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Adsorption and Desorption of Particles and Their Chromatographic Separation

ELI RUCKENSTEIN

Faculty of Engineering and Applied Science
State University of New York at Buffalo
Buffalo, New York 14214

and

DENNIS C. PRIEVE

Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Rates of adsorption/desorption are calculated by considering Born, double-layer, and van der Waals forces. Conditions exist where rates are highly sensitive to particle size, shape, and chemical constitution because diffusion over a potential barrier controls. On this basis, a new separation technique, called potential-barrier chromatography, is suggested.

SCOPE

Removal of suspended solids from a liquid may be required, either to recover valuable products or to remove obnoxious particulates. Clarification of dilute aqueous suspensions is frequently performed in deep-bed granular filters, where the grains provide a surface on which the particles may adsorb. If two types of particles differ in their adsorption rate, separation of them may be accomplished by selectively adsorbing one species on the grains. Furthermore, reversibility of adsorption would allow chromatographic separation of particle mixtures, analogous to gas chromatography.

Physical adsorption arises from physical interactions between the suspended particles and the collector, such as van der Waals attraction, double-layer repulsion, and Born repulsion. The total interaction energy, as a function of the particle-collector gap width, displays either one minimum and no maximum or two minima and one maximum. Several mechanisms for chromatographic sep-

aration of particle species may be classified by the shape of the interaction energy profile. At low ionic strengths, a large maximum in the profile is expected, which represents an insurmountable energy barrier, preventing particle adsorption. Particle residence times then are determined by the particle's velocity which, owing to hydrodynamics alone, is greater than the average fluid velocity by an amount dependent on particle size. This corresponds to hydrodynamic chromatography. Conversely, at high ionic strength no maximum is expected, and particles rapidly adsorb on the surface. The residence time is now determined by adsorption and desorption rates and is expected to be substantially greater than fluid residence time. Finally, at moderate ionic strengths, a surmountable energy barrier is developed which allows adsorption and desorption, but at reduced rates which depend on the height of the barrier.

The present paper focuses on the latter situation, where chromatographic separation of suspended particle species is expected to be most selective. Rates of adsorption and desorption over an energy barrier are calculated as a function of the particle radius and ionic strength in order to predict the sensitivity of the rate to these properties.

CONCLUSIONS AND SIGNIFICANCE

When the Born, double-layer, and van der Waals forces act over distances that are short compared to the diffusion boundary-layer thickness, and when these forces form an energy barrier, the adsorption and desorption rates may be calculated by lumping the effect of the interactions into a boundary condition on the usual convective-diffusion equation. This condition takes the form of a first-order, reversible reaction on the collector's surface. The apparent rate constants and equilibrium collector capacity are explicitly related to the interaction profile and are shown to have the Arrhenius form. They do not depend on the collector geometry or flow pattern. Under conditions where the apparent reaction controls the rate, an exponential sensitivity to particle size is predicted. Decreasing ionic strength is observed to enhance this sensitivity, but at the cost of lower rates. Similar sensitivity is also expected for properties related to chemical constitution. By giving careful attention to the choice of column packing and the ionic strength of the carrier solution, the particle's residence time may be controlled by the adsorption/desorption of particles over an energy barrier. This process is defined here as potential-barrier chromatography. It promises to be much more selective toward particle properties than gel or hydrodynamic chromatography.

Early experiments on flocculation revealed that it may be induced by adding electrolyte to the solution in which the sol is suspended and can sometimes be reversed by dialyzing the electrolyte from the floc. The DLVO theory (Verwey and Overbeek, 1948) adequately explains flocculation but does not allow for reversibility. If only van der Waals attractions and electrostatic double-layer repulsions are considered, the particles in the floc are held together in an infinitely deep energy well, regardless of the ionic strength. Hamaker (1937*a*) qualitatively explained reversibility by considering short-range Born repulsion among the interactions. Then the energy well is not infinitely deep, and its depth becomes dependent on ionic strength.

Measurements of the rate of deposition of particles, suspended in a moving phase, onto a surface also change dramatically with ionic strength (Marshall and Kitchener, 1966; Hull and Kitchener, 1969; Fitzpatrick and Spielman, 1973; Clint et al., 1973). This indicates that repulsive double-layer forces are also of importance to the transport rates of particulate solutes. When the interactions act over distances that are small compared to the diffusion boundary-layer thickness, the rate of transport can be computed (Ruckenstein and Prieve, 1973; Spielman and Friedlander, 1974) by lumping the interactions into a boundary condition on the usual convective-diffusion equation. This takes the form of an irreversible, first-order reaction on the surface. A similar analysis has also been performed for the case of unsteady deposition from stagnant suspensions (Ruckenstein and Prieve, 1975).

In the present paper, the previous analysis for moving suspensions is extended to allow reversible deposition by including the short-range Born repulsion. The apparent surface reaction is then shown to be reversible and first order in both directions and thus is analogous to gas adsorption at low surface coverage. Applications include solid-liquid separations, particle separation, and chromatography.

