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

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Electrical Aspects of Adsorbing Colloid Flotation. VI. Electrical Repulsion between Floc Particles

DAVID J. WILSON

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

Adsorption isotherms are calculated for precipitate and floc foam flotation within the framework of a Gouy-Chapman model which includes both the electrical attractions of the floc particles to the surface and their electrical repulsions for each other. The canonical ensemble is used, and algebraic expressions are found for approximating the sum of products of cluster integrals. Algebraic expressions for the surface excess of adsorbed floc are obtained which involve three reasonably simple integrals. The dependence of the adsorption isotherms on temperature, ionic strength, surface potentials of the floc and the air–water interface, ionic charge, and floc particle size is investigated.

INTRODUCTION

Foam flotation methods have been studied extensively with the object of removal of trace metals and other substances from wastewaters; our first two references include relatively recent reviews (*1*, *2*). Encouraged by Zeitlin's work on adsorbing colloid flotation (*3*, *4*), we have used this very efficient technique for the removal of a number of metals, arsenate, and fluoride (*5*). The magnitude of the electrical attraction between the ionic surfactant-covered air–water interface and the charged floc particles decreases markedly with increasing ionic strength, as was observed by Sheiham and Pinfold (*6*) and others. We have used the Gouy-Chapman model of the electric double layer (*7*, *8*) to calculate equilibrium isotherms and rate processes for precipitate and adsorbing colloid flotation (*9*–*13*). Jorné and Rubin used this model to explain the effects of ionic size and charge on selectivity in foam fractionation (*14*).

Our previous calculations of adsorption isotherms of floc particles at surfaces took floc–floc interactions into account only roughly by means of an excluded volume approach (*11*, *12*) in which floc–floc interactions were treated as one-dimensional hard "sphere" forces. A later paper (*13*) included an approach in which floc–floc interactions were approximated by (a) excluded volume and (b) deleting the interaction energies with the surface of all floc particles in the site but that nearest the surface. The changes in the absorption isotherms which resulted from this change were sufficient to cause us to feel somewhat uneasy about these simplified models, despite their ability to account for the dependence of flotation efficiency on ionic strength, temperature, zeta potential of floc, and surfactant concentration.

The statistical mechanics of nonideal gases (*15*, *16*) provides us with the machinery for developing a more realistic method of calculating adsorption isotherms. We use the canonical ensemble for a single adsorption site and assume that the various sites comprising the surface and the adjacent solution are independent of each other.

ANALYSIS

We take as one site a portion of air–solution interface and the column of liquid of which this portion of surface is the base; the cross-sectional area is of such size as to permit floc particles to be wholly included within the column. The canonical partition function for the site is given by

$$Q(N) = \frac{1}{N!\,h^N}\int_0^L \cdots \int_0^L \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\left\{-\beta\left[\sum_{i=1}^{N} \frac{{p_i}^2}{2m} + \sum_{i=1}^{N} u(x_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v(r_{ij})\right]\right\} \prod_{l=1}^{N} dp_l dx_l \tag{1}$$

Here N = number of floc particles in the assembly
m = mass of a floc particle
$\beta = 1/kT$
p_i = momentum of ith particle
x_i = distance of center of ith particle from the surface
$u(x_i)$ = interaction potential of ith particle with the surface

$v(r_{ij}) = v(x_i - x_j)$ = interaction energy of ith and jth particles
L = length of assembly

The integrations over the momenta are trivial, yielding

$$Q(N) = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{1}{N!} \int_0^L \cdots \int_0^L \exp\left\{-\beta\left[\sum_{i=1}^{N} u(x_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v(r_{ij})\right]\right\} \prod_{l=1}^{N} dx_l \tag{2}$$

We let

$$\exp\left[-\beta u(x_k)\right] - 1 = g(x_k) \equiv g_k \tag{3}$$

$$\exp\left[-\beta v(r_{ij})\right] - 1 = f(r_{ij}) \equiv f_{ij} \tag{4}$$

Note that $g_k \to 0$ as x_k becomes large and $f_{ij} \to 0$ as $|r_{ij}|$ becomes large. So

$$Q(N) = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{1}{N!} \int_0^L \cdots \int_0^L \prod_{k=1}^{N} [g_k + 1] \prod_{i=1}^{N-1} \prod_{j=i+1}^{N} [f_{ij} + 1] \prod_{l=1}^{N} dx_l \tag{5}$$

Let us examine integrals of the form

$$\begin{aligned}\int_0^L \int_0^L (1 + g_1)(1 + g_2) f_{12}\, dx_1\, dx_2 &= \int_0^L \int_0^L f_{12}\, dx_1\, dx_2 + \int_0^L \int_0^L g_1 f_{12}\, dx_1\, dx_2 \\ &\quad + \int_0^L \int_0^L g_2 f_{12}\, dx_1\, dx_2 + \int_0^L \int_0^L g_1 g_2 f_{12}\, dx_1\, dx_2\end{aligned} \tag{6}$$

In the first term on the right-hand side we change variables; $r = x_2 - x_1$, $x_1 = x_1$. The first integral becomes

$$\int_0^L dx_1 \int_{-\infty}^{\infty} f(r)\, dr \equiv Lb, \qquad b = \int_{-\infty}^{\infty} f(r)\, dr \tag{7}$$

In the second term we make the same change of variable, obtaining

$$\int_0^L g(x_1)\, dx_1 \int_{-\infty}^{\infty} f(r) dr \equiv cb, \qquad c = \int_0^L g(x_1)\, dx_1 \tag{8}$$

Similarly, the third integral in Eq. (6) is equal to cb. We set

$$\int_0^L \int_0^L g_1 g_2 f_{12}\, dx_1\, dx_2 = d \tag{9}$$

and note that the upper limits of the integrations can be reduced to a few Debye lengths, since $g_i \cong 0$ when x_i is larger. We can therefore write the integral on the left-hand side of Eq. (6) as

$$\int_0^L \int_0^L (1 + g_1)(1 + g_2) f_{12}\, dx_1\, dx_2 = Lb + 2cb + d \tag{10}$$

We rewrite Eq. (5) as

$$Q = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{1}{N!} \int_0^L (g_1 + 1) \int_0^L (g_2 + 1) \cdots \int_0^L (g_N + 1) \times \left\{1 + \sum^{M} f_{ij} + \sum\sum^{M(M-1)/2} f_{ij} f_{kl} + \sum\sum\sum^{M(M-1)(M-2)/6} f_{ij} f_{kl} f_{mn} + \cdots\right\} \prod_{p=1}^{N} dx_p \tag{11}$$

where $M = N(N - 1)/2$ is the number of terms occurring in the first summation as i ranges from 1 to $N - 1$ and j ranges from $i + 1$ to N.

