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Electrical Aspects of Adsorbing Colloid Flotation. IV. Stripping Column Operation

John W. Wilson[a]; David J. Wilson[a]; James H. Clarke[b]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE [b] CENTER FOR INDUSTRIAL WATER QUALITY MANAGEMENT, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

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Electrical Aspects of Adsorbing Colloid Flotation. IV. Stripping Column Operation

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JOHN W. WILSON and DAVID J. WILSON
DEPARTMENT OF CHEMISTRY

JAMES H. CLARKE
CENTER FOR INDUSTRIAL WATER QUALITY MANAGEMENT
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

The operation of a continuous flow foam flotation column in the stripping mode is analyzed under steady-state conditions. The effects of diffusive mixing, nonlinear adsorption isotherms, and finite rate of mass transport between the surface and bulk phases are taken into account in the differential equations from which column efficiencies are calculated. Adsorption isotherms are calculated by means of statistical mechanics for systems having coulombic interactions.

INTRODUCTION

The foam flotation literature has been reviewed by Somasundaran (*1*, *2*), Lemlich (*3*, *4*), and others; the technique is of particular interest as a method for removing trace quantities of heavy metals and other hazardous substances from aqueous systems. Several mathematical models for foam flotation columns have been described in the literature; these generally consist of equations derived from steady-state material balance considerations at the ends of the column (*3*, *5*, *6*). An integral part of these models is the assumption of instantaneous equilibrium between the surface and the bulk phases. Also, they are confined to the plug flow regime. Goldberg and Rubin (*7*) reviewed a number of these models and also presented a model applicable to a stripping column without solute transfer in the countercurrent region. Wang et al. (*8*) treated continuous bubble fractionation and presented a model which includes axial dispersion and the use of equilibrium absorption isotherms. Cannon and Lemlich (*9*) presented a detailed analysis based upon the assumption of linear isotherms, and Lee has given a somewhat similar treatment (*10*).

We here present an approach derived from Wilburn's analysis of two-phase countercurrent extraction (*11*). He includes effects of diffusion, convection, and mass transfer, and assumes a linear isotherm. We analyze a continuous flow foam flotation column operating at steady-state in the stripping mode, and we include effects of diffusion and turbulence, rate of mass transfer, and nonlinear isotherms. We then focus on the calculation of these isotherms for the case of the floc foam flotation, extending our previous work on this problem and putting it on a somewhat firmer footing (*12–14*).

ANALYSIS

We take Eqs. (1) and (2) as our starting point:

$$0 = D_l V \frac{d^2c}{dx^2} + v_l V \frac{dc}{dx} + \frac{k_1 S^2}{V + SK}(\Gamma - Kc) \tag{1}$$

$$= D_s S \frac{d^2\Gamma}{dx^2} - v_s S \frac{d\Gamma}{dx} - \frac{k_1 S^2}{V + SK}(\Gamma - Kc) \tag{2}$$

Terms are defined as follows:

D_l	effective diffusion constant in the liquid phase
D_s	effective diffusion constant in the surface phase
V	volume of liquid contained in 1 cm^3 of foam
S	surface area contained in 1 cm^3 of foam
v_l	velocity of liquid downward
v_s	velocity of surface upward
K	equilibrium isotherm; $K = \Gamma/c$ at equilibrium
Γ	surface concentration of solute
c	concentration of solute in liquid

c_{Feed}	concentration of solute in column influent
k_1	rate constant governing mass transport between the surface phase and the liquid phase
x	distance from base of column
l	column length

The boundary conditions of the problem are determined in the following way. First, solvent material balance at β (see Fig. 1) yields

$$v_l V' = v_s S\delta + v_l V \tag{3}$$

where δ is the film thickness of drained film and $v_l V'$ is the flow rate of column influent. Solute material balance at β yields

$$v_l V' c_{\text{Feed}} - v_s S\Gamma(l) = v_l V c(l) - v_s S\Gamma(l) + D_l V \frac{dc}{dx}(l) + D_s S \frac{d\Gamma}{dx}(l) \tag{4}$$

