Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Huang, Shang-Da and Wilson, David J.(1975) 'Electrical Aspects of Adsorbing Colloid Flotation II. Theory of Rate Processes', Separation Science and Technology, 10: 4, 407 — 415
To link to this Article: DOI: 10.1080/00372367508058029
URL: http://dx.doi.org/10.1080/00372367508058029

SEPARATION SCIENCE, 10(4), pp. 407–415, 1975

Electrical Aspects of Adsorbing Colloid Flotation
II. Theory of Rate Processes

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Abstract

The kinetic and equilibrium factors affecting the rate of precipitate flotation are analyzed by means of the Gouy-Chapman model. Kinetic effects are found to be extremely rapid, and the rate of precipitate flotation is due to equilibrium considerations. Removal efficiency as a function of inert salt concentration goes through a maximum at about 10^{-5} *M* for films 300 Å thick. Removal efficiency increases with increasing zeta potential of the film surface and with increasing charge on the precipitate particles.

INTRODUCTION

It has been noticed by a number of workers that the efficiency of precipitate flotation and of adsorbing colloid flotation decreases with increasing ionic strength of the solution being foamed (*1–4*). Sheiham and Pinfold (*4*) ascribed this to, among other factors, the effect of the ionic strength on the attractive force between the precipitate particles and the surfactant film. The Gouy-Chapman theory of the electric double layer was used by Verwey and Overbeek (*5*) to analyze the stability of lyophobic collids, and later by Jorné and Rubin (*6*) to account for the effects of ionic charge and size on the selectivity of foam fractionation. We recently used it to calculate the free energy causing the attractive force between precipitate particles and a charged surfactant film, as suggested by Sheiham and

Pinfold, and found that the energies involved were ample to account for precipitate flotation, and that their magnitude and range decreased with increasing ionic strength in a way consistent with the decreasing efficiency of removal with increasing ionic strength (7). We here extend this approach to examine (a) the rate of attainment of equilibrium of charged colloidal particles initially uniformly distributed between the two charged surfaces of a film, and (b) the extent to which the resulting equilibrium distribution results in separation of the precipitate from the bulk solution.

ANALYSIS AND RESULTS

We consider one square centimeter of a film of thickness L, with $\psi(x)$ the potential of the solution composing the film at a distance x from the left side of the film. We let

η = viscosity of solution
r_0 = effective radius of charged colloidal particles
D_r = diffusion constant of colloidal particles
q = electric charge per colloidal particle
$c(x, t)$ = concentration of particles at point x at time t

The differential equation describing the variation of the concentration of colloidal particles with time and position is then

$$\frac{\partial c}{\partial t} = D_r \frac{\partial^2 c}{\partial x^2} + \frac{q}{6\pi r_0 \eta} \frac{\partial}{\partial x}\left[\frac{\partial \psi}{\partial x} c\right] \tag{1}$$

At equilibrium we have $c(x, t) = c_e(x)$, for which

$$\frac{\partial}{\partial x}\left[D_r \frac{\partial c_e}{\partial x} + \frac{q}{6\pi r_0 \eta} \frac{\partial \psi}{\partial x} c_e\right] = 0 \tag{2}$$

This yields

$$D_r \frac{\partial c_e}{\partial x} + \frac{q}{6\pi r_0 \eta} \frac{\partial \psi}{\partial x} c_e = A \tag{3}$$

a constant, and since $\partial c_e/\partial x = \partial \psi/\partial x = 0$ when $x = L/2$ (from symmetry), $A = 0$. Solution of Eq. (3) then yields

$$c_e(x) = c_e(L/2) \exp\left\{\frac{q[\psi(L/2) - \psi(x)]}{6\pi r_0 \eta D_r}\right\} \tag{4}$$

Evidently $6\pi r_0 \eta D_r = kT$, so we can write Eq. (1) as

$$\frac{\partial c}{\partial t} = \frac{1}{6\pi r_0 \eta}\left[kT\frac{\partial^2 c}{\partial x^2} + q\frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial x}c\right)\right] \tag{5}$$

and

$$c_e(x) = c_e(L/2)\exp\left\{\frac{q}{kT}[\psi(L/2) - \psi(x)]\right\} \tag{6}$$

From Eq. (5) we see that variations in r_0 and η merely change the time scale of the process; we therefore set $6\pi r_0 n = 1$.