We now make the usual approximations used in summing the cluster integrals in the calculation of the partition function for a nonideal gas. We assume that N is sufficiently large that the great bulk of the terms $f_{ij} f_{kl} f_{mn} \ldots$ has no indices in common, and that we need keep only the terms of highest power in N in the coefficients of the factors $f_{ij} f_{kl} f_{mn} \cdot \ldots$ On making these approximations, we find that Eq. (11) becomes

$$Q = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{1}{N!} \left\{(L + c)^N + (L + c)^{N-2} \frac{N^2}{2} [(L + c)b + bc + d] + (L + c)^{N-4} \frac{N^4}{8} [(L + c)b + bc + d]^2 + (L + c)^{N-6} \frac{N^6}{48} [(L + c)b + bc + d]^3 + \cdots\right\} \tag{12}$$

To the same level of approximation as used above we can then write Eq. (12) as

$$Q(N) = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{1}{N!} (L + c)^N \left[1 + \frac{N}{L + c}\left(\frac{b}{2} + \frac{bc + d}{2(L + c)}\right)\right]^N \tag{13}$$

For bulk solution, a large distance from the surface, $c = d = 0$, and the partition function is given by

$$Q_\infty(N') = \left(\frac{2\pi mkT}{h^2}\right)^{N'/2} \frac{1}{N'!} L^{N'} \left[1 + \frac{N'}{L} \frac{b}{2}\right]^{N'} \tag{14}$$

The chemical potential of a floc particle is given by

$$\mu = -kT\left(\frac{\partial \log_e Q}{\partial N}\right)_{T,L} \tag{15}$$

and at equilibrium the chemical potential of a particle in an assembly a large distance from the surface, μ_∞, must be equal to the chemical potential of a particle near the surface, μ. We find that

$$\begin{aligned}\mu_\infty = {} & -kT\log\left(\frac{2\pi mkT}{h^2}\right)^{1/2} + kT\log\left[\frac{N'}{L}\left(\frac{1}{1+(N'b/2L)}\right)\right] \\ & - kT\frac{N'b/2L}{1+(N'b/2L)}\end{aligned} \tag{16}$$

and

$$\begin{aligned}\mu = {} & -kT\log\left(\frac{2\pi mkT}{h^2}\right)^{1/2} + kT\log\left[\frac{N}{L+c}\,\frac{1}{1+\dfrac{N}{L+c}\left(\dfrac{b}{2}+\dfrac{bc+d}{2(L+c)}\right)}\right] \\ & -kT\frac{\dfrac{N}{2(L+c)}\left(b+\dfrac{bc+d}{L+c}\right)}{1+\dfrac{N}{2(L+c)}\left(b+\dfrac{bc+d}{L+c}\right)}\end{aligned} \tag{17}$$

We wish to determine the excess of floc particles in the assembly adjacent to the surface as compared to the assembly of identical size in the bulk solution, $N - N' \equiv \Delta N$. For finite N, N', and L, this is not readily done; however, if we pass to the limit of large N, N', and L, a rather simple formula for ΔN results. We proceed as follows.

Let

$$N'/L = \sigma; \qquad N = L\sigma\left(1 + \frac{\Delta N}{L\sigma}\right)$$

We anticipate that $\Delta N/L\sigma \to 0$ as $L \to \infty$. Expansion of μ in descending powers of L yields, through terms of order L^{-1},

$$\mu = \mu_\infty + \frac{kT}{L}\left[\frac{\Delta N}{\sigma} - c - \frac{\Delta Nb + d\sigma}{2+\sigma b} - \frac{\sigma b}{2+\sigma b}\left(\frac{\Delta N}{\sigma} + \frac{d}{b} - \frac{\Delta Nb + d\sigma}{2+\sigma b}\right)\right] \tag{18}$$

The requirement that $\mu = \mu_\infty$ then yields

$$\Delta N = c\sigma\left(1 + \frac{\sigma b}{2}\right)^2 + d\sigma^2\left(1 + \frac{\sigma b}{4}\right) \tag{19}$$

On recalling that $c > 0$, b and $d < 0(u(x_i) < 0, v(r_{ij}) > 0)$, we note that ΔN goes through a maximum at

$$\sigma_{\max} = \frac{-4 + 2[(cb + 4d)/(cb + d)]^{1/2}}{3b} \tag{20}$$

and a minimum (for which ΔN is negative) at

$$\sigma_{\min} = \frac{-4 - 2[(cb + 4d)/(cb + d)]^{1/2}}{3b} \tag{21}$$

both positive values. We also note that $\Delta N = 0$ for

$$\sigma_1 = 0$$

$$\sigma_2 = \frac{-2}{b}\left[1 - \left(\frac{d}{cb + d}\right)^{1/2}\right] \tag{22}$$

and

$$\sigma_3 = \frac{-2}{b}\left[1 + \left(\frac{d}{cb + d}\right)^{1/2}\right] \tag{23}$$

Values of ΔN calculated for $0 < \sigma < \sigma_2$ are presumed to be valid; for $\sigma_2 < \sigma$ our formula probably has no physical significance. The maximum attainable value for ΔN, $\Delta N_{\max}$, is given by

$$\Delta N_{\max} = \left(\frac{cb^2}{4} + \frac{db}{4}\right)\sigma_{\max}(\sigma_{\max} - \sigma_1)(\sigma_{\max} - \sigma_2) \tag{24}$$

obtained by writing Eq. (19) in factored form.

We now calculate the integrals b, c, and d defined in Eqs. (8) and (9). The evaluation of c proceeds as follows:

$$c = \int_0^L \{\exp[-\beta u(x)] - 1\}\, dx \tag{25}$$

where $u(x) = +\infty$, $0 < x < l/2$, and $u(x)$, $x > l/2$ is the electrical free energy of two plane parallel surfaces (each of area l^2) separated by a distance $x - l/2$ minus their free energy at infinite separation. The two surfaces are kept at known potentials of opposite sign, ψ_0 (negative) and ψ_1 (positive). Then

$$c = +\int_0^\infty \{\exp[-\beta G_a(\xi)] - 1\}\, d\xi \tag{26}$$

where, as was shown earlier (*13*),

$$G_a = \frac{Dl^2}{8\pi}\left\{-\int_{\psi_0}^{\psi_1} \frac{H(\xi) + C\log\dfrac{(1 + B\cosh w)^2}{(1 + B)(1 + B\cosh w_0)}}{\left[H(\xi) + C\log\dfrac{1 + B\cosh w}{1 + B\cosh w_0}\right]^{1/2}}\,d\psi \right.$$

$$\left. + \int_{\psi_0}^{\psi_1} \frac{H(\infty) + C\log\dfrac{(1 + B\cosh w)^2}{(1 + B)(1 + B\cosh w_0)}}{\left[H(\infty) + C\log\dfrac{1 + B\cosh w}{1 + B\cosh w_0}\right]^{1/2}}\,d\psi\right\} \tag{27}$$

$$w = \beta ez\psi, \qquad w_0 = \beta ez\psi_0$$

$$H(\infty) = C\log\frac{1 + B\cosh w_0}{1 + B}, \qquad C = 2A/\beta ezB$$

$H(\xi)$ is defined by

$$\xi = \int_{\psi_0}^{\psi_1} \frac{d\psi}{\left[H(\xi) + C\log\dfrac{1 + B\cosh w}{1 + B\cosh w_0}\right]^{1/2}} \tag{28}$$

$$A = \frac{8\pi zec_\infty}{(1 - 2c_\infty/c_{\max})D}, \qquad B = \frac{2c_\infty}{c_{\max} - 2c_\infty}$$

z = |charge| of ions in the electrolyte solution (a 1-1 electrolyte)
e = electronic charge
c_∞ = electrolyte concentration, "molecules"/cc
$c_{\max}$ = maximum possible electrolyte concentration
D = dielectric constant of the solution

The calculation of b is done as follows:

$$b = \int_{-\infty}^{\infty} \{\exp[-\beta v(r)] - 1\}\,dr \tag{29}$$

where $v(r) = \infty$, $|r| < l$, and $v(r)$, $|r| > l$ is the electrical free energy of two plane parallel surfaces (each of area l^2) separated by a distance $r - l$ minus their free energy at infinite separation. Both surfaces are kept at the (positive) surface potential of the floc, ψ_1. Equation (29) can then be rewritten as

$$b = -2l + 2\int_0^{\infty} \{\exp[-\beta G_r(\xi)] - 1\}\,d\xi \tag{30}$$

where $G_r(\xi)$ is calculated as follows.