Solute material balance at α yields

$$v_l V c(0) = v_l V c(0) - v_s S\Gamma(0) + D_l V \frac{dc}{dx}(0) + D_s S \frac{d\Gamma}{dx}(0) \tag{5}$$

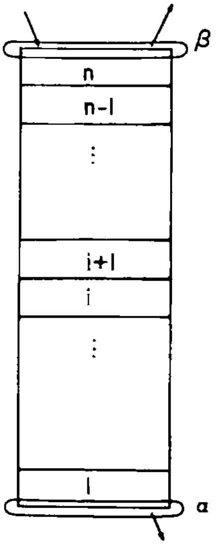

FIG. 1. Material balance diagram of the column.

The requirement that there be no net flux out of the bottom of the column via the surface phase yields

$$0 = v_s\Gamma(0) - D_sS\frac{d\Gamma}{dx}(0) \tag{6}$$

Solute material balance on the liquid phase at the top of the column yields

$$v_lV'c_{\text{Feed}} = v_lVc(l) + D_lV\frac{dc}{dx}(l) \tag{7}$$

Equations (4) through (7) can be simplified and combined to yield boundary conditions identical to those used by Mišek and Rod for countercurrent extraction (*15*):

$$\frac{V}{V'}c(l) + \frac{VD_l}{v_lV'}\frac{dc}{dx}(l) = c_{\text{Feed}} \tag{8}$$

$$\frac{d\Gamma}{dx}(l) = 0 \tag{9}$$

$$v_s\Gamma(0) - D_s\frac{d\Gamma}{dx}(0) = 0 \tag{10}$$

$$\frac{dc}{dx}(0) = 0 \tag{11}$$

We regard K as a function of c (nonlinear isotherm), and solve the differential Eqs. (1) and (2) as follows. We subdivide the column into n compartments as indicated in Fig. 1, and define

$$\xi_i = (x_{i-1} + x_i)/2 \tag{12}$$

$$K_i = K[c(\xi_i)] \tag{13}$$

We shall be constructing an iterative quasilinearization method (*16*) whereby we make an initial choice of the K_i [based on the calculation of $c(x)$ when $K(c)$ is set equal to $K(0)$]. In the ith compartment our differential equations are now

$$0 = -v_sS\frac{d\Gamma^i}{dx} + SD_s\frac{d^2\Gamma^i}{dx^2} - \frac{k_1S^2}{V + SK_i}(\Gamma^i - K_ic^i) \tag{14}$$

$$= v_lV\frac{dc^i}{dx} + VD_l\frac{d^2c^i}{dx^2} + \frac{k_1S^2}{V + SK_i}(\Gamma^i - K_ic^i) \tag{15}$$

We solve these in the ith region by setting $c^i(x) = c^i \exp \lambda^i x$, $\Gamma^i(x) = \Gamma^i \exp \lambda^i x$ to obtain

$$0 = \Gamma^i\left(SD_s\lambda^{i2} - v_sS\lambda^i - \frac{k_1S^2}{V + SK_i}\right) + c^i\frac{k_1S^2K_i}{V + SK_i} \tag{16}$$

$$= \frac{\Gamma^ik_1S^2}{V + SK_i} + c^i\left(VD_l\lambda^{i2} + v_lV\lambda^i - \frac{k_1S^2K_i}{V + SK_i}\right) \tag{17}$$

The requirement that Γ^i and $c^i \neq 0$ yields

$$0 = \begin{vmatrix} \left(SD_s\lambda^{i2} - v_sS\lambda^i - \dfrac{k_1S^2}{V + SK_i}\right) & \dfrac{k_1S^2K_i}{V + SK_i} \\ \dfrac{k_1S^2}{V + SK_i} & \left(VD_l\lambda^{i2} + v_lV\lambda^i - \dfrac{k_1S^2K_i}{V + SK_i}\right) \end{vmatrix} \tag{18}$$

