion energies (instead of EDL energies calculated by using h as a separation distance) are used to predict theoretical collision efficiencies, smaller α values will be obtained. It is well documented that theoretical predictions of α greatly underestimate observations,^{6-8,29,36} so using $h - 2\Delta$ in EDL calculations instead of h will make theoretical predictions poorer. It was therefore decided in this work to use the actual separation distance between the surfaces (h) in the EDL interaction calculations. This practice is commonly used in theoretical predictions of deposition and coagulation rates.^{4-9,50}

Theoretical collision efficiencies were calculated using the procedure described earlier in the theoretical section. EDL repulsion energies were calculated by using the procedure described above. A value of 1×10^{-20} J for the Hamaker constant of the glass-water-polystyrene system was chosen. A comparable value for similar interacting media was used by others.^{8,53} The theoretical stability curves of latex particles A-C are presented in Figure 6. A common feature of the curves, as found in other theoretical deposition studies,^{4,7,8,36} is the drastic drop of α to 0 below a certain KCl concentration. The stability of the particles increases with particle size as

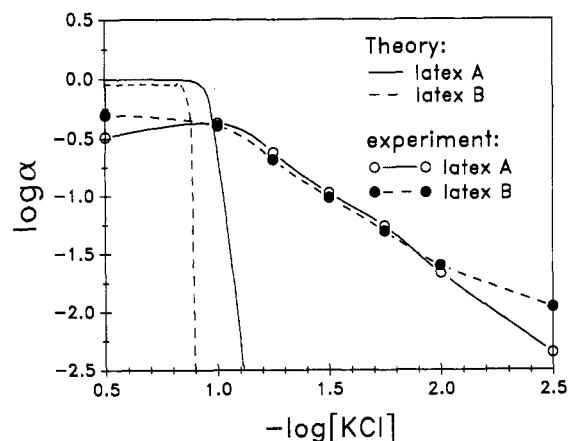


Figure 7. Comparison of theoretical and experimental stability curves of latices A and B (KCl concentration in M). Other parameters are as those given in Figures 5 and 6.

evidenced from the larger slopes of $\log \alpha$ - $\log C_s$ curves and the higher critical deposition concentrations for larger particles. The theoretical and experimental stability curves of latices A and B are presented in Figure 7. The experimental curves are in marked contrast with theory. The experimental collision efficiencies decrease gradually with decreasing KCl concentration whereas theoretical values decrease sharply. Also, the slope of the experimental stability curves and the critical deposition concentrations are independent of particle size while model predictions are sensitive to the size of the particles. The disagreement between observations and theory increases markedly with increasing particle size as a result of the higher energy barriers predicted for larger particles.

At electrolyte concentration levels higher than the critical deposition concentration, the experimental collision efficiencies are lower than the theoretical values, which approach unity. This discrepancy may be attributed to the procedure used to calculate α_{exp} (eq 16). In this equation, α_{exp} is calculated from the ratio of the experimental single-collector efficiency to the theoretical collection efficiency η_0 (eq 12). The latter may overestimate the real value since hydrodynamic interactions are not included. As a result, experimental collision efficiencies smaller than unity can be obtained. A similar explanation was suggested by Gregory and Wishart,⁷ who obtained α_{exp} values smaller than unity for deposition in the absence of energy barriers. Another possible explanation is the presence of structural (hydration) forces due to hydration of counterions at the interface. These forces may be important at high ionic strengths. As particles approach the surface, some dehydration of the ions would have to occur, leading to a repulsion.⁵⁴ In this case, reduced deposition rates may be obtained despite the absence of EDL repulsive forces. Repulsive hydration forces may also explain the anomalous observation with latex A in which α_{exp} decreases upon increasing KCl concentration from 10^{-1} to $10^{-0.5}$ M (runs A8, A9 as compared to A10, A11). Reduced coagulation rates upon increasing salt concentration have been also observed by Healy et al.,⁵⁵ who explained these rates by invoking hydration forces.

