Separation Science and Technology

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

Electrical Aspects of Adsorbing Colloid Flotation. III. Excluded Volume Effects

John W. Wilson[a]; David J. Wilson[a]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

To cite this Article Wilson, John W. and Wilson, David J.(1976) 'Electrical Aspects of Adsorbing Colloid Flotation. III. Excluded Volume Effects', Separation Science and Technology, 11: 1, 89 — 102

To link to this Article: DOI: 10.1080/01496397608085304

URL: http://dx.doi.org/10.1080/01496397608085304

SEPARATION SCIENCE, 11(1), pp. 89–102, 1976

Electrical Aspects of Adsorbing Colloid Flotation. III. Excluded Volume Effects

JOHN W. WILSON and DAVID J. WILSON

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

The separation rates of precipitate flotation separations are calculated from a simple model and a more exact model based upon the Gouy-Chapman approach. The finite volume of the floc particles is taken into account, and the dependence of separation rates on ionic strength surface potential, charge of floc particles, and concentration of floc particles is determined.

INTRODUCTION

Most precipitate flotation and adsorbing colloid flotation processes depend upon electrical interactions between the surfactant film and the (charged) particles of precipitate being removed (*1*, *2*). The adverse effect of increased ionic strength on these separations has been noted by a number of workers (*3–6*), and was attributed by Sheiham and Pinfold (*3*) to the effect of the ionic atmospheres of the film and particles in weakening the attractive forces. Jorné and Rubin (*7*) used the Gouy-Chapman theory of the electrical double layer to explain the effects of ionic size and charge on the selectivity of foam fractionation. We used this model, following the approach of Verwey and Overbeek (*8*), to calculate the free energy of attraction between precipitate particles and charged surfactant films (*9*) and to investigate the kinetic and equilibrium factors affecting the rate of precipitate flotation (*10*). We here extend this approach to take into account the finite volume of the precipitate particles; we relax the requirement implicit in our earlier analysis that the concentration of colloidal particles be extremely low. This extension was suggested by our observation, obvious even to the naked eye, that in the flotation of $Fe(OH)_3$ or $Al(OH)_3$ with sodium lauryl sulfate the surface films are frequently quite densely covered with the precipitate. We outline first a simple approach which is also applicable (at least semiquantitatively) to flotation not involving electrical forces; we then present a more elaborate and precise attack on the problem of the flotation of precipitates in which the forces are electrical. We assume the occurrence of local equilibrium between surface and adjacent liquid, as supported by our earlier work (*10*).

SIMPLE MODEL

Here we analyze a simple model for the adherence of colloidal particles to a surface film. We assume that the interaction potential of a floc particle is given by

$$V(x) = -V_0, \qquad 0 \le x \le Ma$$
$$V(x) = 0, \qquad x > Ma \tag{1}$$

where M is a positive integer and a is equal to a mean length of a floc particle. Thus a particle may be regarded as bound to the surface if it is within a distance Ma of the surface. We take a square of area a^2 on the surface and partition the volume of liquid to its right (see Fig. 1) into cubes of volume a^3; each one of these cubes can contain a maximum of one floc

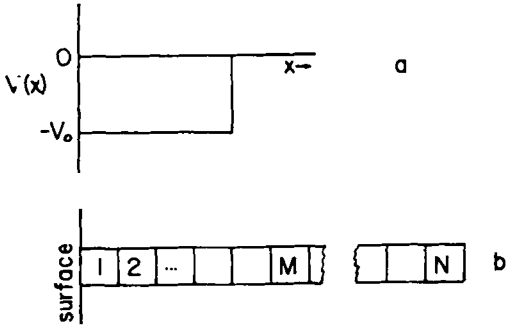

FIG. 1. (a) Potential energy of a floc particle as a function of distance from the surface in the simple model. (b) Partitioning of the liquid volume in the vicinity of the surface into cells.

particle. Let us assume that in a volume of Na^3 of solution we have s floc particles. We wish to calculate the average number of these particles which are bound to the surface; this is done as follows.