We solve this secular equation (which has one zero root) to get the λ_j^i, (c_j^i, Γ_j^i), $j = 1, 2, 3, 4$. We choose the $c_j^i = 1$ for all i and j, which then permits calculation of the Γ_j^i from Eqs. (16) or (17). Then

$$c^i(x) = \sum_{j=1}^{4} \alpha_j^i \exp \lambda_j^i x \tag{19}$$

$$\Gamma^i(x) = \sum_{j=1}^{4} \alpha_j^i\Gamma_j^i \exp \lambda_j^i x \tag{20}$$

where the α_j^i are to be determined from (1) the four boundary conditions (Eqs. 8–11), and (2) the requirements that

$$c^i(x_i) = c^{i+1}(x_i) \tag{21}$$

$$\Gamma^i(x_i) = \Gamma^{i+1}(x_i) \tag{22}$$

$$\frac{dc^i}{dx}(x_i) = \frac{d}{dx}c^{i+1}(x_i) \tag{23}$$

$$\frac{d}{dx}\Gamma^i(x_i) = \frac{d}{dx}\Gamma^{i+1}(x_i) \tag{24}$$

$$i = 1, 2, \ldots, n - 1$$

This yields a total of $4n$ equations to be solved for the $4n$ α_j^i. We substitute Eqs. (19) and (20) into (21)–(24) to obtain

$$\begin{pmatrix} 1 & 1 & 1 & 1 \\ \Gamma_1{}^i & \Gamma_2{}^i & \Gamma_3{}^i & \Gamma_4{}^i \\ \lambda_1{}^i & \lambda_2{}^i & \lambda_3{}^i & \lambda_4{}^i \\ \lambda_1{}^i\Gamma_1{}^i & \lambda_2{}^i\Gamma_2{}^i & \lambda_3{}^i\Gamma_3{}^i & \lambda_4{}^i\Gamma_4{}^i \end{pmatrix}$$

$$\begin{pmatrix} \exp \lambda_1{}^i x_i & 0 & 0 & 0 \\ 0 & \exp \lambda_2{}^i x_i & 0 & 0 \\ 0 & 0 & \exp \lambda_3{}^i x_i & 0 \\ 0 & 0 & 0 & \exp \lambda_4{}^i x_i \end{pmatrix} \begin{pmatrix} \alpha_1{}^i \\ \alpha_2{}^i \\ \alpha_3{}^i \\ \alpha_4{}^i \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 1 & 1 & 1 \\ \Gamma_2{}^{i+1} & \Gamma_2{}^{i+1} & \Gamma_3{}^{i+1} & \Gamma_4{}^{i+1} \\ \lambda_2{}^{i+1} & \lambda_2{}^{i+1} & \lambda_3{}^{i+1} & \lambda_4{}^{i+1} \\ \lambda_1{}^{i+1}\Gamma_1{}^{i+1} & \lambda_2{}^{i+1}\Gamma_2{}^{i+1} & \lambda_3{}^{i+1}\Gamma_3{}^{i+1} & \lambda_4{}^{i+1}\Gamma_4{}^{i+1} \end{pmatrix}$$

$$\begin{pmatrix} \exp \lambda_1{}^{i+1} x_i & 0 & 0 & 0 \\ 0 & \exp \lambda_2{}^{i+1} x_i & 0 & 0 \\ 0 & 0 & \exp \lambda_3{}^{i+1} x_i & 0 \\ 0 & 0 & 0 & \exp \lambda_4{}^{i+1} x_i \end{pmatrix} \begin{pmatrix} \alpha_1{}^{i+1} \\ \alpha_2{}^{i+1} \\ \alpha_3{}^{i+1} \\ \alpha_4{}^{i+1} \end{pmatrix}$$

or, in more compact notation,

$$F(i)D(i, i)\boldsymbol{\alpha}(i) = F(i + 1)D(i, i + 1)\boldsymbol{\alpha}(i + 1) \tag{25}$$

Then

$$\boldsymbol{\alpha}(i) = D^{-1}(i, i)F^{-1}(i)F(i + 1)D(i, i + 1)\boldsymbol{\alpha}(i + 1) \tag{26}$$

or

$$\boldsymbol{\alpha}(i) = T(i)\boldsymbol{\alpha}(i + 1)$$

So

$$\boldsymbol{\alpha}(1) = T(1)T(2) \cdots T(n - 1)\boldsymbol{\alpha}(n) \equiv \tau\boldsymbol{\alpha}(n) \tag{27}$$