In principle, Eq. (5) could be solved by separation of variables and expansion in terms of the eigenfunctions of the x-equation. In practice, this is not feasible because of the complex dependence of ψ on x, as illustrated by the work of Verwey and Overbeek (*5*) and of Devereux and deBruyn (*8*). We choose, therefore, to solve Eq. (5) by straight numerical integration. The potential ψ is calculated as a function of position, ionic strength of the solution, dielectric constant, and temperature by the same procedure used in our earlier work (*7*), and then used in Eq. (5).

The right-hand side of Eq. (5) can be approximated in a number of ways by means of finite differences, but one must be careful to choose an expression such that

$$\int_0^{L/2}\frac{\partial c}{\partial t}(x, t)\,dx \cong \sum_n \frac{\partial c_n}{\partial t}(t)\Delta x = 0 \tag{7}$$

$$c_n(t) = c(n\Delta x, t)$$

to avoid failure of the finite difference representation to conserve the total number of colloidal particles. We chose as our approximation

$$\begin{aligned}\frac{\partial c_n}{\partial t}(t) &= \frac{1}{(\Delta x)^2}kT(c_{n+1} - 2c_n + c_{n-1})\\ &\quad + qc_n(\psi_{n+1} - 2\psi_n + \psi_{n-1}) + \frac{q}{2}(\psi_{n+1} - \psi_n)(c_{n+1} - c_n)\\ &\quad + \frac{q}{2}(\psi_n - \psi_{n-1})(c_n - c_{n-1}) \qquad n = 2, \ldots, N-1\\ &= f(c_{n-1}, c_n, c_{n+1})\end{aligned} \tag{8}$$

with boundary conditions

$$kT(c_2 - c_1) + q(\psi_2 - \psi_1)\frac{c_1 + c_2}{2} = 0 \tag{9}$$

$$kT(c_N - c_{N-1}) + q(\psi_N - \psi_{N-1})\frac{c_N + c_{N-1}}{2} = 0$$

Equation (8) is then integrated with respect to t by means of a predictor-corrector method (*9*) having the form

Predictor:

$$\bar{c}_n(t + \Delta t) = c_n(t - \Delta t) + 2\Delta t \frac{\partial c_n}{\partial t}(t) \tag{10}$$

$$\frac{\partial \bar{c}_n}{\partial t}(t + \Delta t) = f[\bar{c}_{n-1}(t + \Delta t), \bar{c}_n(t + \Delta t), \bar{c}_{n+1}(t + \Delta t)]$$

Corrector:

$$c_n(t + \Delta t) = c_n(t) + \frac{\Delta t}{2}\left[\frac{\partial c_n}{\partial t}(t) + \frac{\partial \bar{c}_n}{\partial t}(t + \Delta t)\right]$$

We are interested in the rate at which a nonequilibrium initial concentration of particles [such as $c(x, 0) = \text{constant}$] approaches the final equilibrium distribution given by Eq. (6). We examine this by computing a quantity, $v(t)$, which is essentially the variance of the concentration from that at equilibrium,

$$v(t) = \int_0^{L/2} [c(x_1 t) - c_e(x)]^2 \, dx \Big/ \int_0^{L/2} [c_0(x)]^2 \, dx \tag{11}$$

If the approach to equilibrium is a simple exponential decay with rate constant k, the approach of $v(t)$ to zero is exponential with rate constant $2k$. Thus a semilog plot of $v(t)$ vs t can be expected to yield information about the range of rate constants contributing to the approach to equilibrium.