Our Poisson-Boltzmann equation,

$$\frac{d^2\psi}{dx^2} = \frac{A \sinh \beta e z \psi}{1 + B \cosh \beta e z \psi}$$

has as a first integral

$$\frac{d\psi}{dx} = \left[C \log \frac{1 + B \cosh \beta e z \psi}{1 + B \cosh \beta e z \psi_m} \right]^{1/2} \tag{31}$$

where $\xi/2 \leq x \leq \xi$, $(d\psi/dx)(\xi/2) = 0$, and we wish to have $\psi(\xi) = \psi_1$. We integrate Eq. (31) by means of the following system:

$$\psi_{(n+1)} = 2\psi_{(n)} - 2\psi_{(n-1)} + \frac{(\Delta x)^2 A \sinh w_n}{1 + B \cosh w_n} \tag{32}$$

$$\psi_{(2)} = \psi_{(1)} + \frac{(\Delta x)^2 A}{2} \frac{\sinh w_1}{1 + B \cosh w_1} \tag{33}$$

$$w_j = \beta e z \psi_{(j)}$$

Initially we choose

$$\psi_{(1)} = 2\psi_1 \exp(-\xi/2a)/[1 + \exp(-\xi/a)] \tag{34}$$

where

$$a = \left(\frac{D}{2\pi\beta c_\infty} \right)^{1/2} \frac{1}{2ze}$$

is the Debye length. We carry out the integration, calculate $\psi_1/\psi_{(n)}$, set $\psi_{(1)}{}^{i+1} = \psi_{(1)}{}^{i}(\psi_1/\psi_{(n)}{}^{i})$, $i = 1, 2, \ldots$ until $\psi_{(n)}{}^{i}$ has converged to ψ_1. At this point $\psi_{(1)}{}^{i} = \psi_m$.

We follow Verwey and Overbeek in the calculation of $G_r(\xi)$ (7).

$$\tfrac{1}{2}G_r(\xi) = -\frac{Dl^2}{8\pi\xi/2}[\psi_1 - \psi_m]^2 + l^2 \int_0^1 \int_0^{\xi/2} \frac{\rho'\psi'}{\lambda} \, dx \, d\lambda \tag{35}$$

$$\rho' = \frac{-D}{4\pi} \frac{d^2\psi'}{dx^2} = \frac{-D}{4\pi} \frac{\lambda A \sinh \lambda w'}{1 + B \cosh \lambda w'} \tag{36}$$

$$w' = \beta e z \psi'$$

Now

$$\psi' d\lambda = \frac{\partial}{\partial \lambda}(\lambda \psi') d\lambda - \lambda \frac{\partial \psi'}{\partial \lambda} d\lambda \tag{37}$$

so Eq. (35) can be rewritten as

$$\tfrac{1}{2}G_r(\xi) = -\frac{Dl^2}{4\pi\xi}[\psi_1 - \psi_m]^2 - \int_0^{\xi/2}\int_0^1 \frac{DAl^2 \sinh \lambda w'}{4\pi[1 + B\cosh \lambda w']}\frac{\partial}{\partial \lambda}(\lambda\psi')d\lambda\, dx$$
$$+ \int_0^{\xi/2}\int_0^1 \frac{Dl^2}{4\pi}\frac{\partial \psi'}{\partial \lambda}\frac{\partial^2 \psi'}{\partial x^2}\, d\lambda\, dx \tag{38}$$

We abbreviate this as

$$\tfrac{1}{2}G_r(\xi) = -\frac{Dl^2}{4\pi\xi}[\psi_1 - \psi_m]^2 + I_1 + I_2 \tag{39}$$

On integrating I_1 with respect to λ we obtain

$$I_1 = -\int_0^{\xi/2} \frac{DAl^2}{4\pi\beta ezB}\log\left[\frac{1 + B\cosh w}{1 + B}\right]dx \tag{40}$$

The second integral is shown by Verwey and Overbeek (the proof is not trivial) to be given by

$$I_2 = -\frac{Dl^2}{8\pi}\int_0^{\xi/2}\left(\frac{d\psi}{dx}\right)^2 dx + \frac{D}{4\pi\xi}[\psi_1 - \psi_m]^2 \tag{41}$$

We change the variable of integration to ψ, use Eq. (31), and collect terms to obtain

$$G_r(\xi) = -\frac{Dl^2}{4\pi}C^{1/2}\int_{\psi_m}^{\psi_1}\log\left[\frac{(1 + B\cosh w)^2}{(1 + B)(1 + B\cosh w_m)}\right]$$
$$\times \left\{\log\left[\frac{1 + B\cosh w}{1 + B\cosh w_m}\right]\right\}^{-1/2} d\psi - G_\infty$$
$$w_m = \beta ez\psi_m \tag{42}$$

Here G_∞ is given by

$$G_\infty = -\frac{Dl^2}{4\pi}C^{1/2}\int_0^{\psi_1} 2\left\{\log\left[\frac{1 + B\cosh w}{1 + B}\right]\right\}^{1/2} d\psi \tag{43}$$

Equation (42) is then used to evaluate the integral in Eq. (30).

The double integral d is evaluated in the following way.

$$d = \int_0^L\int_0^L g_1 g_2 f_{12}\, dx_1\, dx_2 \tag{44}$$
$$g_1 = \exp[-\beta u(x_1)] - 1$$
$$g_2 = \exp[-\beta u(x_2)] - 1$$
$$f_{12} = \exp[-\beta v(|x_2 - x_1|)] - 1$$

If

$$x_1 < l/2, \qquad g_1 = -1$$

$$x_1 \geq l/2, \qquad g_1 = \exp[-\beta G_a(x_1 - l/2)] - 1$$

If

$$x_2 < l/2, \qquad g_2 = -1$$

$$x_2 \geq l/2, \qquad g_2 = \exp[-\beta G_a(x_2 - l/2)] - 1$$

If

$$|x_2 - x_1| < l, \qquad f_{12} = -1$$

$$|x_2 - x_1| > l, \qquad f_{12} = \exp[-\beta G_r(|x_2 - x_1| - l)] - 1$$

Since $g_i \cong 0$ for $x_i \gtrsim 5$ Debye lengths, we can reduce the range of the integrations to $0 \leq x_{\max}$, where $x_{\max} \cong 5$ Debye lengths. Furthermore, the integrand is symmetric with respect to interchange of x_1 and x_2, so it may finally be written as

$$d = 2\int_0^{5a}\int_0^{x_1} g_1 g_2 f_{12}\, dx_1\, dx_2 \tag{45}$$

Now there are some features of Eq. (19) which raise some questions about the use of this particular cluster integral approach at higher floc

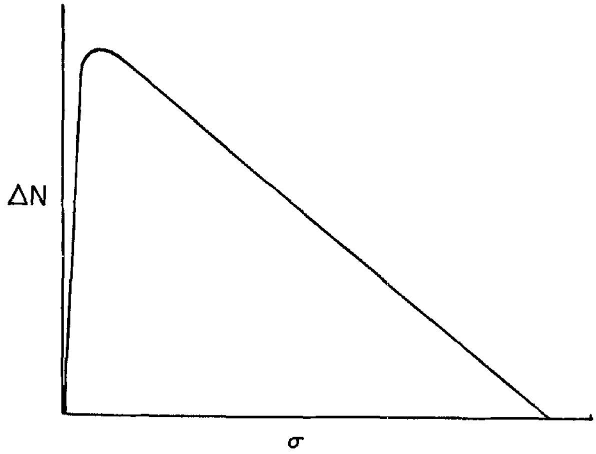

FIG. 1. Schematic isotherm for strong, short-range binding.

concentrations. If there is strong binding of floc particles (binding energy $\gg kT$) which are within a distance δ of the surface, and zero binding of more distant floc particles, on physical grounds a plot of ΔN vs σ should look like that shown in Fig. 1. It is apparent that the cubic equation, Eq. (19), cannot represent isotherms of this type very well. Presumably the flaw lies in the approximations involved in summing the cluster integrals.