A SIMPLIFIED QUANTITATIVE MODEL OF PHYSICAL INTERACTIONS

The van der Waals interaction energy between a sphere and a semiinfinite plate has been estimated, as a function of the sphere-plate separation distance, by Hamaker

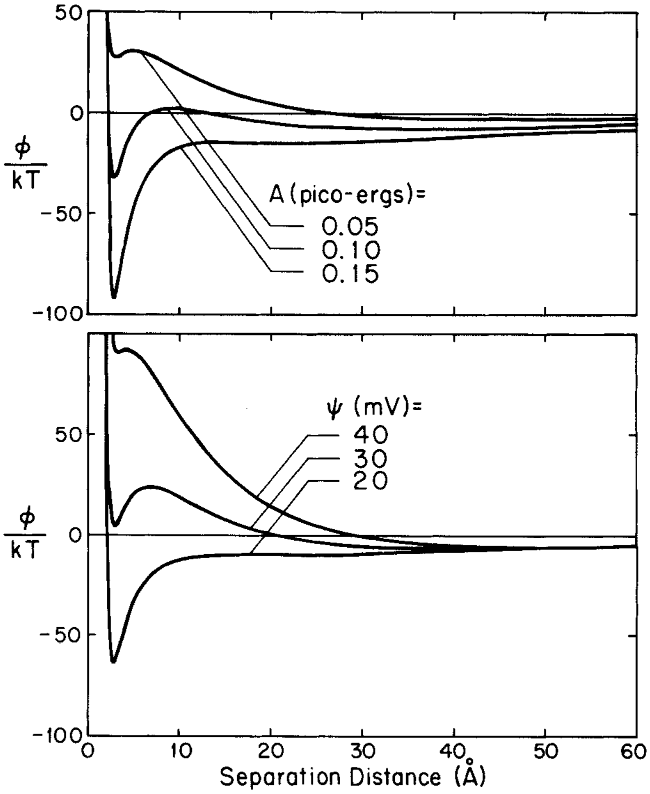

Fig. 1. Effect of (*a*) Hamaker's constant and (*b*) surface potential upon the total interaction energy profile. Unless otherwise indicated, $A = 1 \times 10^{-13}$ erg, $\psi_{S1} = \psi_{S2} = 25$ mV, $\sigma = 5$Å, $n = 0.1$M, $a_p = 0.1\ \mu$m, $\epsilon = 74.3$, and $T = 300$°K.

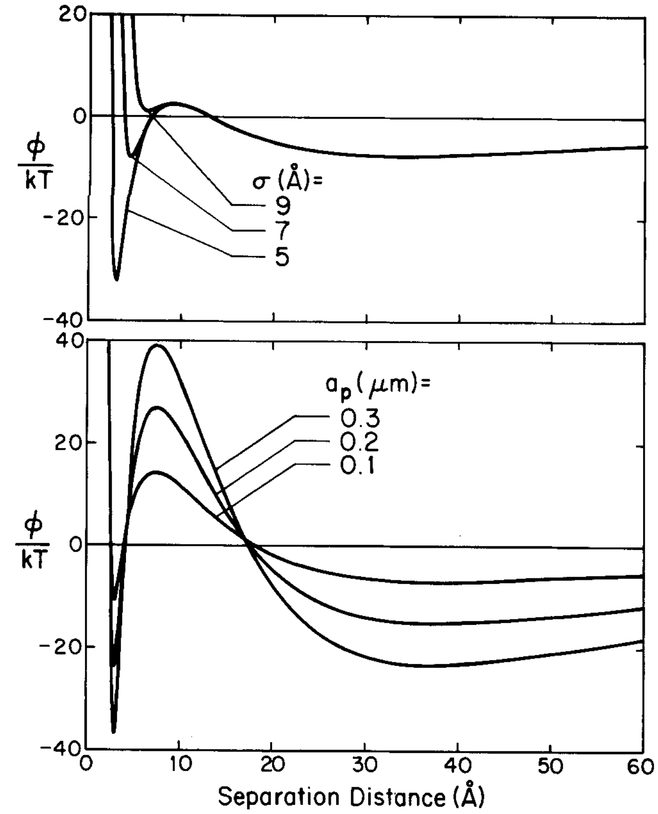

Fig. 2. Effect of (*a*) collision diameter and (*b*) particle radius upon the total interaction energy profile. Other properties have the same value as in Figure 1, except $\psi_{S1} = \psi_{S2} = 28$ mV in (*b*).

(1937*b*), who assumed that the molecular interactions could be linearly superimposed:

$$\phi_6(h) = \frac{A}{6}\left[\ln\left(\frac{h+2a_p}{h}\right) - 2\frac{a_p}{h}\frac{h+a_p}{h+2a_p}\right] \qquad (1)$$

Lifshitz' more recent continuum analysis of the van der Waals interaction (Israelachvili and Tabor, 1973) leads to approximately the same distance dependence but to a more accurate physical interpretation of Hamaker's constant A. However, this distinction becomes unimportant to the present analysis if A is treated as a measurable property.

Born repulsion is a short-range molecular interaction, resulting from the overlap of electron orbitals. It is the twelfth-order term of the empirical Lennard-Jones 6-12 potential. To estimate the Born repulsion between a sphere and a plate, the authors of the present paper assumed these molecular interactions also could be linearly superimposed to obtain

$$\phi_{12}(h) = \frac{A\sigma^6}{7\,560}\left[\frac{8a_p+h}{(2a_p+h)^7} + \frac{6a_p-h}{h^7}\right] \qquad (2)$$

where the collision diameter σ will be treated as a second characteristic property of the solids.

