$\rho$ = density, g/cm$^3$
$\tau$ = shear stress, g/cm s$^2$
$\tau_w$ = wall shear stress, g/cm s$^2$

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# On Reversible Adsorption of Hydrosols and Repeptization

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In a previous paper (Ruckenstein and Prieve, 1976) the reversible deposition of particles from a moving fluid was treated by lumping the effect of the interaction forces between particles and the deposition surface in a boundary condition to the usual convective-diffusion equation. The boundary condition was obtained by analyzing the flux of particles through a very thin layer (~ 100Å) next to the collector's surface. Within this interaction force boundary layer, a quasi steady state was assumed up to a point between the maximum and primary minimum (in the profile of the potential energy of interaction), with quasi equilibrium assumed between that point and the wall (a region in which most of the accumulation is expected to occur). In what follows, this is called approximation A. The goals of this note are: (1) to compare approximation A with approximation B, which assumes quasi steady state over the entire thickness of the interaction force boundary layer, and (2) to extend the analysis to flocculation and repeptization of hydrosols.

In one dimension the equation of continuity for the particles within the thin layer is

$$\frac{\partial c}{\partial t} + \frac{\partial J}{\partial h} = 0$$

where the nomenclature is that of Ruckenstein and Prieve (1976) and J is given by Equation (6) of that same paper. To prevent particles from penetrating the wall at $h = 0$ and to match the concentration at $h = \delta_0$ with that outside the interaction force boundary layer, the following boundary conditions must be imposed:

$$\begin{aligned} J &= 0 \quad \text{at} \quad h = 0 \\ c &= c_i \quad \text{at} \quad h = \delta_0 \end{aligned}$$

where $\delta_0$ is the thickness of the interaction forces boundary layer. The solution of this unsteady problem would allow the accumulation of particles near the surface to be evaluated. More details will be found in Prieve and Ruckenstein (to be published).

When the interaction forces establish an energy barrier that reduces adsorption and desorption rates significantly, particles around the primary minimum ($0 \leq h \leq \delta_2$) have time to achieve quasi equilibrium before their population changes. Then, assuming a quasi steady state for the remainder of the region, we have (alternative A)

$$\begin{aligned} J &= 0 \quad \text{for} \quad 0 \leq h \leq \delta_2 \\ \partial J/\partial h &= 0 \quad \text{for} \quad \delta_2 < h \leq \delta_0 \end{aligned}$$

where $\delta_2$ must be chosen strictly less than $h_{\max}$. This position ($h_{\max}$), corresponding to a maximum in the interaction potential, is unstable; therefore, it is not reasonable to assume quasi equilibrium there.

Note that the boundary condition $J = 0$ at $h = 0$ is automatically satisfied. Using the other boundary condition and Equation (6), we previously obtained Equation (11)

$$-J = \frac{c_i \left( \int_0^{\delta_2} e^{-\phi/kT}\, ds \right) - n_2}{\left( \int_0^{\delta_2} e^{-\phi/kT}\, ds \right) \left( \int_{\delta_2}^{\delta_0} D^{-1}\, e^{\phi/kT}\, ds \right)} \qquad \text{(A)}$$

for the net adsorption rate, where $n_2$ is the number of adsorbed particles per unit area, or

$$n_2 = \int_0^{\delta_2} c ds$$

One may be tempted to replace $h = \delta_0$ by $h = \infty$. However, this causes the integrals to diverge (Prieve and Ruckenstein, 1976) because of the way the diffusion coefficient (or particle mobility) tends to its bulk value. Prieve and Ruckenstein (1976) have shown that for a low potential barrier the integral depends on the value of $\delta_0$. Because it is not possible to define a precise value of $\delta_0$, the lumping of the effect of the interaction forces in a boundary condition is meaningless in this case. If the potential barrier is high enough, the integral is practically independent of $\delta_0$, provided $\delta_0$ is assigned a physically reasonable, finite value. Then the value of the integral will be in agreement with that obtained using the parabolic approximation for the interaction potential around the maximum (Prieve and Ruckenstein, 1976).