As is shown below, it is not difficult to obtain a modified method for summing the cluster integrals to obtain Q_∞. From this we obtain the activity coefficient of the floc particles, and then use a thermodynamic argument to calculate ΔN.

We therefore develop an alternative expression for the canonical partition function Q_∞ for the floc particles at a large distance from the surface, Eq. (14). The chemical potential of a floc particle in the vicinity of the surface is then given by

$$\mu = \mu_0 + G_a(x) + kT \log [\gamma(\sigma)\sigma] \tag{46}$$

where the activity coefficient $\gamma(\sigma)$ is to be calculated from Q_∞. We proceed as follows.

$$Q_\infty(N) = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{1}{N!} L^N \left[1 + \frac{Nb}{2L}\right]^N$$

We rewrite this as

$$\begin{aligned} Q_\infty &= \exp\left(-\frac{2L}{b}\right)\frac{L^N}{N!}\left(1 + \frac{Nb}{2L}\right)^N \exp\left(\frac{2L}{b}\right)A^N \\ A &= \left(\frac{2\pi mkT}{h^2}\right)^{1/2} \\ Q_\infty &= \exp\left(-\frac{2L}{b}\right)\frac{L^N}{N!} e^{-N}e^N\left(1 + \frac{Nb}{2L}\right)^N \exp\left(\frac{2L}{b}\right)A^N \\ &= \exp\left(-\frac{2L}{b}\right)\frac{L^N}{N!} e^{-N}\left(1 + \frac{Nb}{2L}\right)^{2L/b}\left(1 + \frac{Nb}{2L}\right)^N \exp\left(\frac{2L}{b}\right)A^N \end{aligned} \tag{47}$$

on noting that $|b/2L|$ is very small. Then

$$Q_\infty = \frac{A^N L^N}{N!} \exp\left(-\frac{2L}{b} - N\right)\left(1 + \frac{Nb}{2L}\right)^{2L/b+N} \exp\left(\frac{2L}{b}\right) \tag{48}$$

We calculate the chemical potential of a floc particle from Eq. (48):

$$-kT\frac{\partial \log}{\partial N}Q_\infty = \mu_\infty$$

$$= -kT\log A + kT\log\left[\frac{N}{L}\left(\frac{1}{1+(Nb/2L)}\right)\right] \tag{49}$$

We set $N/L = \sigma_\infty$, the number of floc particles per unit length in the bulk solution, and note that the activity coefficient of Eq. (46) is given by

$$\gamma(\sigma) = 1/(1 + \sigma b/2) \tag{50}$$

on comparison with Eq. (49).

We equate chemical potentials in the vicinity of the surface and in the bulk solution to obtain

$$G_a(x) + kT\log\left[\frac{\sigma(x)}{1 + b\sigma(x)/2}\right] = kT\log\frac{\sigma_\infty}{1 + b\sigma_\infty/2} \tag{51}$$

Solving this for $\sigma(x)$ yields

$$\sigma(x) = \frac{\dfrac{\sigma_\infty}{1+\sigma_\infty b/2}\exp\left[-G_a(x)/kT\right]}{1 - \dfrac{b\sigma_\infty/2}{1+b\sigma_\infty/2}\exp\left[-G_a(x)/kT\right]} \tag{52}$$

We then obtain

$$\Delta N = \int_0^\infty [\sigma(x) - \sigma_\infty]\,dx$$

$$= \sigma_\infty(1 + \sigma_\infty b/2)\int_0^\infty \frac{[\exp(-G_a/kT) - 1]\,dx}{1 - (\sigma_\infty b/2)[\exp(-G_a/kT) - 1]} \tag{53}$$

for the net excess of floc particles adsorbed per site. The excess of floc particles adsorbed per cm^2 of surface is then given by $\Delta N(2/b)^2$; evidently the effective length of a floc particle is just $-b/2$.

The result of Eq. (52) is essentially identical to the result we obtained earlier by using a cell model (*11–13*, *17*) if we assume that the length of a cell is given by $-b/2$, which is exact for hard "spheres" in one dimension. We note that the effective size of the floc particles varies relatively little with changes in the ionic strength of the solution; this somewhat surprising result is consistent with the findings of Verwey and Overbeek (*18*). One can easily verify that Eq. (53) can readily yield plots of ΔN vs σ of the sort hypothesized in Fig. 1. This approach puts our cell model and excluded volume calculations on a somewhat more solid footing, inasmuch as we

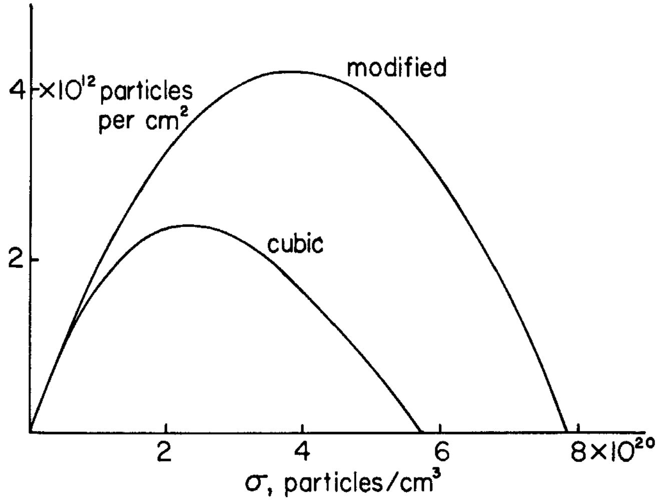

FIG. 2. Comparison of the two methods. $\psi_0 = -20$, $\psi_1 = 20$ mV; $c_\infty = 2 \times 10^{-5}$, $c_{\max} = 10^{-4}$ mole/cm^3; $T = 298$°K; $l = 10^{-7}$ cm; $z = 1$.

now have a clearer picture of what the effective length of a floc particle is in terms of the interparticle potential energies, and we have eliminated the artificial partitioning of the system into cells. This approach also remedies the failure of our previous methods to treat floc–floc repulsions with rigor.

Let us now examine the adsorption isotherms obtained by the two methods we have outlined above. In Fig. 2 we compare adsorption isotherms calculated by Eq. (19) (cubic) and by Eq. (53) (modified). At low concentrations of floc particles the two methods are seen to give essentially identical results, but at higher values of σ the departures are very marked, although qualitatively the curves are similar. All subsequent results were obtained by means of Eq. (53).

Figure 3 shows the expected decrease in adsorption with increasing ionic strength; this result is a feature of all of the models we have explored. Increasing ionic strength decreases the thickness of the double layer and decreases the strength of the attractive force between the floc and the surfactant-coated air–water interface. This model shows an increase in the effective size of the floc particles with decreasing ionic strength due to the increased range of floc–floc electrical repulsion as the ionic strength decreases and the Debye length increases.