When macroscopic surfaces come in contact with polar solvents, such as water, an electrostatic charge can develop on the surface as a result of the loss or gain of a proton or another ion by the surface. This gives rise to a double-layer force between two opposing surfaces. Using the method suggested by Verwey and Overbeek (1948, p. 70) for weak interactions, the authors have calculated the double-layer interaction between two opposing, dissimilar planes (Prieve and Ruckenstein, 1975) and then applied Derjaguin's method (Hogg, Healy, and Fuerstenau, 1966) to obtain the sphere-plane interaction energy:

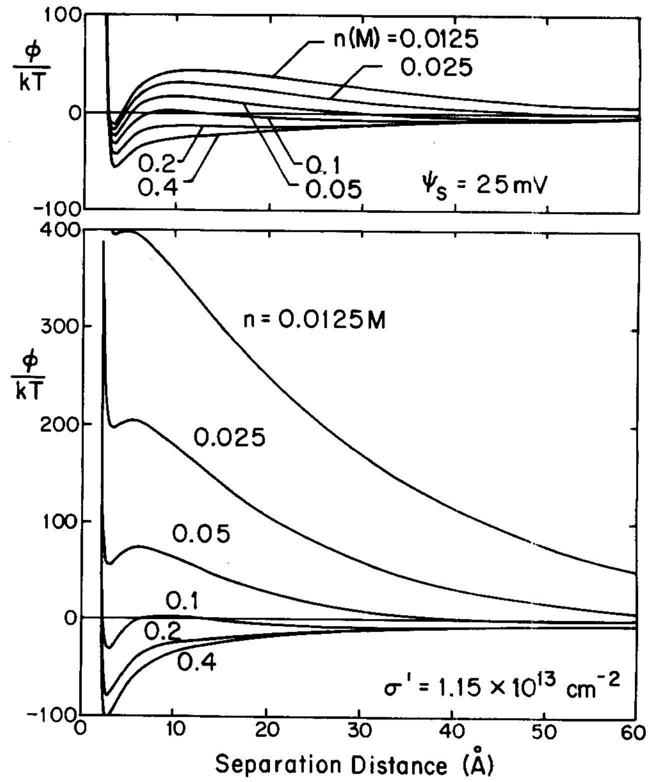

Fig. 3. Effect of ionic strength upon the total interaction energy profile when (*a*) surface potential or (*b*) surface charge density is held fixed. In (*b*), the charge density was chosen so that $\psi_{S1} = \psi_{S2} = 25$ mV when $n = 0.1$M. Other parameters have the same value as in Figure 1.

$$\phi_{DL}(h) =$$

$$16\epsilon\left(\frac{kT}{e}\right)^2 a_p \tanh\left(\frac{e\psi_{S1}}{4kT}\right)\tanh\left(\frac{e\psi_{S2}}{4kT}\right)e^{-\kappa h} \qquad (3)$$

This expression is appropriate for monovalent electrolyte solutions when $\kappa h > 2$ and $\kappa a_p >> 1$.

Summing the contribution from each effect gives the total energy of interaction:

$$\phi(h) = \phi_{12}(h) + \phi_6(h) + \phi_{DL}(h) \qquad (4)$$

Equations (1) to (4) form a simplified quantitative model for the interactions. A number of additional effects, such as surface roughness on the order of σ, solvation of the surface, and elastic deformations resulting from the interactions could also be incorporated in the model. For the present objectives the simplified model of Equations (1) through (4) will be used; however, any expression for $\phi(h)$ can be substituted in the final result of the next section.

Figures 1 to 3 illustrate the quantitative effect of various properties on the interaction profile $\phi(h)$. Four observations are noteworthy. First, there exists a narrow range of Hamaker's constant and surface potentials for which a maximum $[\phi_{\max} = \phi(h_{\max})]$ and two minima $[\phi_{mn1} = \phi(h_{mn1})$ and $\phi_{mn2} = \phi(h_{mn2})]$, exist where $h_{mn2} < h_{\max} < h_{mn1}$. If A is too small (large) or ψ_S too large (small), $\phi_{\max}$ and $\phi_{mn2}(\phi_{mn1})$ merge leaving only one extremum. Since a maximum is assumed in the rate analysis of the next section, the properties A, ψ_{S1}, and ψ_{S2} are restricted to those values (see Figure 4) where three extrema occur. Second, $\phi(h)$ at all h is roughly proportional to the particle radius. Third, holding the charge density fixed when the ionic strength is changed leads to more dramatic changes in $\phi(h)$ than when the surface potential is held fixed. Charge density, surface po-

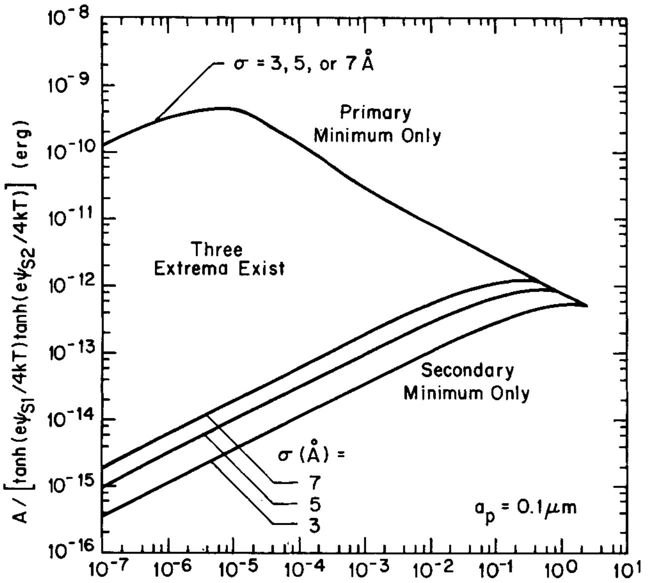

Fig. 4. Map of the region in which the potential energy profile possesses three extrema. Particle radius has practically no effect on the boundaries, except at very low ionic strength. This map was drawn for $a_p = 0.1$ μm.

tential, and ionic strength are related by the Gouy-Chapman equation (Verwey and Overbeek, 1948, p. 32)

$$\sigma' = (2\epsilon kTn/\pi)^{1/2} \sinh (e\psi_S/2kT) \qquad (5)$$

provided the surfaces are widely separated and the electrolyte is univalent. Fourth, depending on ionic strength, the primary minimum (ϕ_{mn2}) may be above the secondary minimum (ϕ_{mn1}). Table 1 summarizes the effect of each parameter on the values of the extrema.