Given s particles and N compartments, M of which are in the bound region, the number of ways in which the particles can be distributed such that $M - j$ of them are bound and $s - M + j$ are free is given by

$$\frac{(N - M)!M!}{(s - M + j)!(N - s - j)!(M - j)!j!}$$

Each of these states of the system has a potential energy $-V_0(M - j)$. The partition function of the system is therefore given by

$$(Pf)_{M,N,s,} = \sum_{j=j_{min}}^{j_{max}} \frac{(N - M)!M! \exp[(M - j)V_0\beta]}{(s - M + j)!(N - s - j)!(M - j)!j!} \tag{2}$$

$$j_{max} = \min(M, N - s), \qquad \beta = 1/kT$$
$$j_{min} = \max(0, M - s),$$

Now we wish to calculate $\bar{n}_b(N, s, M, \beta)$, the average number of bound particles. Evidently $\bar{E} = -\bar{n}_b V_0$, where $\bar{E}$ is the average potential energy of the system. Generally,

$$\partial(Pf)/\partial\beta = -(Pf)\bar{E} \tag{3}$$

so

$$\bar{n}_b = \frac{1}{(Pf)} \frac{\partial(Pf)}{\partial\beta} \frac{1}{V_0} \tag{4}$$

and we finally have

$$\bar{n}_b = \sum_{j=j_{min}}^{j_{max}} \left\{ \frac{(N - M)!M!(M - j) \exp[(M - j)V_0\beta]}{(s - M + j)!(N - s - j)!j!(M - j)!} \right\} \times \left[\sum_{j=j_{min}}^{j_{max}} \left\{ \frac{(N - M)!M! \exp[(M - j)V_0\beta]}{(s - M - j)!(N - s - j)!j!(M - j)!} \right\} \right]^{-1} \tag{5}$$

The number of particles removed per second w is then given by

$$w = 3\dot{V}\bar{n}_b/a^2r \tag{6}$$

where $\dot{V}$ is the gas flow rate and r is the mean bubble radius.

In Fig. 2 are plotted values of $\bar{n}_b$ vs $V_0\beta$ for constant M (bound layer thickness), constant s/N (initial concentration of floc particles), and varying N (essentially the thickness of the liquid layer from which floc particles may

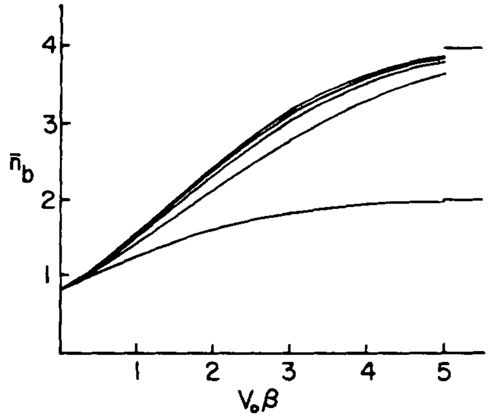

FIG. 2. Effect of varying N at constant concentration. For all runs $M = 4$. From top to bottom, values of N and s are, respectively, 50 and 10, 40 and 8, 30 and 6, 20 and 4, and 10 and 2.

be drawn). We see that saturation of the bound layer occurs somewhere in the vicinity of $V_0\beta = 3$ to 5. Also, as N increases, we see that the sequence of curves rapidly approaches a limit, and it is evident that the results for $N = 40$ to 50 are very close to those which would be obtained in the limit as $N \rightarrow \infty$.

The effect of varying floc particle concentration is shown in Fig. 3 for

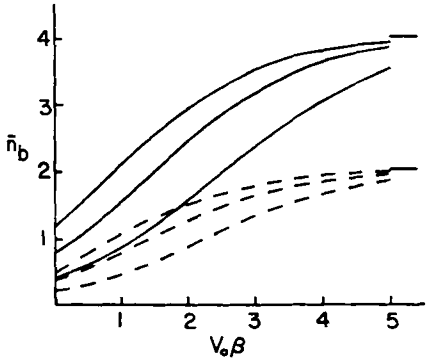

FIG. 3. Effect of varying s at constant N. For the solid curves from top to bottom, s = *15*, *10*, *5*; $N = 50$; and $M = 4$. For the dashed curves from top to bottom, s = *15*, *10*, *5*; $N = 50$; and $M = 2$.

two different bound layer thicknesses. The larger the value of s (for fixed N and M), the larger is the value of $\bar{n}_b$, and the sooner saturation occurs with increasing $V_0\beta$. The results of varying the thickness of the bound layer are exhibited by the two pairs of curves plotted in Fig. 4. In essence, the efficiency of removal is proportional to the bound layer thickness, as one would expect.