In Fig. 1 we plot $v(t)$ vs time for various concentrations μ of an inert 1–1 electrolyte; other parameters are held fixed as indicated. Rate constants for the approach to equilibrium (after the decay of initial transients) are of the order of 1.5 to 2.0×10^7 sec^{-1} for these thin films (300 Å thick), as shown in Table 1. For comparison purposes, the lowest eigenvalues of the simple one-dimensional diffusion problem with absorbing end-points are given in Table 1 as λ_d. Here

$$\lambda_d = \frac{kT\pi}{6r_0\eta(L - 2a_d)^2} \tag{12}$$

where L is the thickness of the film and a_d is the effective thickness of the

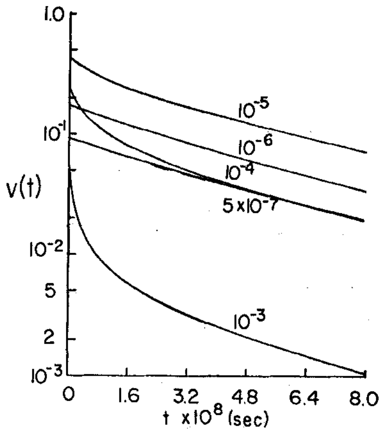

FIG. 1. Dependence of $v(t)$ on salt concentration. For the runs depicted here, $L = 300$ Å, $q = e$, $\zeta = 50$ mV. Solutions were assumed to have the dielectric constant (78.54) and viscosity (0.01 poise) of water at 25 °C in all of our calculations, r_0 was taken to be 10 Å, and the temperature was set equal to 298 °K.

TABLE 1

Systems Studied and Results

L (Å)	μ (moles/liter)	q 4.77×10^{10} esu	ζ (mV)	a_d (Å)	$L - 2a_d$ (Å)	$\lambda_d \times 10^{-6}$ (sec^{-1})	$[v(t)] \times 10^{-6}$ (sec^{-1})	$f \times 100$
300	10^{-7}	1	50	3.06	293.9	5.00	20.2	1.97
300	10^{-4}	1	50	9.68	280.6	5.47	16.2	9.29
300	10^{-5}	1	50	30.6	238.8	7.55	15.6	29.3
300	10^{-6}	1	50	96.8	106.4	38.0	17.9	20.8
300	5×10^{-7}	1	50	137.0	26.0	637	19.0	0
300	10^{-5}	4	50	3.06	238.8	7.55	15.8	97.4
300	10^{-5}	1	100	3.06	238.8	7.55	13.6	66.4
1000	10^{-5}	1	50	3.06	938.8	0.489	4.59	9.16

ionic atmosphere, the Debye length, given by

$$a_d^2 = \frac{DkT}{8\pi N_0 \mu e^2} \tag{13}$$

where N_0 is Avogadro's number and D is the dielectric constant. We note that λ_d should be doubled to make it strictly comparable to the rate constant for the decay of $v(t)$. We see from Table 1 that, while simple diffusion theory gives us time constants of roughly the right magnitude, it is not a good method of approximation.

The effect of varying charge on the colloidal particle is shown in Fig. 2; there is a slight increase in the rate of decay of $v(t)$ due to the increased attractive forces at the sides of the film as the charge increases. The effect of increasing the zeta potential on the rate of decay of $v(t)$ is shown in Fig. 3; somewhat surprisingly, it is smaller for the larger value of the zeta potential. The effect of increasing the film thickness (from 300 to 1000 Å) is shown in Fig. 4; the expected decrease in the rate constant of $v(t)$ with increasing film thickness L is observed.

The large size of the rate constants (approximately 10^7 sec^{-1}) encourages one to assume that there is essentially complete equilibration of the distribution of colloidal particles between the liquid in the interior of the film and the boundary layers. We can then obtain information about the rate of separation by calculating the fractional excess of colloidal particles which are trapped in the boundary layers at equilibrium. We define the boundary layer as that portion of the film between $x = 0$ and $x = a_b$ (or $x = L - a_b$

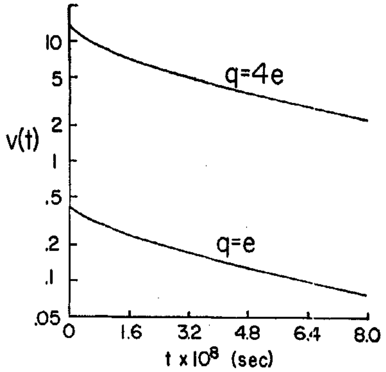

FIG. 2. Dependence of $v(t)$ on particle charge. $L = 300$ Å, $\mu = 10^{-5}$ M, $\zeta = 50$ mV.