EVALUATION OF ADSORPTION/DESORPTION RATES

Transport through the Interaction Boundary Layer

Consider a thin region near to the collector, whose thickness δ_o is defined so that fluid motion can be neglected inside the region, and particle-collector interactions can be neglected outside it. This region is defined as the interaction boundary layer. By denoting by $c(x)dx$ the number of centers per unit surface area located between x and $x + dx$, where $x = h + a_p$, the net flux of particles through the region can be expressed as the sum of contributions from the total interaction force $-d\phi/dh$ and from Brownian motion

$$J = - D(h) \frac{dc}{dh} - m(h) \frac{d\phi}{dh} c \qquad (6)$$

where the particle mobility can be evaluated from Stokes' law, as modified by Brenner (1961) to account for wall effects (which become important when the particle is near the collector)

$$m(h) = \frac{f(h/a_p)}{6\pi\mu a_p} \qquad (7)$$

and where the diffusion coefficient is given by the Nernst-Einstein equation

$$D = mkT \qquad (8)$$

The wall correction $f(H)$ tends to H when $H << 1$ and to unity when $H >> 1$.

Suppose that the interaction forces establish an energy barrier that retards the motion of particles both toward and away from the collector. If this barrier reduces the adsorption and desorption rates significantly, particles near the primary minimum will have time to achieve a balance between the interaction forces and Brownian motion, before their population changes. Integration of Equation (6) with $J \approx 0$ and $D = mkT$ leads to a Boltzmann distribution

$$c(h) = \frac{n_2}{I_2} \exp [- \phi(h)/kT] \text{ for } h < \delta_2 \qquad (9a)$$

where $I_2 = \int_o^{\delta_2} \exp [- \phi(h)/kT]dh$, and δ_2 is the largest h in the interval (h_{mn2}, h_{max}) for which a Boltzmann distribution can be assumed. The integration constant n_2/I_2 was determined so that $\int_o^{\delta_2} c(h)dh = n_2$, where n_2 is the number of particles adsorbed per unit area. These arguments can also be applied near the secondary minimum. Here the equilibrium distribution is given by

$$c(h) = c_i \exp [- \phi(h)/kT] \text{ for } \delta_1 < h < \delta_o \qquad (9b)$$

where δ_1 is the smallest h in the interval (h_{max}, h_{mn1}) for which a Boltzmann distribution can be assumed. In this region the integration constant is calculated as $c_i = c(\delta_o)$, noting that δ_o is defined so $\phi(\delta_o) \approx 0$.

A Boltzmann distribution cannot be obtained in the middle region ($\delta_2 < h < \delta_1$) containing the maximum because particles do not reside in this region long enough to establish an equilibrium. However, this zone is sufficiently thin so that J can be assumed to be constant throughout. Integration of Equation (6) then leads to

$$-J = \{c(h) \exp [\phi(h)/kT]\} \Big|_{\delta_2}^{\delta_1} \left\{ \int_{\delta_2}^{\delta_1} \frac{\exp [\phi(h)/kT]}{D(h)} dh \right\}^{-1} \qquad (10)$$

Evaluating $c(\delta_2)$ from Equation (9a) and $c(\delta_1)$ from Equation (9b), we get

$$-J = K_f c_i - K_r n_2 \qquad (11)$$

where $K_f^{-1} = \int_{\delta_2}^{\delta_1} D^{-1} \exp (\phi/kT)dh$ and $K_r = K_f/I_2$.

TABLE 1. EFFECT OF PHYSICAL PARAMETERS ON EXTREMA IN THE INTERACTION ENERGY PROFILE*

Physical parameter	Effect on extrema				
	ϕ_{mn2}	ϕ_{max}	ϕ_{mn1}	$\phi_{max} - \phi_{mn2}$	$\phi_{max} - \phi_{mn1}$
Hamaker's constant	−	−	−	+	−
Surface potential	+	+	+	−	+
Collision diameter	+	~0	0	−	~0
Particle radius	(+)	(+)	(+)	+	+
Ionic strength					
(constant potential)	−	−	−	−	−
(constant charge)	−	−	−	+	−

* + denotes increase in extremum results from an increase in value of parameter.
− denotes decrease in extremum results from an increase in value of parameter.
(+) denotes increase in absolute magnitude results from an increase in value of parameter.
0 denotes no significant effect.

To determine the net rate of adsorption of particles suspended in a fluid that is flowing over the collector, one may then solve the usual convective-diffusion equation subject to a reversible first-order reaction as the boundary condition, provided the diffusion boundary layer is much thicker than the interaction boundary layer.