Another feature of the experimental stability curves is that the slopes were linear over the entire salt concentration below the critical deposition concentration (0.1 M KCl), with a small decrease in the slope of latices B

(52) Overbeek, J. Th. G. *Adv. Colloid Interface Sci.* **1982**, *16*, 17.

(53) Yoshimura, Y.; Ueda, K.; Mori, K.; Yoshoka, N. *Int. Chem. Eng.* **1980**, *20*, 600.

(54) Gregory, J. Presented at IXEL European Chemistry of Interfaces Conference, Zakopane, Poland, 1986.

(55) Healy, T. W.; Homola, A.; James, R. O. *Faraday Discuss. Chem. Soc.* **1978**, *65*, 156.

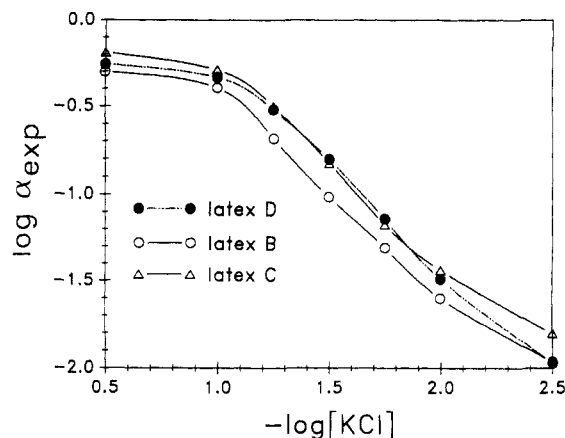


Figure 8. Experimental stability curve of latex D as compared to latices B and C. Latex D has lower surface charge and ζ potential than latices B and C (as shown in Table I and Figure 3). Experimental conditions are similar to those described in Figure 5.

and C at concentration levels below 10^{-2} M. Theoretical stability curves, on the other hand, predict higher slopes at lower salt concentrations. The increase of the theoretical slopes is attributed to the increase in ζ potentials (more negative) with decreasing salt concentrations (Figure 3), thus making the calculated repulsive energy higher. If one considers the ζ potential as a reasonable substitute for the surface potential, then this experimental finding presents another contradiction with the DLVO theory.

Additional evidence for the lack of sensitivity of colloidal stability to particle size is shown in Figure 8, which compares the stability of latex D with latices B and C. Latex D is smaller in size and has lower surface charge and ζ potential compared to latices B and C and as a result is expected to be less stable. However, as shown in that figure, the slope of the stability curve and the critical deposition concentration of latex D are remarkably similar to those of latices B and C.

Possible Explanations for the Observed Discrepancies. The proportionality of VDW and EDL interactions with respect to particle size and hence the direct dependence of the total interaction energy on particle size lies on a firm theoretical foundation. This dependence is obtained by using Derjaguin's⁵⁶ approximation or by rigorously solving for the force between two spheres.^{57,58} Several possible reasons for the observed insensitivity of colloid stability to particle size are discussed below. These were described with more details elsewhere.⁵⁹

1. A Distribution in Surface Potentials. In the calculation of the theoretical collision efficiencies, it is assumed that the surface charge of particles and collectors is uniformly distributed, that all particles have a constant surface potential, and that all collectors also have a constant surface potential for a given solution chemistry. Electrophoretic mobility measurements of various colloidal particles indicate a wide distribution of mobility values.⁶⁰ This indicates that individual particles in a suspension possess different values of surface potentials.