If the quasi steady state approximation is imposed for all $h$, then (alternative B)

$$\frac{\partial J}{\partial h} = 0 \quad \text{for} \quad 0 \leq h \leq \delta_0$$

There is no reason to believe that this approximation is better than the previous one. It represents only another limiting case. The integration of Equation (6) under this assumption leads to a result very similar to Equation (10):

$$-J = (c(h) \exp[\phi(h)/kT])\Big|_h^{\delta_0} \left( \int_h^{\delta_0} \frac{\exp[\phi(s)/kT]}{D(s)} ds \right)^{-1} .$$

Substituting $c(\delta_0) = c_i$, $\phi(\delta_0) = 0$ and the above definition of $n_2$, we obtain

$$-J = \frac{c_i \left( \int_0^{\delta_2} e^{-\phi/kT} ds \right) - n_2}{\int_0^{\delta_2} e^{-\phi(h)/kT} \int_h^{\delta_0} \frac{e^{\phi(s)/kT}}{D(s)} dsdh} \qquad \text{(B)}$$

which differs from (A) in that the denominator is a double integral rather than the product of two integrals.

Obviously, Equations (A) and (B) are not identical. The difference stems from the assumption that $J = 0$ in (A) for $0 \leq h \leq \delta_2$ compared to the assumption $\partial J/\partial h = 0$ in (B) for the same range. But consider the case where $\phi(h)$ possesses a maximum $\phi_{\max}$ and a primary minimum $\phi_{mn2}$ (a secondary minimum may also exist but is not relevant to the current discussion). Also suppose that $\phi_{\max} - \phi_{mn2}$ and $\phi_{\max}$ are large compared to $kT$. (The latter is a necessary condition for the lumping of the effect of the interaction forces into a boundary condition to the convective-diffusion equation and is implicitly assumed in our development.) Then the integrand in the denominator of (B), $e^{-\phi(h)/kT} \int_h^{\delta_0} D^{-1} e^{\phi(s)/kT} ds$, will take on its largest value near the primary minimum ($h = h_{mn2}$) and will decay rapidly as $|h - h_{mn2}|$ becomes non zero. This suggests that the variable lower limit $h$ can be replaced by the constant $h_{mn2}$ without significantly changing the value of the double integral. Now the integral can be factored into the product of two integrals. Since the integrand $D^{-1} e^{\phi/kT}$ assumes its maximum value at $h = h_{\max}$ where $\phi = \phi_{\max}$ and decays rapidly as $|h - h_{\max}|$ differs from zero, we can compress the limits of integration from $(h_{mn2}, \delta_0)$ to $(\delta_2, \delta_0)$ where $h_{mn2} < \delta_2 < h_{\max} < \delta_0$. Under these conditions (A) and (B) are the same.

In the preceding discussion, a particle is said to be adsorbed when it is located near the primary minimum because it is here that the largest rate of accumulation occurs. Mathematically, this region was defined as the interval $0 \leq h \leq \delta_2$, where $\delta_2$ can reasonably be assumed somewhere in the interval $h_{mn2} < \delta_2 < h_{\max}$. Particles near the secondary minimum (if one exists) are not counted as adsorbed because generally the number of particles in its vicinity is not changing much with time compared to those near the primary minimum. For some applications, a definition of adsorbed particles which includes the secondary minimum may be more appropriate.

A similar analysis can also be performed in which flocculation is considered reversible. One must assume of course that elementary particles forming the floc maintain their individuality; thus they have not sintered together to form a single mass.

Suppose we have an electrolyte solution initially containing spherical flocs of radius $a_f$, each composed of many elementary particles of radius $a$, so that $a_f >> a$. Further, suppose that at $t = 0$ the electrolyte solution is suddenly diluted. The lowering of the ionic strength will increase the double layer repulsion between particles in the floc and thereby tend to disrupt it. Of course, some time is required for ions within the interior of the floc to diffuse out; this time is on the order of $t_e \sim a_f^2/D_e$, where $D_e$ is the diffusion coefficient of the electrolyte. Once the ions have had time to diffuse out, the floc could disintegrate into two or more fragments of any size smaller than $a_f$. Considering the potential energy of interaction between two ideally spherical fragments of radii $a_1$ and $a_2$, where $a_1^3 + a_2^3 = a_f^3$, one finds that an energy barrier, roughly proportional to $a_1 a_2/(a_1 + a_2)$ opposes separation of the two fragments. This barrier to separation is smallest when $a_1 << a_2$; hence the detachment of elementary particles from the outer surface of the floc is the most probable event following a lowering of the ionic strength. This would also be true for $t < t_e$ since the exterior of the floc is exposed to lower ionic strength before the interior, and thus the particles of the exterior first experience the increased double layer repulsion.