Plots of $\bar{n}_b$ vs s ($N = 50$)—essentially a concentration variable—give us the shape of the adsorption isotherm. These are shown in Fig. 5 for several

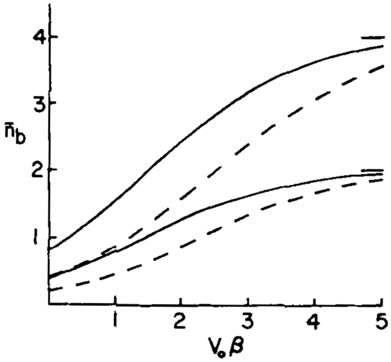

FIG. 4. Effect of varying bound layer thickness. For the solid curves, $s = 10$, $N = 50$, and $M = 4$ (upper) and 2 (lower); for the dashed curves, $s = 5$, $N = 50$, and $M = 4$ (upper) and 2 (lower).

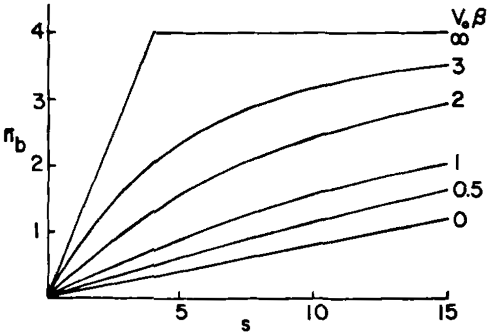

FIG. 5. Adsorption isotherms for the simple model. $N = 50$ and $M = 4$ for all curves. At constant N, s is proportional to floc particle concentration.

TABLE 1

Separation Factors ($N = 50$, $M = 4$)

S	$f(V_0\beta = 3)$	$f(V_0\beta = \infty)$
15	1.92	2.33
10	2.96	4.00
5	4.85	9.00
≤ 4	—	11.50

values of $V_0\beta$. We define a separation factor,

$$f = [\bar{n}_b(V_0\beta)/\bar{n}_b(V_0\beta = 0)] - 1$$

which goes to zero as the interaction causing the separation, and in terms of which the net excess of bound particles is given by

$$\bar{n}_b(V_0\beta) - \bar{n}_b(0) = f\bar{n}_b(0)$$

The separation factors can readily be computed from the data given in Fig. 5; some of these are listed as functions of s, the concentration variable (when N is fixed) in Table 1.

We see that the separation factors generally decrease with increasing concentration of floc particles, a point which we have noted experimentally in work on ferric hydroxide flocs, and which hampers the extension of precipitate or adsorbing colloid flotation methods to high concentrations.

COULOMBIC ATTRACTION

Here we examine a Gouy-Chapman type model in which the coulombic attraction between the charged surface of the film and the floc particles may be reduced by the presence of an ionic atmosphere. We calculate the electric potential $\psi(x)$ in the liquid as a function of the distance from the left surface of the film by integration of

$$\frac{d\psi}{dx} = \frac{\pm\sqrt{2}}{ea_1\beta}[\cosh \beta e\psi - \cosh \beta e\psi(l)]^{\frac{1}{2}} \tag{7}$$

where $a_1^{-2} = \dfrac{8\pi e^2 N_0 c\beta}{D}$

c = concentration of 1–1 electrolyte
D = dielectric constant
e = |electronic charge|
N_0 = Avogadro's Number

$\psi(l)$ = electric potential at midpoint of film
l = half thickness of film
$\beta = 1/kT$

The calculation is outlined in our earlier paper (*9*) and discussed in detail by Verwey and Overbeek (*8*) and by Devereux and de Bruyn (*11*). We then proceed as follows.