Our Eqs. (8)–(11) become

$$c_{\text{Feed}} = \sum_{j=1}^{4} \alpha_j{}^n \exp(\lambda_j{}^n l)\left[\frac{V}{V'} + \frac{VD_l\lambda_j{}^n}{V'v_l}\right] \tag{28}$$

$$0 = \sum_{j=1}^{4} \alpha_j{}^n \exp(\lambda_j{}^n l)\Gamma_j{}^n\lambda_j{}^n \tag{29}$$

$$= \sum_{j=1}^{4} \alpha_j{}^1\Gamma_j{}^1(v_s - D_s\lambda_j{}^1) \tag{30}$$

$$= \sum_{j=1}^{4} \alpha_j{}^1\lambda_j{}^1 \tag{31}$$

or, more compactly,

$$\begin{pmatrix} c_{\text{Feed}} \\ 0 \end{pmatrix} = B\boldsymbol{\alpha}(n)$$

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = A\boldsymbol{\alpha}(1)$$

where A and B are 2×4 matrices defined by Eqs. (28)–(31). On using Eq. (27) with these we obtain

$$\begin{pmatrix} c_{\text{Feed}} \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} B \\ A\tau \end{pmatrix}\boldsymbol{\alpha}(n) \equiv C\boldsymbol{\alpha}(n) \tag{32}$$

Then

$$\boldsymbol{\alpha}(n) = C^{-1}\begin{pmatrix} c_{\text{Feed}} \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{33}$$

and

$$\boldsymbol{\alpha}(i) = T(i)\boldsymbol{\alpha}(i+1) \tag{26}$$

as before. Solute concentrations in the middle of the various compartments are obtained from

$$c^i(\xi_i) = \sum_{j=1}^{4} \alpha_j{}^i \exp(\lambda_j{}^i \xi_i) \tag{34}$$

where ξ_i is given by Eq. (12). These $c^i(\xi^i)$ are then used to calculate a new set of K_i's, at which point we go back to Eq. (18) and repeat the calculation up through Eq. (34). We continue these iterations until results from successive iterations are in sufficiently close agreement.

The amount of solute which is discharged per second in the column effluent is given by

$$v_l V c(0) = v_l V \sum_{j=1}^{4} \alpha_j{}^1$$

The total amount of solute flowing into the column per second is given by $v_l V' c_{\text{Feed}}$. We define a separation parameter, F, as

$$F = Vc(0)/V'c_{\text{Feed}} \tag{35}$$

Let us examine some typical results. Figure 2 exhibits the anticipated decrease in solute concentration in the column effluent as the specific foam area S increases. The effect of varying the surface flow velocity v_s is shown in Fig. 3; we note that it is approximated here that the increased gas flow rate has not affected the wetness of the foam. The dependence of the separation parameter F on the liquid flow velocity v_l is shown in Fig. 4, and is as one would expect. Figure 5 shows the effect of diffusion and

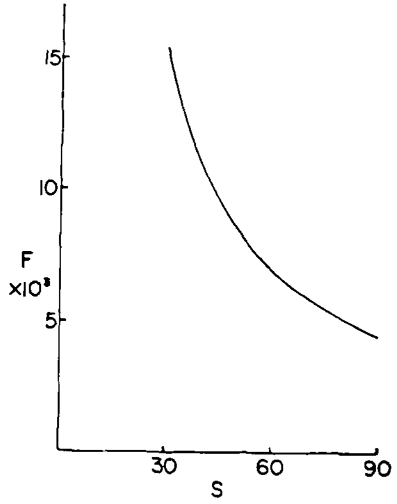

FIG. 2. Dependence of separation factor F on specific foam area S (cm^{-1}). $D_s = D_l = 500$, $v_s = v_l = 1$, $V = 0.0025$, $k_1 = 0.1$, $L = 50$, $c_{\text{Feed}} = 1.4 \times 10^{-7}$ moles/cm³, $a_1 = 6 \times 10^{-3}$, $a_2 = 10^{-8}$; all constants in c.g.s. units.