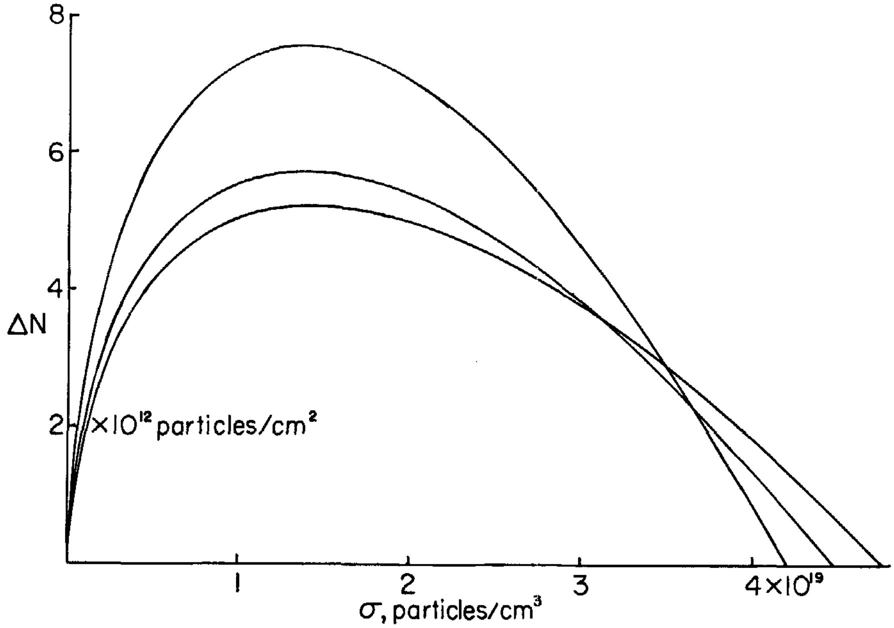

FIG. 3. Effect of ionic strength. $\psi_0 = -100$, $\psi_1 = 100$ mV; $c_\infty = 2 \times 10^{-6}$, 10^{-5}, 2×10^{-5} (top to bottom); $c_{\max} = 10^{-4}$ mole/cm³; $T = 298$ °K; $l = 10^{-7}$ cm; $z = 1$.

The effect of increasing temperature is seen in Fig. 4. Temperature effects are rather small, particularly at small floc concentrations. We note that the relatively slight increase in adsorption with temperature at higher floc concentrations is in the opposite direction from that observed with our earlier models. We believe that this is due to the possibility of closer approaches between floc particles at the higher temperatures.

We see in Fig. 5 the effect of changing the surface potential of the air–water interface, ψ_0. The effect is what one would expect, and is in agreement with the results of our earlier models. On the other hand, the effect of changing the surface potential of the floc, ψ_1, was quite unexpected (Fig. 6). Increasing ψ_1 resulted in a drastic *decrease* in the adsorption except at quite low values of σ, in which range the adsorption increased somewhat. (This increase is not visible in the figure.) The effective volume of the particles, $(b/2)^3$, is very markedly increased by the increased floc–floc repulsions, which apparently more than counterbalance the increased

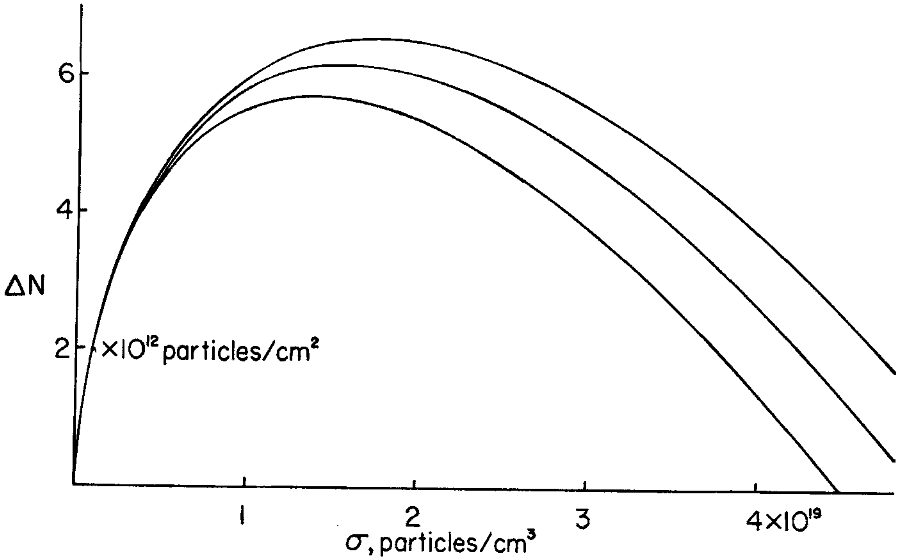

FIG. 4. Effect of temperature. $\psi_0 = -100$, $\psi_1 = 100$ mV; $c_\infty = 10^{-5}$, $c_{\max} = 10^{-4}$ mole/cm³; $T = 340, 320, 298$ °K (top to bottom); $l = 10^{-7}$ cm; $z = 1$.

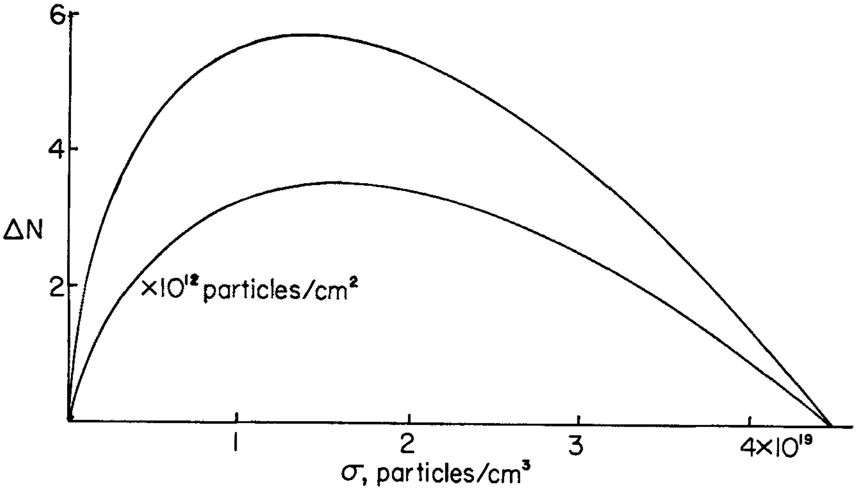

FIG. 5. Effect of ψ_0. $\psi_0 = -100, -50$ (top to bottom), $\psi_1 = 100$ mV; $c_\infty = 10^{-5}$, $c_{\max} = 10^{-4}$ mole/cm³; $T = 298$ °K; $l = 10^{-7}$ cm; $z = 1$.

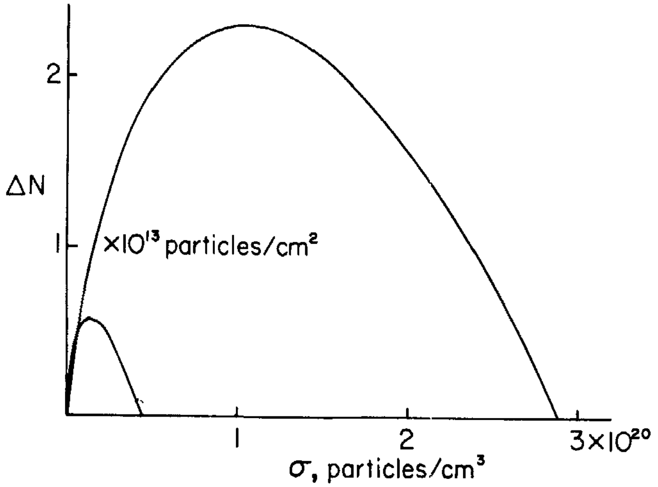

FIG. 6. Effect of ψ_1. $\psi_0 = -100$, $\psi_1 = 50$, 100 mV (top to bottom); $c_\infty = 10^{-5}$, $c_{max} = 10^{-4}$ mole/cm³; $T = 298\,°K$; $l = 10^{-7}$ cm; $z = 1$.