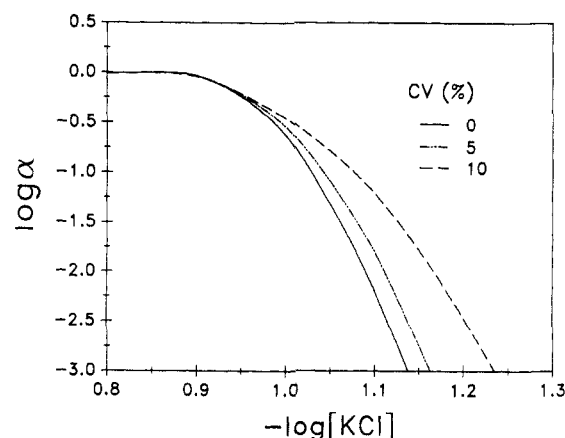


Figure 9. Theoretical stability curves of latex A assuming a Gaussian (normal) distribution of ζ potentials of particles and collectors for various coefficients of variation (CV). The physical and chemical conditions are as those described in Figure 6. The mean collision efficiencies were calculated from eq 17.

The effect of a distribution of surface potential of particles and collectors can be evaluated by calculating the mean value of the theoretical collision efficiency with the surface potentials being considered as random variables. A similar approach has been employed to evaluate the effect of a distribution of surface properties of particles on coagulation rates,⁶¹ the effect of a distribution in ζ potentials on stability ratios in coagulation,⁶² and the effect of a distribution in ζ potentials on deposition rates of non-Brownian particles.⁶³ Hence, the mean value (α_m) is given by

$$\alpha_m = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_1(\psi_1) f_2(\psi_2) \alpha(\psi_1, \psi_2) d\psi_1 d\psi_2 \quad (17)$$

where ψ_1 and ψ_2 are the surface potentials of particles and collectors having jointly independent probability density functions $f_1(\psi_1)$ and $f_2(\psi_2)$, respectively, and $\alpha(\psi_1, \psi_2)$ is the theoretical collision efficiency, calculated from eq 13, with ψ_1 and ψ_2 as random variables. Numerical calculations of eq 17 for various coefficients of variation of surface potentials of particles and collectors were carried out. It was assumed that the surface potentials of particles and collectors are normally distributed. The mean values of the surface potentials were replaced by the measured average ζ potentials. Representative results of these calculations are presented in Figure 9. The effect of a distribution of surface potentials is to decrease the stability (higher α values) and the slopes of $\log \alpha$ - $\log C_s$ curves. However, the experimental α values are still orders of magnitude larger than the predicted values, and the actual slopes of the stability curves are much smaller than those predicted.

2. Hydrodynamic Interaction. In a viscous fluid such as water, the mutual approach of two particles or the approach of a particle toward a surface is hindered by the slow drainage of fluid from the narrowing gap between the surfaces. This phenomenon is referred to as hydrodynamic or viscous interaction. Viscous interaction of a sphere interacting with a planar surface depends on the diameter of the sphere and the distance of separation. Exact solutions for the drag and torque as a function of particle-wall separation are available.⁶⁴⁻⁶⁶

(56) Derjaguin, B. V. *Kolloid Z.* 1934, 69, 155.

(57) Barouch, E.; Matijević, E.; Ring, T. H.; Finlan, J. M. *J. Colloid Interface Sci.* 1978, 67, 1.

(58) Bell, G. M.; Levine, S.; McCartney, L. N. *J. Colloid Interface Sci.* 1970, 33, 335.

(59) Elimelech, M. *Ph.D. Dissertation*, Johns Hopkins University, 1989.

(60) Rajagopalan, R.; Chu, R. Q. *J. Colloid Interface Sci.* 1982, 86, 299.

(61) Prieve, D. C.; Lin, M. M. *J. Colloid Interface Sci.* 1982, 86, 17.

(62) Prieve, D. C.; Ruckenstein, E. *J. Colloid Interface Sci.* 1980, 73, 539.

(63) Tobiasson, J. E. *Ph.D. Dissertation*, Johns Hopkins University, 1987.

(64) Brenner, H. *Chem. Eng. Sci.* 1961, 16, 242.