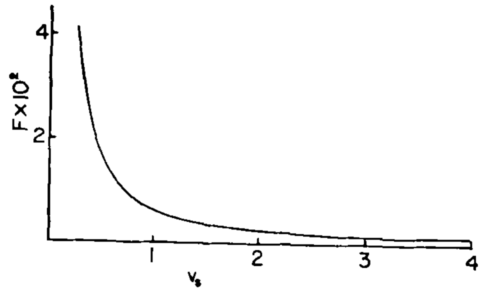

FIG. 3. Dependence of separation factor F on surface velocity v_s (cm/sec). $S = 60$, other parameters as in Fig. 2.

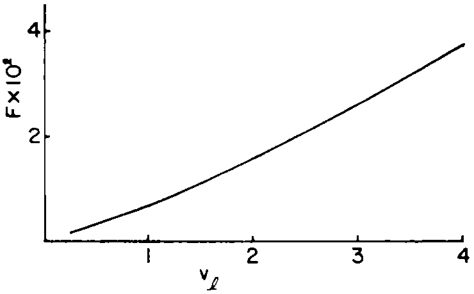

FIG. 4. Dependence of F on liquid velocity (cm/sec). Other parameters as in Figs. 2 and 3.

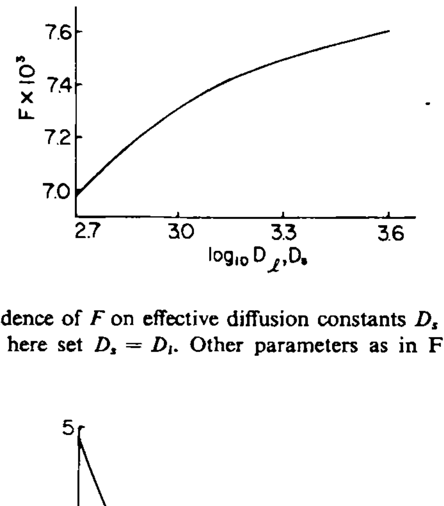

FIG. 5. Dependence of F on effective diffusion constants D_s and D_l (cm²/sec). We have here set $D_s = D_l$. Other parameters as in Figs. 2 and 3.

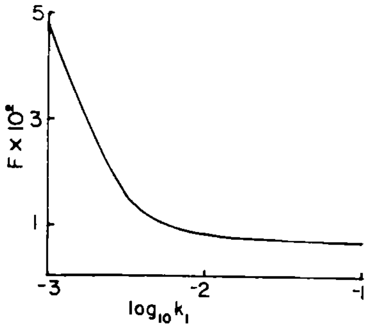

FIG. 6. Dependence of F on mass transfer rate constant k_1 (cm/sec). Other parameters as in Figs. 2 and 3.

turbulent mixing in decreasing the separation efficiency (increasing the separation parameter). The magnitude of k_1, the rate constant governing mass transfer of solute between the surface and the liquid phase, exerts a very marked effect upon the separation efficiency, as demonstrated in Fig. 6.

The isotherms for floc foam flotation which we calculated in our earlier work (*14*) can be approximated rather well by simple Langmuir isotherms,

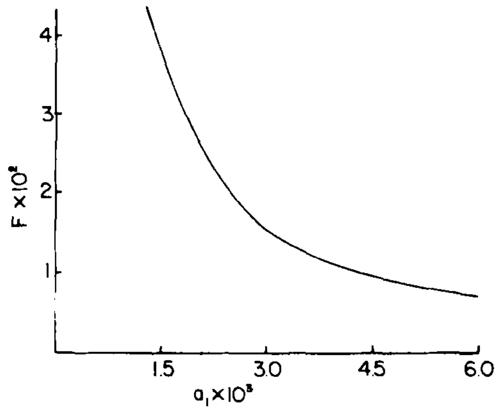

FIG. 7. Dependence of F on Langmuir parameter a_1 (cm). Other parameters as in Figs. 2 and 3.