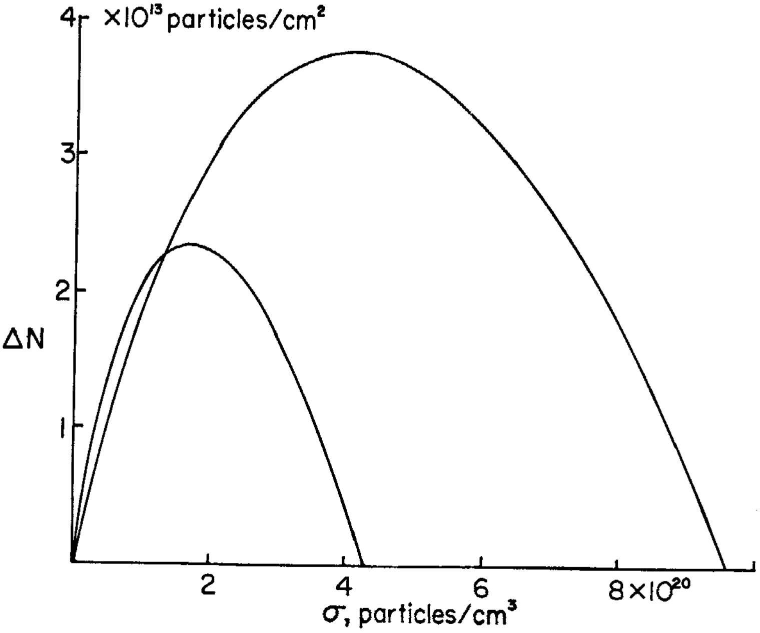

FIG. 7. Effect of floc particle size. $\psi_0 = -100$, $\psi_1 = 100$ mV; $c_\infty = 10^{-5}$, $c_{max} = 10^{-4}$ mole/cm³; $T = 298\,°K$; $l = 5$, 6×10^{-8} cm (top to bottom); $z = 1$.

interface–floc attraction except at quite low floc concentrations. This effect is large enough so that it should be readily accessible to experimental study, and provides an interesting test of the present theory.

The effect of floc particle size, l (a length), is shown in Fig. 7. Increased size causes a larger electrical attraction energy (proportional to l^2) between the interface and the floc, resulting in a more rapid rise of the plot of ΔN vs σ at small values of σ. The increased size of the floc particles and the associated increased magnitude of the floc–floc repulsion energy (also proportional to l^2) results in ΔN–σ plots going through their maximum value of ΔN and returning to $\Delta N = 0$ for smaller values of σ.

The effect of increasing the magnitude of the charge on the inert electrolyte ions from $|z| = 1$ to 2 is shown in Fig. 8. The effect is extremely small at small values of σ, with the curve for $|z| = 2$ lying slightly below that for $|z| = 1$, although this effect is too small to be seen in the figure. At higher values of σ, the effect of $|z|$ upon the floc–floc repulsion (which controls the effective particle size) becomes dominant, and the $|z| = 2$ curve lies above the $|z| = 1$ curve.

Our modification of the method for summing the cluster integrals which leads to Eq. (48) for Q_∞ can also be applied to Eq. (13); the analysis goes through without difficulty and one obtains an expression for ΔN as a

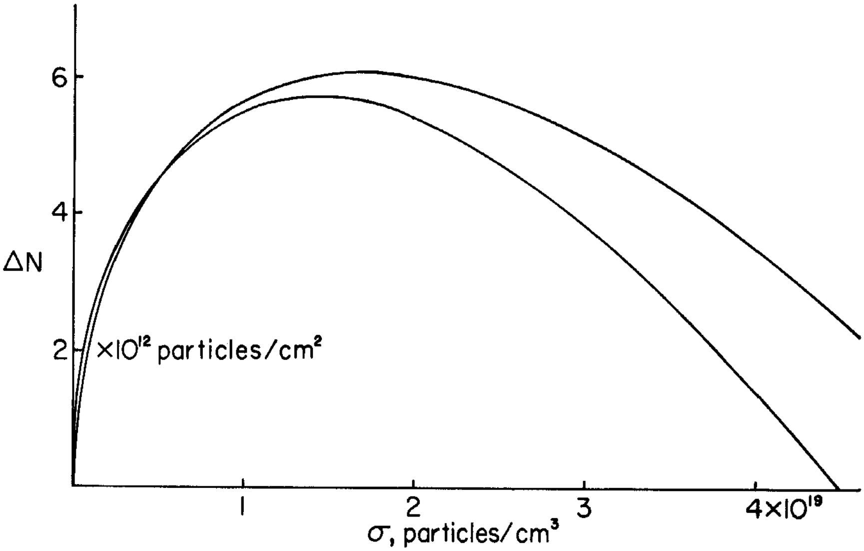

FIG. 8. Effect of z. $\psi_0 = -100$, $\psi_1 = 100$ mV; $c_\infty = 0.25$, 1.0×10^{-5}, $c_{\max} = 10^{-4}$ mole/cm³; $T = 298$°K; $l = 10^{-7}$ cm; $z = 2$, 1 (top to bottom).

function of σ. This is done as follows. We modify Eq. (13) by the introduction of two factors of unity to obtain Eq. (54).

$$Q = \exp\left[-2(L+c)/b\right]\frac{(L+c)^N}{N!}e^{-N}e^N$$

$$\times\left[1+\frac{N}{2(L+c)}\left(b+\frac{bc+d}{L+c}\right]^N \exp\left[2(L+c)/b\right]A^N$$

$$A = \left(\frac{2\pi mkT}{h^2}\right)^{1/2} \tag{54}$$

We note that $e^N \cong (1+(N/x))^x$ for large x, and let

$$x = \frac{2(L+c)}{b+\dfrac{bc+d}{L+c}}$$

Our expression for Q then becomes

$$Q = A^N - \exp\left[-\frac{2(L+c)}{b} - N\right]\frac{(L+c)^N}{N!}\exp\left[\frac{2(L+c)}{b}\right]$$

$$\times\left[1+\frac{N}{2(L+c)}\left(b+\frac{bc+d}{L+c}\right)\right]^{N+[\{2(L+c)\}/\{b+(bc+d)/(L+c)\}]} \tag{55}$$

We then equate the floc chemical potentials calculated from Eqs. (48) and (55); this yields

$$\log\left[\frac{L}{N_\infty}\left(1+\frac{N_\infty b}{2L}\right)\right] = \log\left\{\frac{L+c}{N}\left[1+\frac{N}{2(L+c)}\left(b+\frac{bc+d}{L+c}\right)\right]\right\} \tag{56}$$

Let $N = N_\infty + \Delta N$, $\sigma = N_\infty/L$, and let L and N_∞ become very large, exponentiate both sides of Eq. (56), and expand in powers of L^{-1}. On dropping terms of order L^{-2} and higher, one obtains Eq. (57) for ΔN:

$$\Delta N = c\sigma\left(1+\frac{\sigma b}{2}\right)+\frac{d\sigma^2}{2} \tag{57}$$

The parabolic plots of ΔN vs σ which are obtained are qualitatively correct but have the same flaw mentioned earlier in connection with Eq. (19). This was an unexpected blow and, in view of the ability of the second method described here to eliminate that failing, we did not calculate adsorption isotherms from Eq. (57).