The forward rate constant is evaluated as the integral of exp $[\phi(h)/kT]/D(h)$, which assumes its largest value at $h = h_{\max}$ and decays rapidly as $|h - h_{\max}|$ increases. Then it is reasonable, following Kramers (1940), to expand $\phi(h)$ in a Taylor series about $h = h_{\max}$

$$\phi(h) = \phi_{\max} - \frac{1}{2}\gamma_{\max}(h - h_{\max})^2 \qquad (12)$$

truncating after the second-order term, with $\gamma_{\max} = -d^2\phi/dh^2|_{h=h_{\max}}$. Substituting this parabolic approximation into the definition of K_f and integrating, we get an expression containing error functions. If the maximum is a sharp spike, their arguments become sufficiently large so that the error functions tend to a maximum value of unity, whereupon the expression for the forward rate constant reduces to

$$K_f \approx D(h_{\max}) \left(\frac{\gamma_{\max}}{2\pi kT}\right)^{1/2} \exp\,(-\phi_{\max}/kT) \qquad (13a)$$

Because $D(h)$ varies slowly compared to the exponential, it was replaced by its value $D(h_{\max})$ at the central point of the expansion. Similar arguments can be applied to the definition of I_2 to obtain

$$K_r \approx D(h_{\max}) \frac{(\gamma_{\max}\gamma_{mn2})^{1/2}}{2\pi kT} \exp\left(-\frac{\phi_{\max} - \phi_{mn2}}{kT}\right) \qquad (13b)$$

where $\gamma_{mn2} = +d^2\phi/dh^2|_{h=h_{mn2}}$. Hence the apparent rate constants have the Arrhenius form, with $\phi_{\max}$ as the activation energy for adsorption, $\phi_{\max} - \phi_{mn2}$ as the activation energy for desorption, and ϕ_{mn2} as the heat of adsorption. When saturated, $J = 0$, and the grain capacity is $(K_f/K_r)c_o$. The ratio K_f/K_r is determined mainly by ϕ_{mn2}, which becomes more negative as ionic strength increases (Figure 3), thereby leading to larger K_f/K_r. Particle-particle interactions have implicitly been neglected, which requires the grain capacity to correspond to substantially less than monolayer coverage. This condition is met provided that the bulk particle concentration is sufficiently dilute.

In summary, the expression for the net rate of particle transport through the interaction boundary layer takes the same form as a first-order, reversible, heterogeneous chemical reaction, provided that $\phi_{\max}$ and $\phi_{\max} - \phi_{mn2}$ are large compared to kT, $\min\{\delta_1 - h_{\max}, h_{\max} - \delta_2\}$ $(\gamma_{\max}/2kT)^{1/2} > 2$, $\min\{h_{mn2}, \delta_2 - h_{mn2}\}$ $(\gamma_{mn2}/2kT)^{1/2} > 2$, and δ_o is small compared to the diffusion boundary-layer thickness. An additional assumption is that the particles are not carried over the barrier by their inertia. Therefore, the inertial force on the particle must be small compared to the applied force $-d\phi/dh$

$$|F_{\text{inertia}}| = M \left| V\frac{dV}{dh} \right|$$
$$\approx Mm \left| \frac{d\phi}{dh}\frac{d}{dh}\left(m\frac{d\phi}{dh}\right) \right| << \left| \frac{d\phi}{dh} \right|$$

which is satisfied when $|d(md\phi/dh)/dh| << m^{-1}M^{-1}$. If inertia is not negligible, the problem must be solved by using the more general Fokker-Plank equation (Chandrasekhar, 1943, p. 65).

Transport to a Rotating Disk

As an example, suppose that a fluid containing particles is in contact with a rotating disk. What will be the net rate of adsorption onto the collector disk? Levich (1962) neglected radial variations and solved the usual convective-diffusion equation, taking the concentration as c_i at the disk surface and as c_o far away from the disk. If c_i is eliminated from his solution by imposing Equation (11) at this surface, with $J = -D\, dc/dy|_{y=0}$, the result for the net adsorption rate will be

$$-J = \frac{B}{B+1}(K_f c_o - K_r n_2) \qquad (14)$$

where

$$B = \frac{\alpha D(\infty)}{K_f \Gamma(4/3)} \text{ and } \alpha^3 = \frac{0.170}{D(\infty)}\left(\frac{\omega^3 \rho_f}{\mu}\right)^{1/2}$$

As particles accumulate on the disk, n_2 and J can be expected to change slowly with time. Substituting dn_2/dt for $-J$ and integrating, we get

$$n_2(t) = \frac{K_f}{K_r}c_o + \left(n_{2i} - \frac{K_f}{K_r}c_o\right) \exp\,[-(B+1)K_r t/B] \qquad (15a)$$

and

$$-J(t) = \frac{B}{B+1}(K_f c_o - K_r n_{2i}) \exp\,[-(B+1)K_r t/B] \qquad (15b)$$

At steady state, the number density of adsorbed particles is $K_f c_o/K_r$, regardless of the initial density n_{2i}. Thus, if $n_{2i} < K_f c_o/K_r$, a net adsorption will take place, whereas if $n_{2i} > K_f c_o/Kr$, a net desorption occurs. From Equation (13), K_f/K_r depends primarily on the depth ϕ_{mn2} of the primary minimum which in turn is influenced significantly by the ionic strength (Figure 3).

Transport in Creeping Flow over Cylinders and Spheres

Because the concentration must depend on both angular and radial positions, the exact analysis for cylinders and spheres is considerably more complex than for the rotating disk. However, rigorous calculations of the rate in these geometries with $K_r = 0$ (Ruckenstein and Prieve, 1973) revealed that a dimensionless parameter B always can be defined which uniquely determines the dimensionless area-average flux and, further, that the dependence of this flux on B is nearly identical (±20%) for all geometries examined. Extrapolating this experience to $K_r \neq 0$ one expects, as a first approximation, that Equation (15) may also be applied to cylinder and sphere geometries, provided that n_2 and J are area-average quantities and B is evaluated as $\alpha D(\infty)/K_f\Gamma(4/3)$, where α^3 is $U/2a^2D(\infty)$ or $2\beta U/3a^2D(\infty)$ for a sphere or a cylinder, respectively.