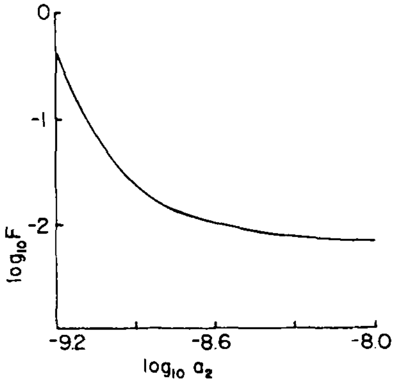

FIG. 8. Dependence of F on Langmuir parameter a_2 (moles/cm^3). Other parameters as in Figs. 2 and 3.

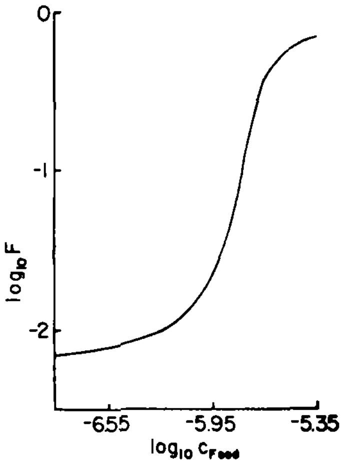

FIG. 9. Dependence of F on c_{Feed} (moles/cm^3). Other parameters as in Figs. 2 and 3.

as is shown later in this paper. For reasons of mathematical convenience we therefore use Langmuir isotherms in our calculations, setting

$$\Gamma = Kc = \frac{a_1}{1 + c/a_2}c$$

The dependence of the separation parameter on a_1 and a_2 is shown in Figs. 7 and 8, and qualitatively is what one would intuitively expect. The effect of this nonlinear isotherm on the separation parameter is also illustrated in Fig. 9, which shows the dependence of separation parameter on feed concentration. As feed concentration increases, the surface film becomes saturated, at which point the separation parameter approaches unity, corresponding to negligible separation.

ADSORPTION ISOTHERMS

In the third paper of this series (referred to as III below) we developed a method for calculating adsorption isotherms for systems in which the attraction between particles and surface is electrical (*14*). The model included the effect of the finite volume of the colloidal particles by means of a cell approach, but included some simplifications and approximations which we have since been able to avoid. We use the notation used in III, and follow a technique given by Hill (*17*).

Let us assume M equivalent, independent, distinguishable sites on our surface film, each one of which can bind 1, 2, . . . , m particles. We let

$$q(s) = \sum_j \exp\left[-\beta\varepsilon_j(s)\right]$$

be the site partition function when the site is occupied by s particles. In detail,

$$q(s) = \sum_{j_1=1}^{j_2-1} \sum_{j_2=2}^{j_3-1} \cdots \sum_{j_s=s}^{m} \sum_{\varepsilon(js)} \exp(-\beta\varepsilon) \tag{36}$$

If a_s sites have s particles bound to them, then the canonical ensemble partition function for the collection of M sites and N particles is given by

$$Q(N, M, T) = \sum_{a_i\text{'s}} M! \prod_{i=0}^{m} \frac{[q(i)]^{a_i}}{a_i!} \tag{37}$$

where the a_i's must satisfy $\sum_{s=0}^{m} a_s = M$ and $\sum_{s=0}^{m} sa_s = N$. Hill then shows that the grand partition function of the system is given by

$$\Xi = \sum_{N=0}^{mM} Q(N, M, T)\lambda^N \tag{38}$$

$$= \sum_{a_i\text{'s}} M! \prod_{i=0}^{m} \frac{[q(i)\lambda^i]^{a_i}}{a_i!} \tag{39}$$

where $\sum_{s=0}^{m} a_s = M$ is our only constraint. But this is evidently just

$$\Xi = [\xi(\lambda, T)]^M \tag{40}$$

where

$$\xi(\lambda, T) = \sum_{s=0}^{m} q(s)\lambda^s \tag{41}$$

The average number of particles per site is then given by

$$\bar{S} = \lambda\left(\frac{\partial \log \xi}{\partial \lambda}\right)_T = \frac{\sum_{s=0}^{m} sq(s)\lambda^s}{\sum_s q(s)\lambda^s} \tag{42}$$