We assume that a floc particle occupies a volume of a^3 cm^3, and we examine the rectangular parallelepiped of liquid extending to the right of a square of film surface of area a^2 (see Fig. 1). We assume that this volume contains s floc particles and that it encloses a total of N cubes of volume a^3. We regard particles in the first M of these compartments (going from left to right) as being bound to the surface; M is chosen such that $q\psi[(M - \frac{1}{2})a] \leqslant -\beta^{-1}$, $q\psi[(M + \frac{1}{2})a] > -\beta^{-1}$, where q is the charge of a particle. We neglect the electrical interactions between the floc particles so that the potential energy of a given configuration of s particles is given by

$$V(j_1, j_2, \ldots, j_s) = q \sum_{i=1}^{s} \psi(j_i) \tag{8}$$

where $\psi(j_i)$ is the electric potential at a distance $(j_i - \frac{1}{2})a$ from the film surface. Here $(j_i - \frac{1}{2})a$ is the distance of the ith particle from the film surface.

The partition function of the system is then given by

$$(Pf) = \sum_{j_1=1}^{j_2-1} \sum_{j_2=2}^{j_3-1} \cdots \sum_{j_{s-1}=s-1}^{j_s-1} \sum_{d_s=s}^{N} \exp\left[-\sum_{i=1}^{s} q\beta\psi(j_i)\right] \tag{9}$$

and the probability of any particular configuration $(l_1, l_2, \ldots, l_s)$ is given by

$$P(l_1, l_2, \ldots, l_s) = \exp\left[-\sum_{i=1}^{s} q\beta\psi(l_i)\right](Pf)^{-1} \tag{10}$$

We let

$$\begin{aligned} U(p) &= 0, p > 0 \\ &= 1, p < 0 \end{aligned}$$

The number of bound particles associated with the state $(l_1, l_2, \ldots, l_s)$ is given by

$$n_b(l_1, l_2, \ldots, l_s) = \sum_{i=1}^{s} U(l_i - M) \tag{11}$$

Then the average number of bound particles is given by

$$\bar{n}_b = \sum_{l_1=1}^{l_2-1} \sum_{l_2=2}^{l_3-1} \cdots \sum_{l_{s-1}=s-1}^{l_s-1} \sum_{l_s=s}^{N} P(l_1, l_2, \ldots, l_s) \sum_{i=1}^{s} U(l_i - M) \quad (12)$$

The number of particles removed per second is given by Eq. (6), as before.

The electric potential was calculated and the average number of bound particles per area a^2 of surface computed on the XDS Sigma 7 computer of the Vanderbilt Computer Center. A typical calculation of $\bar{n}_b$ requires about 80 sec of machine time.

The effect of increasing ionic strength on $\bar{n}_b$, which is proportional to the separation rate, is shown in Fig. 6. The separation rate is seen to decrease markedly with increasing ionic strength, as was also noted in our earlier approach. Figure 7 illustrates the dependence of separation rate on the charge of the colloidal particles; the expected increase of separation rate with increasing magnitude of charge is observed, with $\bar{n}_b$ increasing by roughly one unit for each unit increase of charge magnitude. This rate of increase of $\bar{n}_b$ is more rapid at higher surface potentials.

Figure 8 shows the adsorption isotherms for two values of the surface potential (50 and 100 mV). The lower curve (50 mV) approaches asymptotically a maximum value of 2.0 with increasing s; the upper curve approaches 3.0 asymptotically. Both curves are rather similar in appearance to the isotherms for our simpler model shown in Fig. 5, suggesting the utility of the latter (use of which requires less than a tenth of the machine time required by the more exact approach).