As an illustration of how the method of Ruckenstein and Prieve can be extended to repeptization of flocculated sols, assume that the detachment of elementary particles is the only possible event following dilution of the electrolyte and further assume, for the sake of simplicity, that free elementary particles do not flocculate, except to reassociate with the original floc. Let $J(r)$ denote the flux of elementary particle centers through the imaginary spherical surface of radius $r$, concentric with the floc's center and let $4\pi r^2 c(r)dr$ denote the number of particle centers located between $r$ and $r + dr$, relative to the floc's center. Using approximation B, but taking into account the spherical geometry, one obtains

$$N = 4\pi r^2 J(r) = \frac{n - c_\infty \int_0^{\delta_2} e^{-\phi/kT} dh}{\frac{1}{4\pi} \int_0^{\delta_2} e^{-\phi(h)/kT} \int_h^\infty D^{-1} (a + a_f + s)^{-2} e^{\phi(s)/kT} dsdh} = K_r' n - K_f' c_\infty \qquad \text{(C)}$$

where $n = \int_0^{\delta_2} c \, dh$ and $c_\infty$ is the number of free elementary particles per unit volume. Because $a_f >> \delta_2$, the curvature effect was neglected in the definition of $n$.

When $a_f >> a$, the potential energy of interaction between an elementary particle and a floc is equivalent to the potential energy $\phi(h)$ between a particle and a flat plate; thus $\phi(h)$ used by Ruckenstein and Prieve (1976) still applies. Furthermore, if the conditions necessary for Equation (13) of that paper apply, then the rate constants for reversible flocculation may be calculated as $K_f' = 4\pi a_f^2 K_f$ and $K_r' = 4\pi a_f^2 K_r$, where $K_f$ and $K_r$ are given by Equation (13).

Multiplying Equation (C) by the number of flocs per unit volume, $c_f$, yields the net rate of increase in free elementary particles $c_\infty$ per unit volume, or:

$$\frac{dc_\infty}{dt} = N c_f = K_r' n c_f - K_f' c_\infty c_f. \qquad \text{(D)}$$

As elementary particles detach from the floc, the radius $a_f$ gradually decreases so that the sum of the number of free elementary particles and the number of elementary parti-

TABLE 1. REPEPTIZATION RATES AND EQUILIBRIA[a]

| Ionic strength (mol/l) | $\frac{\phi_{mn2}}{kT}$ | $\frac{\phi_{\max}}{kT}$ | $K_r'$ (cm$^2$/sec) | $K_f'$ (cm$^3$/sec) | $\tau$ (sec) | $c_\infty^*$ (cm$^{-3}$) |
|---|---|---|---|---|---|---|
| 0.08 | $-21.4$ | 2.93 | $6.1 \times 10^{-10}$ | $2.6 \times 10^{-9}$ | 3.8 | $6.8 \times 10^{8}$ |
| 0.07 | $-18.2$ | 5.26 | $1.7 \times 10^{-9}$ | $2.8 \times 10^{-10}$ | 36 | $1.8 \times 10^{10}$ |
| 0.06 | $-13.8$ | 8.55 | $5.1 \times 10^{-9}$ | $1.1 \times 10^{-11}$ | 900 | $1.3 \times 10^{12}$ |