We assume, as in III, that

$$\varepsilon(j_1, j_2, \ldots, j_s) = \sum_{k=1}^{s} \varepsilon(j_K) \tag{43}$$

The energy of any configuration of s particles at the site is simply the sum of the independent one-particle energies. This permits us to write

$$q(s) = \sum_{j_1=1}^{j_2-1} \sum_{j_2=2}^{j_3-1} \cdots \sum_{j_s=s}^{m} \left[\sum_{\varepsilon(j_1)} \sum_{\varepsilon(j_2)} \cdots \sum_{\varepsilon(j_s)} \exp \left\{ -\beta \sum_{i=1} \varepsilon(j_i) \right\} \right]$$

$$= \sum_{j_1} \sum_{j_2} \cdots \sum_{j_s} \prod_{j_i=1}^{s} [Pf(j_i)] \tag{44}$$

where $[Pf(j_i)]$ is a one-particle partition function for a particle in compartment j_i. We write $[Pf(j_i)]$ as $\exp[-\beta V(j_i)]q(j_i)$, where $V(j_i)$ is the binding energy of a particle in compartment j_i to the surface.

On substituting Eq. (44) into Eq. (41) we obtain

$$\xi = \sum_{s=0}^{m} \lambda^s \sum_{j_1=1}^{j_2-1} \sum_{j_2=2}^{j_3-1} \cdots \sum_{j_s=s}^{m} \prod_{j_i=1}^{s} q(j_i) \exp[-\beta V(j_i)]$$

$$= \prod_{j_i=1}^{m} \{1 + q(j_i)\lambda \exp[-\beta V(j_i)]\} \tag{45}$$

From this result and Eq. (42) we readily obtain

$$\bar{S} = \sum_{k=1}^{m} \frac{\lambda q(k) \exp[-\beta V(k)]}{1 + \lambda q(k) \exp[-\beta V(k)]} \tag{46}$$

Now $q(k)$ involves partition function factors associated with a particle in a box, essentially, and with rotational motions. This is true for all k, and we therefore make the reasonable approximation that $q(k) = q$, independent of k, which yields

$$\bar{S} = \sum_{k=1}^{m} \left[1 + \frac{\exp[\beta V(k)]}{\lambda q} \right]^{-1} \tag{47}$$

Now

$$\log \lambda q = \beta\mu_{\text{total}} - \beta\mu_{\text{internal}}$$

$$= \beta\mu_{\text{configurational}}$$

where the μ's represent chemical potentials. III showed that

$$\beta\mu_{\text{configurational}} = \log \frac{\sigma}{1 - \sigma} \tag{48}$$

where σ is the "density of particles in the bulk liquid," the average number of particles in L compartments a large distance away from the surface, divided by L. This then yields our previous result for $\bar{S}$:

$$\bar{S} = \sum_{k=1}^{m} \left[1 + \frac{1-\sigma}{\sigma} \exp\left[\beta V(K)\right] \right]^{-1} \tag{49}$$

We define S_{excess} as

$$S_{\text{excess}} = \bar{S} - M\sigma \tag{50}$$

the net excess of particles bound per site in the surface layer, an alternative and perhaps somewhat better criterion than the binding energy criterion we used in III. Substitution of Eq. (49) in (50) then yields

$$S_{\text{excess}} = \sigma(1-\sigma) \sum_{k=1}^{m} \frac{1 - \exp \beta V(k)}{\sigma[1 - \exp \beta V(k)] + \exp \beta V(k)} \tag{51}$$

This formula is well adapted to calculating isotherms for bubbles rising through bulk liquid and for wet foams.