RESULTS AND DISCUSSION

Evaluation of Apparent Rate Constants

Figure 5 shows the dependence of the apparent adsorption rate constants upon particle radius and ionic strength for two extreme cases: surface potential or charge density held fixed as the ionic strength is changed, where the ψ_S, σ', and n are related by Equation (5). These results were obtained by using trial-and-error procedures on a digital computer to locate the three extrema in Equation (4) for each set of conditions. Then the necessary functions were evaluated and substituted into Equations (13).

One feature of Figure 5 is the enormous variation in the rate constants (tens of orders of magnitude) resulting from relatively small changes in particle size or ionic strength. Measurements of deposition rates, under condi-

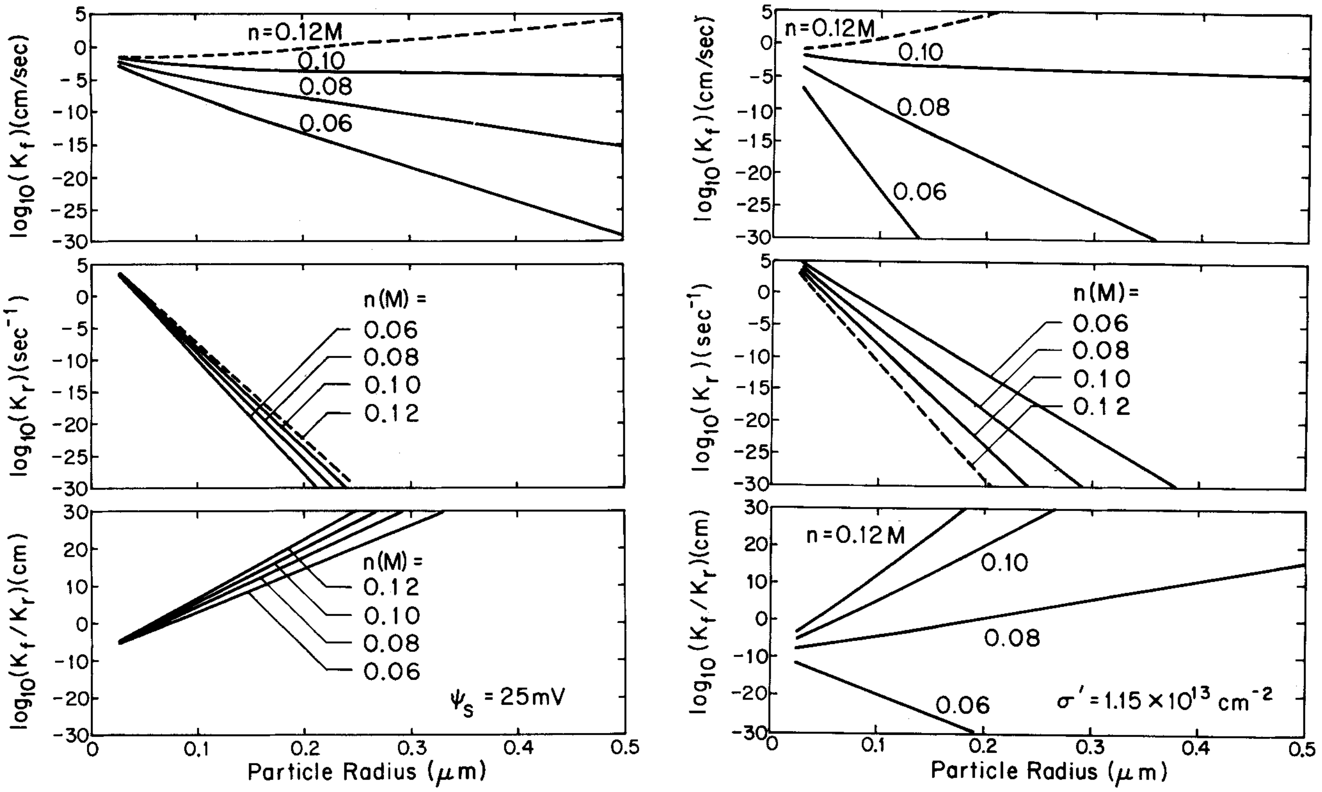

Fig. 5. Effect of particle radius and ionic strength upon the adsorption/desorption rate constants and the collector capacity when *(a)* surface potential is 25 mV at all ionic strengths or *(b)* surface charge density is the same at all ionic strengths. Charge density in *(b)* is chosen as in Figure 3*b*, while other parameters have the same values as in Figure 1.

tions where the interaction forces are rate limiting (rates then reflect K_f) by Clint et al. (1973) and Hull and Kitchener (1969) indeed do show great sensitivity to ionic strength and in the direction indicated but not as great as inferred from Figure 5. Oversensitivity in the predictions undoubtedly results from inaccuracies in the estimation of the interaction energy and its dependence upon ionic strength. Small errors in the interaction energy are greatly amplified by the exponentiation in Equations (13). Available expressions for the energy are not sufficiently accurate for quantitative rate predictions. However, they can be used, as in the present paper, to make qualitative predictions of the rate. Furthermore, this sensitivity may be exploited to study the nature of the total particle-surface interaction by measuring the rates of deposition and equilibrium surface coverage.