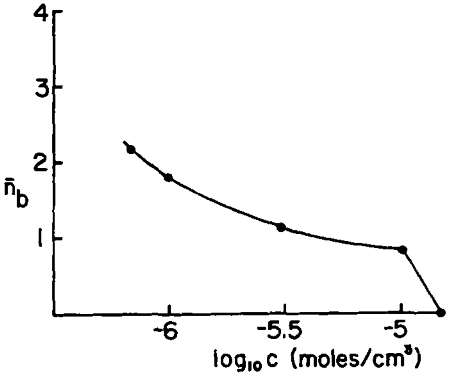

FIG. 6. Effect of ionic strength c on separation rate, coulombic model. $\psi_l = 50$ mV, $q = -1$ (-4.77×10^{-10} esu), $a = 10$ Å, $s = 4$, and $N = 20$.

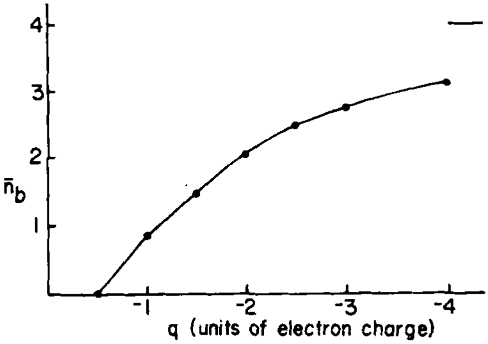

FIG. 7. Effect of floc charge on separation rate, coulombic model. $\psi = 50$ mV, $c = 10^{-5}$ moles/cm^3, $a = 10$ Å, $s = 4$, and $N = 20$.

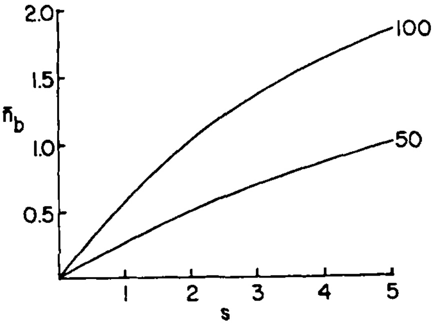

FIG. 8. Adsorption isotherms for the coulombic model. $\psi = 100$ mV (upper curve) and 50 mV (lower curve), $a = 10$ Å, $q = -1$, $c = 10^{-5}$ moles/cm^3, and $N = 20$.

The approach outlined above is well adapted to dealing with thin films, but requires extremely large amounts of computer time if one wishes to apply it to thick films or to bubbles rising through bulk liquid. We therefore examine the case of an infinitely thick film, for which $N \to \infty$ (see Fig. 1b). We assume that the density of particles per unit cell at very large distances from the surface is σ, and we take the potential energy zero to be that of a particle a great distance from the surface. Since we can have no more than one particle in a given "state" (i.e., in a given cell), we must use Fermi-Dirac statistics. We follow Hill (*12*) in calculating the mean number of particles in cell j:

$$n_j = \{\exp[(V(x_j) - \mu)/kT] + 1\}^{-1} \tag{13}$$

where V is the potential energy and μ the chemical potential.

The chemical potential of the particles is calculated as follows. At equilibrium the chemical potential is independent of x, so it may be calculated at large values of x where $V(x) = 0$. We consider N cells containing s particles, where $\sigma = s/N$. For this assembly

$$\Omega = \frac{N!}{s!(N-s)!}$$

gives the number of possible states from which, with use of Stirling's formula, the entropy is given by

$$S = k \log_e \left[\frac{N^N}{s^s(N-s)^{N-s}}\right] = \frac{-F}{T} \tag{14}$$

The chemical potential is then given by

$$\mu = -T\left(\frac{\partial S}{\partial s}\right)_{N,T} = \beta^{-1} \log_e\left(\frac{\sigma}{1-\sigma}\right) \tag{15}$$

So

$$n_j = \left[\frac{1-\sigma}{\sigma}\exp(\beta V(x_j)) + 1\right]^{-1} \tag{16}$$