An attempt to relate the anomaly with respect to particle size in slow coagulation to the hydrodynamic interaction was presented by Derjaguin and Muller⁶⁷ and Honig et al.⁶⁸ The hydrodynamic interaction was included in the classical Fuchs⁶⁹ expression of the stability ratio W . Their calculations showed, however, that the effect of hydrodynamic interaction on the slope of the $\log W$ - $\log C_0$ curve is very small. Similar results are expected in deposition. Prieve and Ruckenstein⁷⁰ reported that the effect of hydrodynamic interactions on deposition rates of Brownian particles is small (compared to larger particles). The approximate analytical expression (eq 13) which was used to evaluate the theoretical collision efficiencies, although partially corrected for hydrodynamic interaction, still predicts a significant effect of particle size.

Recent studies⁷¹ indicate that another mechanism which is not included in modern theories of deposition and coagulation can increase the hydrodynamic resistance. This additional resistance is caused by the friction of liquid against the counterions of the interacting diffuse double layers. A quantitative expression for the stability ratio of slow coagulation which incorporates this viscous resistance was derived by van de Ven.⁷² It appears that the effect of this resistance is to increase the stability of particles; this results in an increase in the critical coagulation (or deposition) concentration and in the slope of the stability curves. It is therefore concluded that such hydrodynamic interactions cannot resolve the disparity with respect to particle size.

3. Dynamics of Interaction. In the classical theory of colloid stability, two possibilities of interactions are distinguished: interaction at constant surface potential and at constant surface charge. These theories may be classified as "static" since the various dynamic processes taking place during interaction and collision are not considered. The constant surface potential interaction case as used in this research (eq 2) yields the lowest EDL repulsion energy. Using other static EDL expressions such as constant surface charge¹⁷ or an intermediate case²⁵ will result in higher repulsions and hence less agreement of observed α values with theoretical predictions.

Studies of interfacial electrodynamics^{73,74} point out that it is possible that by considering the dynamics of interacting double layers some basis for the apparent insensitivity of colloidal stability to particle size may be gained. It was found that the extent of lateral adjustment of charge during interaction is dominated by hydrodynamic drag. Since the drag force depends on particle size, it may counteract the effect of the particle size on the rate of coagulation and deposition. However, no theory which treats rigorously the dynamics of interaction exists. In a complete theory of dynamic EDL interaction, the repulsion should be a function of not only the distance of separation but also of the velocity at which surfaces approach each other and of the various fluxes of ions at the interface during interaction. These fluxes disturb the nature

of the double layer and may have a significant effect on the rate of coagulation and deposition.

4. Deposition in Secondary Minima. Secondary minima in the total energy of interaction profile can be obtained at moderate to large separation distances (usually larger than several nanometers). For given chemical conditions, the depth of the secondary minimum increases with particle size and the Hamaker constant of the interacting media. Coagulation of Brownian particles in secondary minima is possible, in principle, if the resultant of the force from the thermal energy of the particles and the fluid drag force is insufficient to drive the particles out of the secondary minima. Indirect evidence for this phenomenon has been reported by numerous investigators.^{22,75,76}

Wiese and Healy¹⁷ argued that the apparent independence of the stability ratio on particle size in coagulation experiments can be understood in terms of an energetic rather than a kinetic criterion for colloid stability. By incorporating both primary and secondary minima coagulation, the anomalous particle size effects were shown to be in agreement with the DLVO theory. Several other studies relating anomalous particle size effects to coagulation in secondary minima have been reported.^{16,18,19} These semiquantitative studies, however, did not consider the effects of fluid shear which can prevent this type of coagulation.

Significant deposition in secondary minima in the experimental system employed in this research is very unlikely. Theoretical analysis of the trajectory of a non-Brownian particle around a sphere in a creeping flow, based on a force balance, predicts that collection in a secondary minimum is possible only in a small region at the rear stagnation point of the spherical collector.^{8,77-79} Similar predictions are expected for Brownian particles; particles trapped in a secondary minimum will translate and rotate due to fluid drag and shear until they reach the rear stagnation point where the net force (sum of VDW, EDL, and fluid drag forces) on the particle is zero. Furthermore, the width of the secondary minimum region is of the order of a few nanometers, which implies that at most one particle can be collected by each collector.