We next outline another approach to summing the cluster integrals appearing in Eq. (11). As before we write

$$\int_0^L \int_0^L (1 + g_1)(1 + g_2)f_{12}\, dx_1\, dx_2 = Lb + 2cb + d$$

and assume that N is sufficiently large that the great bulk of the terms $f_{ij}f_{kl}f_{mn}\ldots$ in Eq. (11) has no indices in common. This permits us to carry out the integrations indicated in Eq. (11) to obtain

$$Q(N) = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{(L + c)}{N!} \sum_{n=0}^{M} \frac{M!}{n!(M - n)!}\left[\frac{b + [(bc + d)/(L + c)]}{L + c}\right]^n$$

$$M = N(N - 1)/2 \tag{58}$$

This can be rewritten as

$$Q(N) = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{(L + c)^N}{N!}\left[1 + \frac{b + [(bc + d)/(L + c)]}{L + c}\right]^{N(N-1)/2} \tag{59}$$

Note that, in contrast to our earlier approaches leading to Eqs. (13) and (55), no approximations are made with regard to keeping only dominant terms in the coefficients of the series.

We obtain the canonical partition function for a similar quantity of bulk solution, $Q_\infty(N_\infty)$; by setting $c = d = 0$ in Eq. (59):

$$Q_\infty(N_\infty) = \left(\frac{2\pi mkT}{h^2}\right)^{N_\infty/2} \frac{L^{N_\infty}}{N_\infty!}\left[1 + \frac{b}{L}\right]^{N(N-1)/2} \tag{60}$$

We let

$$x = \left(b + \frac{bc + d}{L + c}\right)\bigg/(L + c)$$

$y = b/L$, and note that when L is permitted to become large, $x = y(1 + d/bL)$.

Equating floc chemical potentials for two systems then yields

$$\frac{\partial \log Q}{\partial N} = \frac{\partial \log Q_\infty}{\partial N_\infty} \tag{61}$$

or

$$-\log N + \log (L + c) + (N - 1/2) \log (1 + x)$$
$$= -\log N_\infty + \log L + (N_\infty - 1/2) \log (1 + y) \tag{62}$$

We let $\Delta N = N - N_\infty$, $\sigma = N_\infty/L$, and calculate ΔN in the limit as N_∞ and $L \to \infty$ with σ fixed:

$$\Delta N = \frac{\sigma(c + d\sigma)}{1 - b\sigma} \tag{63}$$

This expression for the adsorption isotherm can also be obtained by an alternative route starting with Eq. (13),

$$Q(N) = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{(L + c)^N}{N!} \left[1 + \frac{N}{2(L + c)}\left(b + \frac{bc + d}{L + c}\right)\right]^N \tag{13}$$

We examine the last factor, noting that

$$\exp u = \lim_{N \to \infty} \left(1 + \frac{u}{N}\right)^N$$

Evidently we must choose

$$u = \frac{N^2}{2(L + c)}\left(b + \frac{bc + d}{L + c}\right) \tag{64}$$

which yields for the partition function

$$Q(N) = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \frac{(L + c)^N}{N!} \exp\left[\frac{b}{2(L + c)}\left(1 + \frac{c + d/b}{L + c}\right)N^2\right] \tag{65}$$

The partition function of the floc in a similar quantity of bulk solution is given by setting c and $d = 0$ as before:

$$Q_\infty(N_\infty) = \left(\frac{2\pi mkT}{h^2}\right)^{N_\infty/2} \frac{L^{N_\infty}}{N_\infty!} \exp\left(\frac{b}{2L} {N_\infty}^2\right) \tag{66}$$

We equate the chemical potentials of the floc in the two systems to obtain

$$\begin{aligned} 0 = {} & \log\left(1 + \frac{c}{L}\right) - \log\left(1 + \frac{\Delta N}{N_\infty}\right) \\ & + \frac{bN_\infty}{L}\left(1 + \frac{c}{L}\right)^{-1}\left(1 + \frac{c + d/b}{L + c}\right)\left(1 + \frac{\Delta N}{N_\infty}\right) - \frac{bN_\infty}{L} \end{aligned} \tag{67}$$

On passing to the limit as N_∞ and $L \to \infty$ and solving for ΔN, we recover Eq. (63) for the adsorption isotherm.

Some isotherms calculated from Eq. (63) are shown in Figs. 9 and 10. In Fig. 9 we see the effect of varying the ionic strength of the solution; the results at low floc concentrations are rather similar to those shown in Fig. 3, but at higher floc concentrations the two methods show very marked departures. Figure 10 exhibits the temperature dependence of the adsorption isotherms calculated from Eq. (63); these results should be compared with Fig. 4. Again, very marked departures are seen between the two methods at higher floc concentrations. The parabolic appearance of the isotherms and the very strong dependence on both T and c_∞ of the values of σ for which ΔN returns to zero lead us to place more reliance on the earlier method.

We can, however, calculate the activity coefficient of the floc from Eq. (60) and then use the earlier method for calculating adsorption isotherms, Eqs. (46) through (53). The chemical potential calculated from Eq. (60) is

$$\mu_\infty = -kT\log\left(\frac{2\pi mkT}{h^2}\right)^{1/2} + kT\log\frac{N}{L} - kT(N - 1/2)\log\left(1+\frac{b}{L}\right) \qquad (68)$$

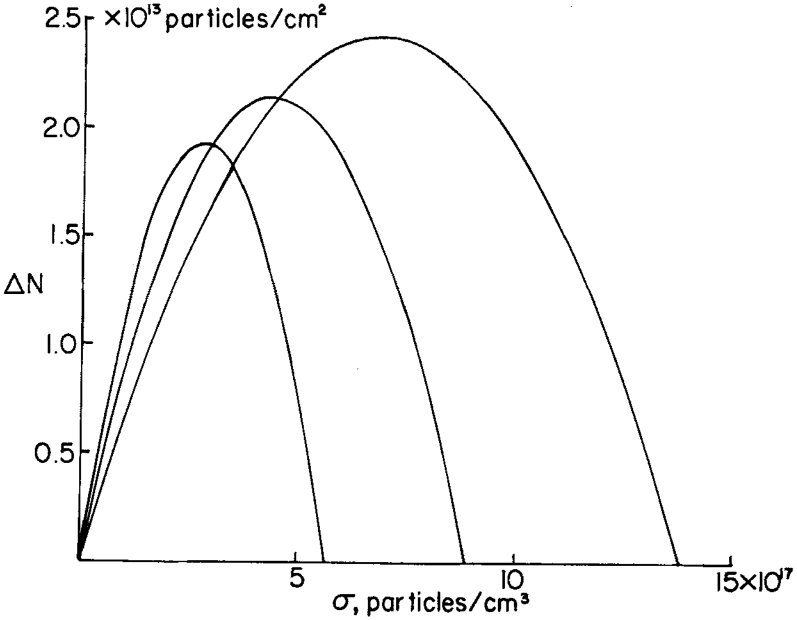

FIG. 9. Effect of ionic strength. Isotherms calculated by Eq. (63). $\psi_0 = -100$, $\psi_1 = 100$ mV; $c_\infty = 2 \times 10^{-5}$, 10^{-5}, and 5×10^{-6} mole/cm³ (top to bottom); $c_{max} = 10^{-5}$ mole/cm³; $T = 298$°K; $l = 10^{-7}$ cm; $z = 1$.