The average number of bound particles is then given by

$$\bar{n}_b = \sum_{j=1}^{M} n_j \tag{17}$$

where M is chosen such that

$$V(x_M) \leq -kT, \qquad V(x_{M+1}) > -kT$$

The electric potential in the vicinity of a charged plane surface of a solution of 1–1 electrolyte of infinite extent was first determined by Gouy and Chapman; the result, available in standard surface chemistry texts (*13*), is

$$x = \frac{a_1}{2} \log_e\left[\frac{(\cosh e\psi\beta/2 + 1)(\cosh e\psi_0\beta/2 - 1)}{(\cosh e\psi\beta/2 - 1)(\cosh e\psi_0\beta/2 + 1)}\right]. \tag{18}$$

For the simple model having the potential energy function shown in

Fig. 1(a), our result is

$$\bar{n}_b = M\bigg/\left[\frac{1-\sigma}{\sigma}\exp(-V_0\beta)+1\right] \tag{19}$$

if $V_0\beta$ is large (> 6, say), one can simplify this to obtain

$$\bar{n}_b = M\bigg/\left[\frac{\exp(-V_0\beta)}{\sigma}+1\right] \tag{20}$$

a simple Langmuir isotherm. For smaller values of $V_0\beta$ the isotherms are illustrated in Fig. 9.

Equation (17) was used to calculate adsorption isotherms at various values of the ionic strength (Fig. 10), temperature (Fig. 11), and surface potential (Fig. 12). The dependence on ionic strength and surface potential is what one would expect on simple physical grounds, but the nature of the temperature dependence is less obvious. Increasing the temperature results in two counteracting effects; the increased thermal energy of the particles tends to decrease separation efficiencies, while the more diffuse character of the ionic atmosphere of the surface tends to increase separation efficiencies. We see in Fig. 11 that the former effect is dominant, but that the temperature dependence is generally rather weak. Between 298 and 325°C (actually 310 and 320°C), however, there is a very marked change with temperature. This occurs when the number of bound compartments M decreases from 4 to 3, which it does discontinuously (M must be an integer). Evidently experimental work is needed to determine whether this feature is real or is merely an artifact resulting from our rather simple model. One would expect that the range of sizes of floc particles would

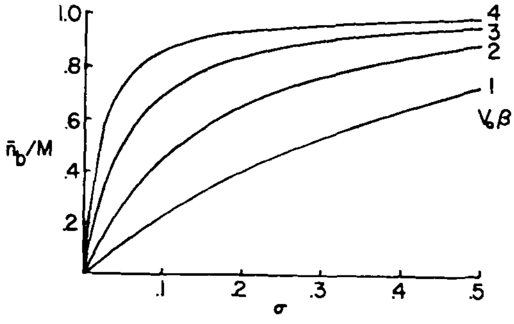

FIG. 9. Adsorption isotherms for the simple model, thick film approximation.

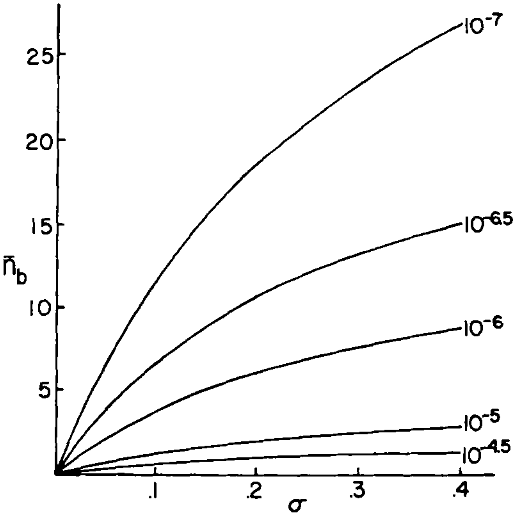

FIG. 10. Dependence of adsorption isotherms on ionic strength (moles/cm³) for the coulombic model, thick film approximation. $\psi_0 = 50$ mV, $T = 298$ °K, $q = -1$, and $a = 10$ Å.