Attractive forces for submicron particles in secondary minima are small and can be overcome by fluid drag forces. The fluid drag force for a given particle can be controlled by changing the approach velocity of the fluid toward the collector. Experimental collision efficiencies for latices A and C were determined from deposition experiments at higher approach velocity, 0.377 cm/s as compared to 0.136 cm/s in the previous deposition runs. The stability curves, as determined from these experiments, are compared in Figure 10. The slopes of the curves are similar at both velocities. If deposition of latex particles in secondary minima is possible, it is expected that the threefold increase of the approach velocity would have an effect on the concentration profile in the secondary minima. Therefore, the experimental collision efficiencies would be different at both velocities. However, as observed, the stability curves are remarkably similar, indicating that significant deposition in secondary minima is not likely to occur.

(65) Goldman, A. J.; Cox, R. G.; Brenner, H. *Chem. Eng. Sci.* 1967, 22, 637.

(66) Goldman, A. J.; Cox, R. G.; Brenner, H. *Chem. Eng. Sci.* 1967, 22, 653.

(67) Derjaguin, B. V.; Muller, V. M. *Dokl. Akad. Nauk SSSR (Engl. Transl.)* 1967, 176, 738.

(68) Honig, E. P.; Roeberson, G. J.; Wiersema, P. H. *J. Colloid Interface Sci.* 1971, 36, 97.

(69) Fuchs, N. Z. *Phys.* 1937, 89, 736.

(70) Prieve, D. C.; Ruckenstein, E. *AIChE J.* 1974, 20, 1178.

(71) Muller, V. M. *Langmuir* 1987, 3, 621.

(72) van de Ven, T. G. M. *J. Colloid Interface Sci.* 1988, 124, 138.

(73) Dukhin, S. S.; Lyklema, J. *Langmuir* 1987, 3, 94.

(74) van Leeuwen, H. P.; Lyklema, J. *Ber. Bunsen-Ges. Phys. Chem.* 1987, 91, 288.

(75) Schenkel, J. H.; Kitchener, J. A. *Trans. Faraday Soc.* 1960, 56, 161.

(76) Kotera, A.; Furusawa, K.; Kudo, K. *Kolloid Z. Z. Polym.* 1970, 240, 837.

(77) Spielman, L. A.; Cukor, P. M. *J. Colloid Interface Sci.* 1973, 43, 51.

(78) Payatakes, A. C.; Tien, C.; Turian, R. M. *AIChE J.* 1974, 20, 889.

(79) Rajagopalan, R.; Tien, C. *AIChE J.* 1976, 22, 523.

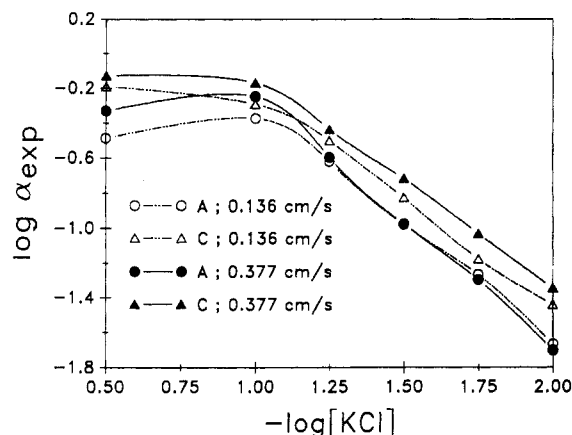


Figure 10. Experimental stability curves of latices A and C at different approach velocities (KCl concentration in M). Bed depth = 20 cm, porosity = 0.4, collector diameter = 0.2 mm, temperature = 24 °C, and pH = 6.7.

5. Surface Roughness. The poor agreement between observations and theory in studies concerned with the kinetics of coagulation and deposition has been attributed to several factors. Among these factors is the surface roughness of particles and collectors. The disparity with respect to particle size was also attributed to surface roughness.¹³ It was suggested that the total interaction energy may be determined by the radii of curvature of the protrusions rather than the curvature of the interacting particles.