Because the rate constants have the Arrhenius form and the apparent activation energies are nearly proportional to particle radius (Figure 2*b*), the semilog plots of K_f and K_r against a_p are nearly linear, as shown in Figure 5. The slope of the K_f lines is negative at low ionic strengths, where $\phi_{\max}$ is positive, and positive at high ionic strength, where $\phi_{\max}$ is negative (Figure 3). Since $\phi_{\max} - \phi_{mn2}$ must be positive, the slope of the K_r lines is always negative. Similarly, the sign of the slope of the K_f/K_r lines is determined by the sign of ϕ_{mn2}. Ionic strength has a more profound effect on the rate when the surface charge is held fixed rather than the surface potential. This follows directly from the effect of ionic strength on the interaction energy.

Implications for Particle Removal

If a particular type of particle is to be removed from a suspension by adsorption onto the grains of a packed bed, then clearly the maximum rate will be achieved by choosing grains having a charge opposite to the particles so that no energy barrier exists. However, such grains may saturate quickly and be difficult to regenerate. Regeneration may be easier if the grains have the same charge as the particles. By adsorbing at high ionic strengths, Figure 5 shows that the rate of adsorption (K_f), as well as the grain's capacity ($n_{2f}/c_o = K_f/K_r$) to hold adsorbed particles, will be most favorable. When grains and particles have the same charge, regeneration of the saturated grains may be possible by purging the bed with a particle free solution having low ionic strength, since this corresponds to the maximum rate of desorption (K_r) and the minimum grain capacity (K_f/K_r). However, even at the lowest ionic strength, the desorption rate for a given system may be insufficient for practical regeneration. One solution might be to choose a different grain material to give the system a smaller Hamaker constant or larger collision diameter. A second anticipated problem is the sintering which may occur between the particles and grains. Such strong bonds would prevent desorption. Possibly, this may be averted by strongly adsorbing certain molecules on the grains which prevent sintering but still allow the particle to get close enough to physically adsorb.

Implications for Particle Separation

Suppose that two or more different types of particles are dispersed in water to form a mixed suspension. A means to separate one component of the mixture from the others is to selectively adsorb that component on the grains of a packed bed, while the remaining components pass through. Selectivity of physical adsorption results from differences in particle size, shape, or chemical constitution where the latter will affect the surface potential, Hamaker's constant, and collision diameter. Variation in the adsorption rate constant K_f with particle size can be seen in Figure 5. From these curves it can be concluded that selectivity, based on size, improves as the ionic strength becomes different from the value where $\phi_{\max}$ is changing sign (0.1M for the system of Figure 5). By

TABLE 2. CHROMATOGRAPHIC TECHNIQUES FOR SEPARATION OF SUSPENDED PARTICLES

Technique	Mechanism	Basis of separation
Permeation chromatography	Movement of particles into and out of pores in packing grains	Particle size
Hydrodynamic chromatography	Movement of particles into and out of regions having low fluid velocity external to the grains	Particle size
Potential-barrier chromatography	Brownian movement of particles over a potential-energy barrier to become physically attached to or detached from the surface of grains	Particle size, particle constitution (surface charge density, collision diameter of surface molecules, Hamaker constant)

decreasing the ionic strength below 0.1M, the separation factor ($d \ln K_f/d\, a_p$) is enhanced at the cost of decreasing adsorption rates and grain capacity. Although both the separation factor and K_f are enhanced above 0.1M, no energy barrier exists. Then, convective diffusion can be expected to control the rate, making the adsorption less selective. By operating at lower ionic strengths, the rate becomes controlled by the resistance to transport through the interaction boundary layer, which can be expected to be much more sensitive to particle size than the resistance of the diffusion boundary layer (decaying exponential vs. cube root).

Chromatographic Separation of Suspended Particles

If the desorption rate is sufficiently large, chromatographic separation and analyses of mixed suspensions become possible. Dependence of adsorption and desorption rates upon particle properties causes some components of a pulse of mixed particles carried through a packed bed to be eluted more quickly than others. This mechanism is analogous to conventional gas chromatography, and all the formalisms developed for the latter may be applied.

Gel and hydrodynamic chromatography (Determan, 1968; DeMarzio and Guttman, 1969) are two other methods for particle size analysis. They differ from the method proposed above in the mechanism by which particles are retained in the bed. When the packing contains pores which are permeable to some but not all of the particles, those particles which are small enough to enter the pores through Brownian motion will require a larger average residence time. This is the mechanism of gel (permeation) chromatography. Hydrodynamic chromatography results from the nonuniformity in the velocity profile between grains; pores are not required. Because the center of smaller particles is able to move closer to the surface of grains, these particles have a lower average velocity.

Physical interactions between particles and grains can greatly affect, and sometimes overwhelm, hydrodynamic chromatography. For example, if particles and grains bear like charges, so that a strong repulsive force develops, none of the particles will be able to get as near to the wall as in the absence of the force. Consequently, all particles move more rapidly through the bed. This effect has been observed at low ionic strengths by Small (1974). Conversely, strong attractive forces may cause rapid physical adsorption of the particles, whereupon the residence time becomes controlled by the time between adsorption and desorption. Then hydrodynamics are much less important. Finally, when both attractive and repulsive forces act, adsorption still occurs, but a surmountable energy barrier now can develop which will control the adsorption and desorption rates. Separation under these conditions is defined here as potential-barrier chromatography (see Table 2). At sufficiently high ionic strengths, where the energy barrier is surmountable, Figure 4 shows that the range of A, ψ_{S1}, and ψ_{S2} corresponding to the existence of a maximum is narrow. However, if a surmountable barrier can be achieved, the rates of adsorption and desorption will be very sensitive to particle size (see Figure 5). Sensitivity to the surface charge density and Hamaker constant likewise could be demonstrated. Consequently, the selectivity of the new proposed potential-barrier chromatography is anticipated to be substantially better than when rapid adsorption occurs in the absence of an energy barrier (ordinary diffusion controls rate) or when no adsorption takes place owing to an insurmountable barrier (hydrodynamic chromatography). Furthermore, separation of particles having the same size, but different chemical constitution, can also be performed by potential-barrier chromatography, due to the sensitivity to the charge on the particle's surface, its collision diameter and Hamaker constant. Finally, shape selectivity may also be possible, based on differences in the interaction between a plane collector and disks or spheres of the same volume and chemical constitution.