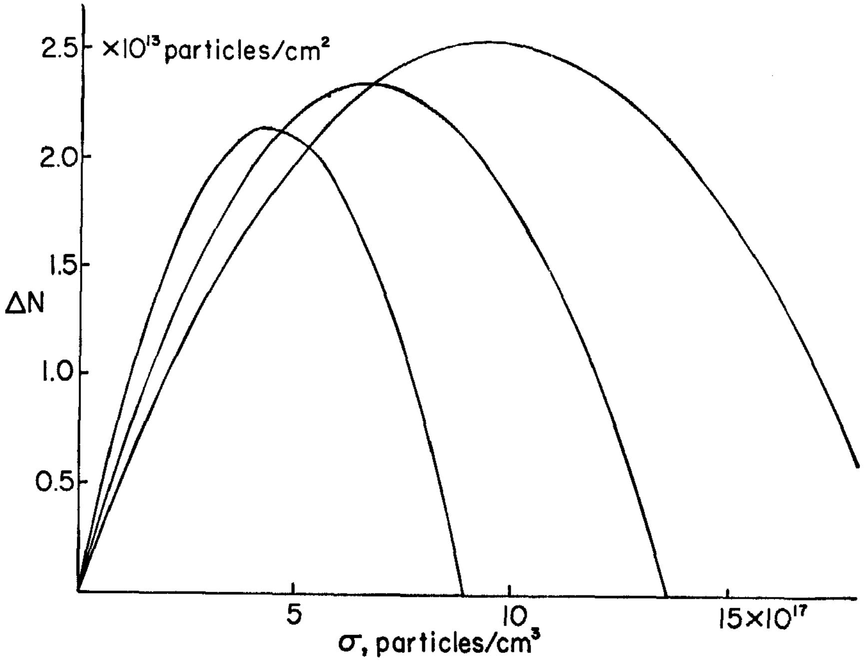

FIG. 10. Effect of temperature. Isotherms calculated by Eq. (63). $\psi_0 = -100$, $\psi_1 = 100$ mV; $c_\infty = 10^{-5}$, $c_{\max} = 10^{-4}$ mole/cm³; $T = 340$, 320, 298 °K (top to bottom); $l = 10^{-7}$ cm; $z = 1$.

On letting $\sigma = N/L$ we obtain for the activity coefficient

$$\gamma = \frac{1}{\left(1 + \dfrac{b\sigma}{N}\right)^N} \cong \exp\,(-b\sigma) \tag{69}$$

and the floc chemical potential is given by

$$\mu_\infty = \mu_0 + kT \log\,[\sigma \exp\,(-b\sigma)] \tag{70}$$

at large distances from the air–solution interface.

Equating μ_∞ to the chemical potential of the floc a distance x from the interface then yields

$$\sigma(x) \exp\,[-b\sigma(x)] = \exp\,[-G_a(x)/kT]\sigma_\infty \exp\,[-b\sigma_\infty] \tag{71}$$

This is then solved iteratively for $\sigma(x)$, and ΔN is evaluated by

$$\Delta N = \int_0^\infty [\sigma(x) - \sigma_\infty]\, dx \tag{72}$$

The dependence on ionic strength of isotherms computed by this method is shown in Fig. 11. We note the usual decrease in the extent of floc adsorption with increasing ionic strength, but the behavior of the isotherms at high floc concentrations departs very markedly from that of isotherms calculated by Eq. (53), in which the activity coefficient is given by Eq. (50) instead of Eq. (69). The isotherms calculated using Eq. (69) do not appear to go through a maximum with increasing σ and then decrease to zero, as was observed with our other approaches. The temperature dependence of the isotherms is shown in Fig. 12; it is seen to be very weak over the entire

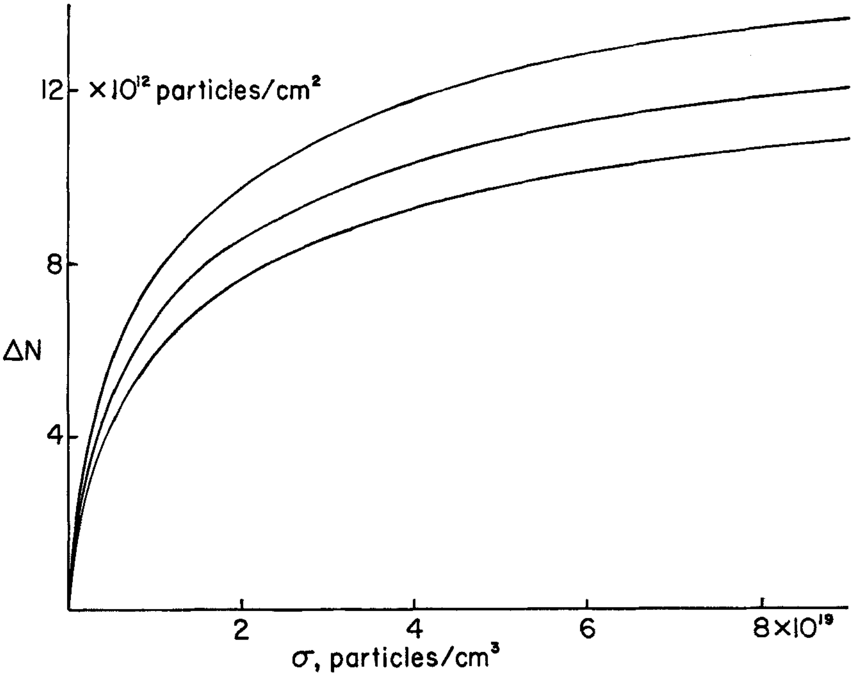

FIG. 11. Effect of ionic strength. Isotherms calculated by Eqs. (71) and (72). All parameters as in Fig. 9.

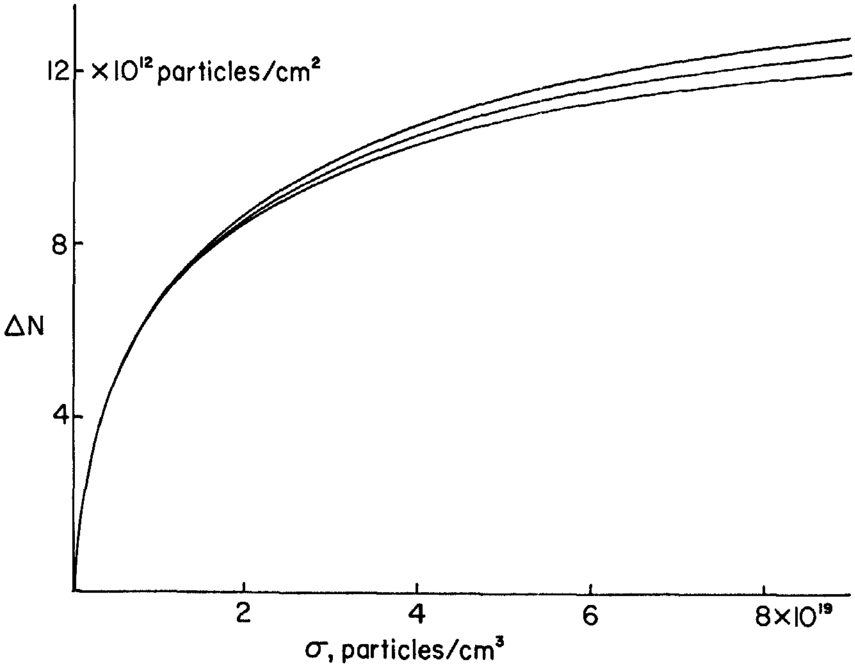

FIG. 12. Effect of temperature. Isotherms calculated by Eqs. (71) and (72). All parameters as in Fig. 10.

range of floc concentration, in moderate contrast to the results shown in Fig. 4 and very marked contrast to the plots of Fig. 10.

In summary, we note that we have presented here four different methods of calculating charged floc adsorption isotherms on charged surface films. The shapes of the isotherms calculated by the different approaches, and the dependences of the isotherms on system variables (surface potentials, temperature, ionic strength, etc.) are sufficiently different to make it possible to discriminate between these methods, and also the ones proposed earlier (*12*, *13*) experimentally. We note that the major problem in all of the approaches described here is obtaining an adequate approximation to the cluster integral sums at the higher floc concentrations.

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