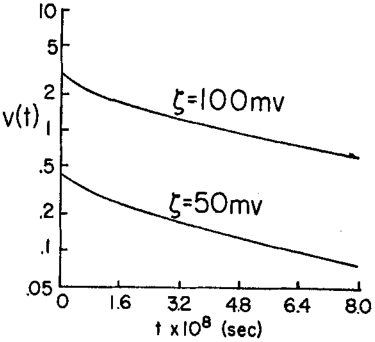

FIG. 3. Dependence of $v(t)$ on zeta potential of the film surface. $L = 300$ Å, $\mu = 10^{-5}\ M, q = e$.

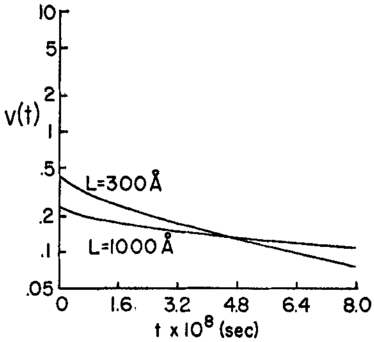

FIG. 4. Dependence of $v(t)$ on film thickness. Here $q = e$, $\mu = 10^{-5}\ M$, $\zeta = 50$ mV.

and $x = L$), where a_b is chosen such that

$$q[\psi(a_b) - \psi(L/2)] = -kT \tag{14}$$

Then the fractional excess of particles which are trapped at the surface at equilibrium is given by

$$f = \int_0^{a_b} [c_e(x) - c_0(x)]\,dx \bigg/ \int_0^{L/2} c_0(x)\,dx \tag{15}$$

when we make use of the symmetry of the system. This fractional excess is plotted against the $\log_{10}$ of the inert salt concentration in Fig. 5. We see

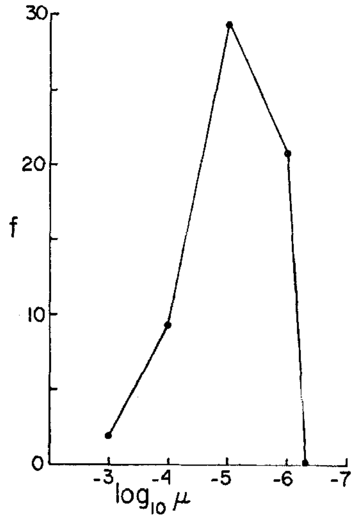

FIG. 5. Dependence of f on salt concentration. Here $q = e$, $\zeta = 50$ mV, $L = 300$ Å.

here a rather interesting effect; the fractional excess goes through a maximum at a salt concentration of about 10^{-5} M. At salt concentrations higher than this, the Debye length and also a_b are quite small, and therefore the volume over which the potential energy of a colloidal particle is more than kT less than its potential energy in the middle of the film is correspondingly small; relevant plots are shown in our earlier work (7). This reduces the amount of material which can be trapped in the boundary layer. As the salt concentration goes below 10^{-5} M, $\psi(L/2) \to \psi(0)$, and again a progressively smaller and smaller volume of the film is at a potential such that the potential energy of a particle in that volume is more than kT less than the potential energy of a particle in the middle of the film. With films 300 Å thick, the optimal range of salt concentration is evidently 10^{-4} to 10^{-6} M; with thicker films this range would be shifted to lower values.

In Table 1 we also see the effects of increasing the zeta potential and of increasing the charge on the colloidal particles. Both result in a very marked increase in f; i.e., more efficient separations, as one would expect.

CONCLUSIONS

Our results indicate that the rates of precipitate flotation separations are controlled by the equilibrium between the concentration of particles in the boundary layer and that in the interior of the foam, rather than by the kinetics of migration to the boundary layer, which are extremely rapid. Boundary layer trapping increases with decreasing salt concentration at salt concentrations above about 10^{-5} M for films 300 Å thick, and decreases with decreasing salt concentration at lower salt concentrations. Boundary layer trapping of the colloidal particles increases with increasing zeta potential of the film surface and with increasing particle charge. And, as indicated in Table 1, increasing the film thickness (from 300 to 1000 Å) markedly decreases the efficiency of separation.

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Received by editor August 26, 1974