[a] Values of parameters used in these calculations include $a = 10^{-5}$ cm, $a_f = 10^{-3}$ cm, $c_f = 10^{8}$ cm$^{-3}$, $\sigma = 2.5$A, $\epsilon = 74.3$, $T = 300$°K, $\psi = -10$mV at 0.1 mol/l (recomputed from Gouy-Chapman equation at lower ionic strengths, assuming surface charge is unchanged) and $A = 1.769 \times 10^{-14}$ erg (chosen so that $\phi_{\max} = 0$ at 0.1 mol/l). *For Notations see Ruckenstein and Prieve (1976).*

cles in flocs equals a constant, $c_o$, per unit volume. Equation (D) can be integrated exactly, taking into account the changes of $K_r'$ and $K_f'$ with time. However, more insight into the problem can be obtained from the simple equation obtained in the limiting case when the amount of dilution of the electrolyte is small so that nearly all the elementary particles remain in the flocs. Then $K_r'$ and $K_f'$, which are proportional to $a_f^2$, remain nearly constant. Interpreting $n$ as the number of elementary particles attached per unit area to the floc and assuming hexagonal close packing, then $n = (\sqrt{3})/6a^2$. As particles detach from the floc, new particles underneath are exposed so that $n$ is practically independent of time. Then (D) integrates to yield

$$(c_\infty^* - c_\infty(t)) = (c_\infty^* - c_{\infty i})e^{-t/\tau}$$

where $c_\infty^* = K_r' n/K_f'$, $\tau = 1/K_f' c_f$ and $c_{\infty i} = c_\infty(t = 0)$.

Table 1 shows some values of the time constant $\tau$ and the equilibrium concentration $c_\infty^*$ obtained from these equations, employing the simplified model of the interaction forces developed by Ruckenstein and Prieve (1976). As might be expected, lowering the ionic strength makes the primary minimum, $\phi_{mn2}$, less deep, thus shifting the equilibrium in favor of more detached elementary particles, $c_\infty^*$. However, decreasing the ionic strength increases the time $\tau$ to reach equilibrium, in spite of the fact that the repeptization rate, $K_r'n$, is increasing. This can be rationalized by observing that both the repeptization rate $K_r' n$ and the equilibrium concentration $c_\infty^*$ are increased by dilution, but $c_\infty^*$ increases faster so that a longer time $\tau$ is needed to reach equilibrium. Of course, the analysis here could be generalized to allow the recombination of singlets to form doublets, the combination of singlets and doublets to form triplets and quadruplets, etc. Finally, an equilibrium distribution of floc sizes should be obtainable.

In this note, an equation is established for the rate of reversible adsorption on the basis of the quasi steady state assumption over the entire thickness of the interaction force boundary layer. When an interaction force boundary layer occurs ($\phi_{\max} >> kT$), we find that the approximation of quasi steady state over part of the region and quasi-equilibrium over the other part leads to practically the same rate as the approximation of quasi steady state over the entire region if $\phi_{\max} - \phi_{mn2} >> kT$. Hence, either approximation is equally appropriate. A simple analysis of the repeptization of colloids is discussed on the basis of the equation established for reversible adsorption.

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# High Peclet Number Mass Transfer to a Sphere in a Fixed or Fluidized Bed

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The mass transfer from a moving fluid to a solid particle situated in a fixed or fluidized bed is encountered in a large number of industrial processes (chemical reactors, filters, etc.). Practically important and very attractive is the case of low Reynolds number (creeping) flow of the fluid through the bed. In this case, an analytical solution is possible. It is based on Levich's (1962) well-known solution for the mass transfer to a single sphere falling in an infinite fluid with velocity $U_o$. His solution applies for the case where the diffusion coefficient of the species $D$ is low; in other words, the characteristic Peclet number $Pe$ of the process is high ($Pe \geqq 1\,000$). As pointed out by several authors, this requirement is met in most practical cases. In this situation, the mass transfer occurs in a very thin concentration boundary layer near the solid sphere, for which the spherical geometry can be neglected. Mass transfer to a single sphere can be expressed in terms of the Sherwood number as

$$Sh = 0.997 \cdot Pe^{1/3} \tag{1}$$

Equation (1) was also obtained by Friedlander (1961) and Lochiel and Calderbank (1964), while a second-order correction to this expression was introduced by Acrivos and Goddard (1965, 1966).

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