A simple approach to assess the effect of surface roughness on the total interaction energy and the collision efficiency is given below. Roughness is assigned to particles and collectors as small half-spheres protruding from their surfaces. As a first approximation, the total interaction energy is calculated as a superposition of interactions. Thus, for the case of a smooth sphere interacting with a rough collector, the interaction energy is the sum of (i) particle-half-sphere protrusion interaction, ϕ_i , and (ii) particle-smooth collector interaction, ϕ_{ii} . The distance of closest approach between particles and a collector in this case is determined by the size of protrusions on the surface of the collector. On the basis of this picture, the total interaction energy as a function of the separation distance (h) between a particle and a half-sphere protrusion of radius a_r is the sum

$$\phi_T(h) = \phi_i(h) + \phi_{ii}(h + a_r) \quad (18)$$

Scanning electron micrographs of the clean 0.2-mm glass beads were taken at magnifications of 50–100 K. Small-scale irregularities were observed on the surface of the glass beads. Protrusions of various sizes (up to 50 nm) and heights (up to 20 nm) are present on the surface with an average spacing of about 300 nm. Several pits with irregular shape and an estimated depth of up to 20 nm were also observed.

Calculations of interaction energies for the case of smooth particles interacting with rough surfaces, for various protrusion sizes, were carried out. The results showed that the total interaction energy and the height of the energy barrier decrease in the presence of roughness. This is a result of the smaller contribution from the particle-smooth collector repulsion (ϕ_{ii}) owing to the presence of a distance of closest approach. Representative results of ϕ_i , ϕ_{ii} , and ϕ_T are presented in Figure 11. The height of the energy barrier as obtained by using this analysis is $23kT$ as compared to $212kT$ when roughness is not included. The calculations of ϕ_T for various protrusion sizes also showed that as the protrusion increases above

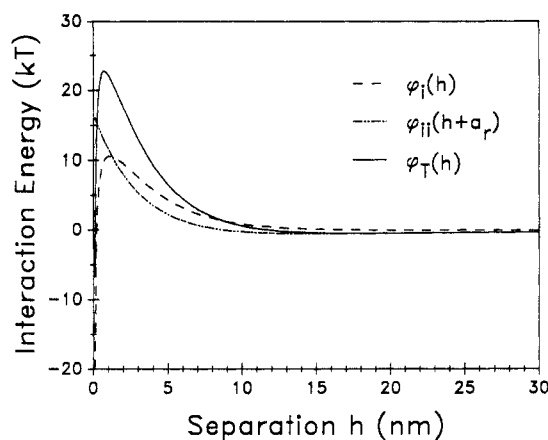


Figure 11. Interaction energy curves of a rough collector with a protrusion having a radius of curvature of 10 nm interacting with smooth particles. The following parameters were used: particle diameter = 0.4 μ m, ζ potentials of particles and collectors = -45 and -30 mV, respectively, Hamaker constant = 10^{-20} J, ionic strength = 0.01 M, and temperature = 24 °C.

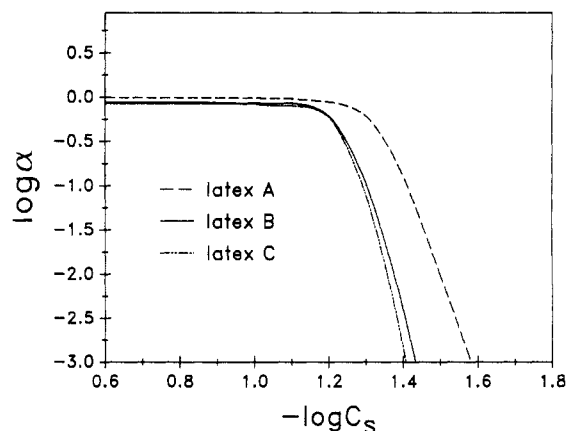


Figure 12. Theoretical stability curves of latices A–C with rough collectors. The radius of curvature of protrusions on collectors has been taken as 10 nm. The following parameters were used: surface potentials of particles and collectors were replaced by the mean measured ζ potentials, collector diameter = 0.2 mm, approach velocity = 0.136 cm/s, porosity = 0.4, and temperature = 24 °C.