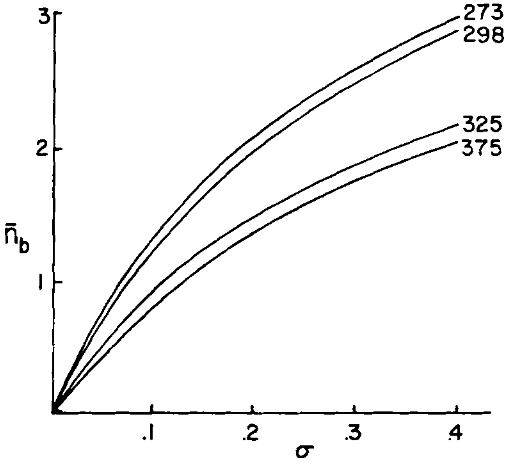

FIG. 11. Dependence of adsorption isotherms on temperature (°K) for the coulombic model, thick film approximation. $\psi_0 = 50$ mV, $q = -1$, $a = 10$ Å, and $c = 10^{-5}$ moles/cm³.

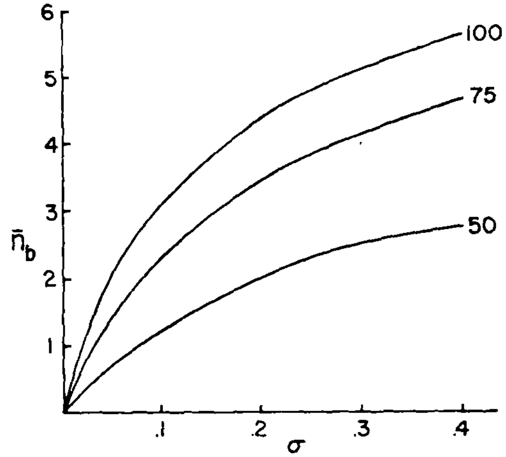

FIG. 12. Dependence of adsorption isotherms on surface potential (mV) for the coulombic model, thick film approximation. $T = 298\,^\circ K$, $q = -1$, $a = 10$ Å, and $c = 10^{-5}$ moles/cm^3.

tend to smooth out this sharp temperature discontinuity, and that other criteria for determining the number of particles being removed might result in the smoothing or even the removal of the discontinuity.

In conclusion, our results yield strongly nonlinear isotherms for fairly concentrated systems. These suggest that calculations of foam flotation column efficiencies should take into account these nonlinear isotherms; we hope to extend the lumped parametric approach of Cannon and Lemlich (*14*) and of Kown and Wang (*15*) to do this. For thick films with coulombic interactions we find a rather weak dependence of removal rate on temperature, and generally we find increasing removal rates with increasing surface potential and floc particle charge, and with decreasing ionic strength.

REFERENCES

1. R. Lemlich, ed., *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972.
2. P. Somasundaran, *Sep. Purif. Methods*, *1*, 1 (1972).
3. I. Sheiham and T. A. Pinfold, *J. Appl. Chem.*, *18*, 217 (1968).
4. R. B. Grieves and D. Bhattacharyya, *Separ. Sci.*, *4*, 301 (1969).
5. A. J. Rubin and W. L. Lapp, *Ibid.*, *6*, 357 (1971).
6. B. B. Ferguson, C. Hinkle, and D. J. Wilson, *Ibid.*, *9*, 125 (1974).

7. J. Jorné and E. Rubin, *Ibid.*, *4*, 313 (1969).
8. E. J. W. Verwey and Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.
9. J. W. Wilson and D. J. Wilson, *Separ. Sci.*, *9*, 381 (1974).
10. S.-D. Huang and D. J. Wilson, *Ibid.*, *10*, 405 (1975).
11. O. F. Devereux and P. L. de Bruyn, *Interaction of Plane-Parallel Double Layers*, MIT Press, Cambridge, Massachusetts, 1963.
12. T. L. Hill, *An Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, Massachusetts, 1960, p. 438.
13. A. W. Adamson, *Physical Chemistry of Surfaces*, 2nd ed., Wiley-Interscience, New York, 1967, p. 212.
14. K. D. Cannon and R. Lemlich, *Chem. Eng. Progr. Symp. Ser.*, *Water*, *No. 124*, *68* (1972).
15. B. T. Kown and L. K. Wang, *Separ. Sci.*, *6*, 537 (1971).

Received by editor July 22, 1975