The results of calculations of S_{excess} as a function of σ are shown in Figs. 10, 11, 12, and 13. Figure 10 shows the effect of increasing ionic strength on the isotherm; Fig. 11 that of increasing surface potential ψ_0; Fig. 12 that of increasing charge on the floc particles; and Fig. 13 that of increasing temperature. These results are quite similar to those obtained by our earlier technique except for two points. First, these plots go through

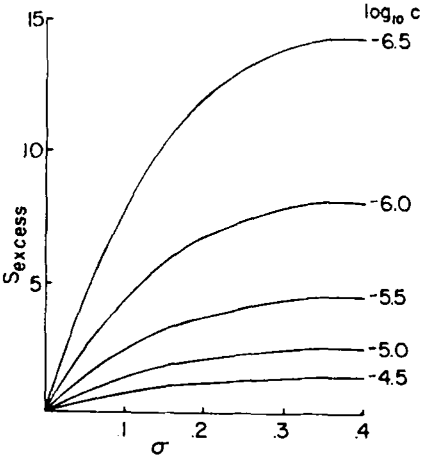

FIG. 10. Dependence of isotherms on ionic strength (moles/cm^3). $q = 4.77 \times 10^{-10}$ esu, $\psi_0 = -50$ mV, cell length = 10 Å, $T = 298$°K.

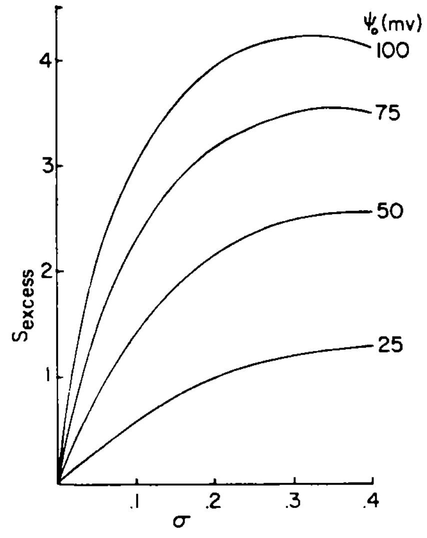

FIG. 11. Dependence of isotherms on surface potential ψ_0 (mV). Other parameters as in Fig. 10; $c = 10^{-5}$ moles/cm^3.

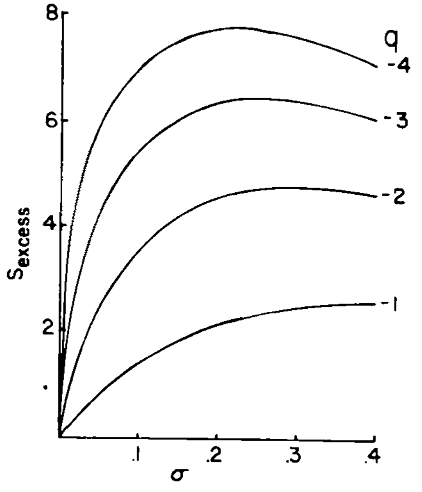

FIG. 12. Dependence of isotherms on floc particle charge ($q = 4.77 \times 10^{-10}$ esu). Other parameters as in Figs. 10 and 11.

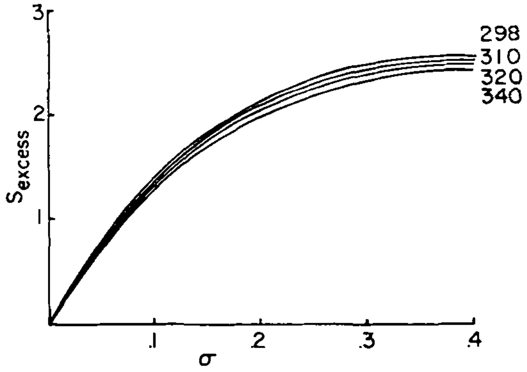

FIG. 13. Dependence of isotherms on temperature (°K). Other parameters as in Figs. 10 and 11.

a maximum (readily visible in Figs. 11 and 12) and actually go to zero as σ approaches unity. This is due simply to the fact that it is physically impossible for the local floc particle density to exceed unity, so that the difference between local floc particle density and σ must approach zero as σ → unity. For reasonable values of σ (zero to 0.3, say), the curves can be matched by Langmuir curves to less than 10% error by a nonlinear least squares routine.

The second difference from our earlier results (using the binding energy criterion) is a more reasonable temperature dependence, as shown in Fig. 13. The binding energy criterion results in marked discontinuities in the temperature dependence which we have not seen in our experimental results and believe to be artifacts of that model. Our present approach eliminates these discontinuities and gives us a rather weak temperature dependence similar to that observed in our preliminary experimental work.

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