a certain size the energy barrier starts to increase as a result of the larger repulsion caused by the particle-protrusion interaction (ϕ_i). This is caused by the increase in the radius of curvature of the protrusion.

Theoretical calculations of the collision efficiency for the case of interaction of particles with rough surfaces were carried out. Similar equations as used before were utilized. The total interaction energy was calculated from eq 18. Stability curves of latices A–C assuming a typical size of collector protrusions are shown in Figure 12. The results show that the slopes of the stability curves are much less sensitive to particle size, yet, the magnitude of these slopes is still much larger than the experimental results. It is also shown that the critical deposition concentrations are still dependent on particle size, as opposed to observations.

The simple model presented assumes that the number of protrusions on the collector is not a limiting factor. This assumption is acceptable since the average distance between protrusions on the glass bead collectors is about 300 nm, as indicated previously. For surfaces with a small number of protrusions, the probability of finding a protrusion on the surface should be included, which will result in a decrease of the collision efficiencies. It should also be emphasized that the model particles and

collectors utilized in this research are smoother and more spherical than most real particles and surfaces of practical interest. Other modifications may include distribution of sizes of protrusions, a possibility of contact with more than one protrusion, and the possibility that the radius of curvature is smaller than the height of the protrusion. The last possibility will cause a marked decrease in the collision efficiency and consequently a better agreement with theory.

The effect of roughness on colloid stability as discussed above is for *static* EDL interaction theories. Surface roughness may also have a notable effect on interfacial dynamics of interaction.^{73,74} The current understanding of dynamics of interaction is very poor and its effect on colloidal stability cannot be assessed quantitatively.

Conclusions

A theoretical framework for particle size effects in deposition of Brownian particles in the presence of repulsive colloidal interactions has been developed. The theory indicates that the magnitude of the slopes of the stability curves ($\log \alpha - \log C_s$ curves) and the critical deposition concentrations are sensitive to particle size. Deposition experiments with model particles and surfaces in a well-defined system show that the slopes of the stability curves as well as the critical deposition concentrations are *insensitive* to particle size, in a marked contrast to theoretical predictions.

Several hypotheses for the observed discrepancies with respect to particle size effects were evaluated. It was shown that (i) a distribution in surface potentials, (ii) hydrody-

namic interaction, (iii) deposition in secondary minima, and (iv) equilibrium (static) aspects of surface roughness cannot explain the observed discrepancies. It is most likely that the discrepancies with respect to particle size effects are related to the failure of the DLVO theory to consider dynamics of interaction. Interfacial electrostatics of interaction, coupling of electrostatics and hydrodynamics, and the possible effects of surface roughness on dynamics of interaction are presumed to have a significant effect on the kinetics of particle-particle interaction.

It is concluded that for any *real* interacting colloidal particles or particles interacting with surfaces, the collision efficiency is *independent* of particle size. Colloidal particles with comparable surface chemical properties will exhibit similar colloidal stability, at a given solution chemistry, regardless of their size. The classical DLVO theory breaks down at very close separation between interacting particles where interfacial phenomena such as coagulation and deposition are important. The theory is incapable of predicting quantitatively the kinetics of particle-particle or particle-surface interactions. It is imperative that the dynamics of interaction and its relation to colloid stability and to the anomalous particle size effect be better understood.

Acknowledgment. We acknowledge the support of the U.S. Environmental Protection Agency under Research Grant R812760. The authors also thank John E. Tobiasson of the University of Massachusetts for reviewing the manuscript.

Registry No. Polystyrene, 9003-53-6.