Applications to Other Problems

By including Born repulsion in the calculation of the interaction energy profile, the primary minimum ϕ_{mn2} is finite and depends on ionic strength. Allowing the primary to be above the secondary minimum ϕ_{mn1}, one is able to explain the large equilibrium separation (about 90 Å) which is known to occur between biological cells. Without short-range repulsion, the primary energy well becomes infinitely deep, and h_{mn2} (<10 Å) is the only stable equilibrium separation.

Hamaker (1937*a*) has suggested that short-range repulsion is responsible for repeptization (reverse of flocculation). By repeating the analysis of this paper for interactions between unequal spheres, one could calculate both flocculation and repeptization rates and, in principal, thereby predict the distribution of floc sizes, including the limiting equilibrium distribution.

NOTATION

a = radius of collector, cm
a_p = particle radius, cm
A = Hamaker's constant, erg
B = $\alpha D(\infty)/K_f\Gamma(4/3)$
c = local particle concentration, particles/cm^3
c_i = particle concentration at interface between the interaction and diffusion boundary layers (at $h = \delta_o$), particles/cm^3
c_o = particle concentration in bulk of solution, particles/cm^3
D = local diffusion coefficient, cm^2/s
e = protonic charge, statcoul
f = local wall correction factor for D and m
h = minimum separation distance between particle and collector surfaces, cm
H = h/a_p
I_2 = $\int_0^{\delta_2} \exp\,[-\phi(h)/kT]dh$, cm

J = particle flux, particles/(cm^2-s)
k = Boltzmann constant, erg/°K
K_f = $\left\{ \int_{\delta_2}^{\delta_1} \frac{\exp[\phi(h)/kT]}{D(h)} dh \right\}^{-1}$, cm/s
K_r = K_f/I_2, s^{-1}
m = local particle mobility, (cm/s)/dyne
M = mass of a single particle, g
n = ionic strength of bulk solution, ions/cm^3*
n_2 = number of adsorbed particles, particles/cm^2
n_{2i} = initial value of n_2, particles/cm^2
n_{2f} = final value of n_2, particles/cm^2
T = absolute temperature, °K
U = approach velocity, cm/s
y = distance measured normal to collector, cm

Greek Letters

α = $[(0.170/D(\infty))(\omega^3\rho_f/\mu)^{1/2}]^{1/3}$, cm^{-1}
β = $1 - 0.5 \ln (2aU\rho_f/\mu)$
γ = $|d^2\phi/dh^2|$, erg/cm^2
Γ = Gamma function
δ_o = thickness of interaction boundary layer, cm
δ_1 = smallest h in the interval $h_{\max} < h < h_{\text{mn1}}$ for which a Boltzmann distribution of particles may be assumed, cm
δ_2 = largest h in the interval $h_{\text{mn2}} < h < h_{\max}$ for which a Boltzmann distribution of particles may be assumed, cm
ϵ = fluid dielectric constant
κ = $(8\pi ne^2/\epsilon kT)^{1/2}$, cm^{-1}
μ = fluid viscosity, g/(cm-s)
ρ_f = fluid density, g/cm^3
σ = collision diameter, cm
σ' = electrostatic surface charge density, statcoul*
ϕ = total potential energy of interaction, erg
ϕ_6 = van der Waals energy of interaction, erg
ϕ_{12} = Born energy of interaction, erg
ϕ_{DL} = double-layer energy of interaction, erg
ψ_{Si} = electrostatic potential of surface i, statvolt*
ω = disk rotation speed, rad/s

Subscripts

max = evaluated at the maximum of $\phi(h)$
mn1 = evaluated at the secondary minimum of $\phi(h)$
mn2 = evaluated at the primary minimum of $\phi(h)$

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* A consistent set of units has been specified above for each symbol, although more convenient units are sometimes employed in the text (for example, mV instead of statvolts).

Constitutive Equation for Vapor Drift Velocity in Two-Phase Annular Flow

A constitutive equation for a vapor drift velocity which specifies the relative motion between phases in the drift flux model is developed for two-phase annular flows. The constitutive equation is derived by taking into account the interfacial geometry, the body force field, and the interfacial momentum transfer, since these macroscopic effects govern the two-phase diffusions. A comparison of the model with three sets of experimental data obtained over a wide range of flow parameters shows a satisfactory agreement.

MAMORU ISHII
T. C. CHAWLA
and
NOVAK ZUBER

Argonne National Laboratory
Reactor Analysis and Safety Division
9700 South Cass Avenue
Argonne, Illinois 60439

Correspondence concerning this paper should be addressed to M. Ishii. N. Zuber is with the Reactor Safety Division, U.S. Nuclear Regulatory Commission, Washington, D. C.