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Surfactant Recovery in Adsorbing Colloid Flotation

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Abstract

The displacement of surfactants from floc–water interfaces by salts is examined by statistical mechanical methods. The effect of added salts on the adsorption isotherm is exhibited, and it is found that surfactant condensed films can readily be displaced. This may markedly improve the economics of adsorbing colloid flotation by facilitating surfactant recovery. Preliminary experimental results supporting the theory are presented; Na_2CO_3 is used to displace sodium lauryl sulfate from $Fe(OH)_3$. The viscous drag forces on floc particles attached to rising bubbles are calculated for bubbles having diameters in the range 0 to 1 mm. At the upper end of this range these forces appear to be large enough to reduce the efficiency of foam flotation.

INTRODUCTION

Foam flotation methods show considerable promise for the removal of a variety of pollutants from wastewaters; the literature in this field has been recently reviewed by several authors (*1–3*). Zeitlin's bench-scale studies of adsorbing colloid flotation (*4–7*) caused us to apply the technique to the treatment of a number of industrial wastes (*8*) and to investigate two models for floc particle-bubble attachment (*9–11*).

A matter of considerable impact on the economics of foam flotation is the extent to which surfactant can be recovered for recycling. Within the framework of the Fuerstenau-Somasundaran-Healy model (*12–18*), one expects that a very substantial fraction of the surfactant in the collapsed foamate from floc foam flotation will be adsorbed on the floc sludge, interfering with the settling of the sludge and the recovery of the surfactant. An analysis of the adsorption isotherms of the surfactant on the floc and the effect on these of varying ionic strength were given in an earlier paper (*10*) in which the adsorption of nonsurfactant ions into the primary layer on the floc, and the competition of surfactant and nonsurfactant ions for sites in the primary layer, were neglected. We here present an analysis which takes these effects into account. Our results indicate the feasibility of displacing surfactant ions from the floc sludge by the addition of nonsurface-active salts.

We also examine the effect of bubble size on the viscous drag forces tending to drag attached floc particles away from rising bubbles.

ANALYSIS

We first look at the simple case in which the surfactant ions do not interact with each other; this is readily seen to yield Langmuir-type adsorption isotherms for the surfactant ion and the nonsurface-active competing ion.

N_S = number of surface sites/cm^2

θ_A = fraction of sites occupied by surfactant ions A

θ_B = fraction of sites occupied by nonsurface-active ions B

c_A = bulk concentration of A

c_B = bulk concentration of B

At equilibrium the rates of adsorption and desorption of A (and also of B) are equal yielding

$$k_{A_f} N_S \theta_A = k_{A_r} c_A N_S (1 - \theta_A - \theta_B) \tag{1}$$

$$k_{B_f} N_S \theta_B = k_{B_r} c_B N_S (1 - \theta_A - \theta_B) \tag{2}$$

Solution of these equations leads in the usual way to

$$\theta_A = \frac{b_A c_A}{(1 + b_A c_A + b_B c_B)} \tag{3}$$

$$\theta_B = \frac{b_B c_B}{(1 + b_A c_A + b_B c_B)} \tag{4}$$

where $b_A = k_{Ar}/k_{Af}$ and $b_B = k_{Br}/k_{Bf}$. We see, as expected, that increasing c_B results in decreasing θ_A, displacing surfactant from the floc particle surface. The model, however, is rather unrealistic, in that it neglects the van der Waals interactions of the hydrocarbon chains of the surfactant ions which, as Fuerstenau and his co-workers have observed experimentally (*12–18*), have a profound effect on the shapes of the adsorption isotherms. Surface condensation may occur, resulting in a sudden increase in θ_A from slightly greater than zero to slightly less than one with a slight decrease in temperature or a slight increase in surfactant concentration.

We next attack the problem of competition for surface sites when interactions between the surfactant ions are significant. We use an approximate method described by Fowler and Guggenheim (*19*).

We let

z = number of nearest neighbors of a site

N_A = number of sites occupied by A

N_B = number of sites occupied by B

N_{XY} = average number of pairs of sites occupied by X and Y;
X, Y = A, B or 0 (empty)

We take into account the A-A pair interaction energy, $2w/z$, as follows:

$$4N_{AA}N_{00} = N_{A0}^2 \exp(-2w/zkT) \tag{5}$$

$$4N_{BB}N_{00} = N_{B0}^2 \tag{6}$$

$$2N_{00}N_{AB} = N_{A0}N_{B0} \tag{7}$$

$$2N_{AA} + N_{A0} + N_{AB} = zN_A \tag{8}$$

$$2N_{00} + N_{A0} + N_{B0} = z(N_S - N_A - N_B) \tag{9}$$

$$2N_{BB} + N_{B0} + N_{AB} = zN_B \tag{10}$$

(This is a straightforward extension of the approach used for a single adsorbed species in Ref. *19*.) A lengthy series of successive eliminations finally yields a remarkably simple equation for N_{AA}:

$$4(D - 1)N_{AA}^2 - [4(D - 1)N_A + 2N_S]zN_{AA} + Dz^2N_A^2 = 0 \tag{11}$$

where $D = \exp(-2w/zkT)$. This is identical to Fowler and Guggenheim's

Eq. (1010,1). We follow these authors to obtain

$$N_{AA} = zN_S\left\{\frac{\theta_A}{2} - \frac{\theta_A(1-\theta_A)}{\beta+1}\right\} \tag{12}$$

$$\beta = [1 - 4\theta_A(1-\theta_A)(1-D)]^{1/2} \tag{13}$$

The expression for the chemical potential of A is given by (*19*)

$$\frac{\mu_A}{kT} \equiv \log\lambda_A = \log\frac{\theta_A}{1-\theta_A-\theta_B} - \log a_A{}^\circ(T) + \frac{w}{kT} + \frac{1}{2}z\log\frac{(\beta-1+2\theta_A)(1-\theta_A)}{\theta_A(\beta+1-2\theta_A)} \tag{14}$$

where $a_A{}^\circ(T)$ is the partition function for the internal degrees of freedom of the surfactant ion. We note that

$$a_A{}^\circ(T) = \exp(\chi_A/kT)j_A(T) \tag{15}$$

where $j_A(T)$ is the partition function for the internal motions of a surfactant ion in bulk solution and χ_A is the binding energy of an isolated surfactant ion to the floc–water interface.

In solution we assume the chemical potential of a surfactant ion to be given by

$$\frac{\mu_A}{kT} = \text{const} - \frac{5}{2}\log T + \log c_A - \log j_A(T) \tag{16}$$

Equating Eqs. (14) and (16) then yields

$$\log\frac{1-\theta_A-\theta_B}{\theta_A} - \frac{\chi_A}{kT} + \frac{w}{kT} + \frac{z}{2}\log\frac{(\beta-1+2\theta_A)(1-\theta_A)}{\theta_A(\beta+1-2\theta_A)} + \frac{5}{2}\log T = \log\frac{c_A}{c_A{}^\circ} = \log c'_A \tag{17}$$

where $c_A{}^\circ$ is determined by the constant in Eq. (16).

In similar but simpler fashion,

$$\log\frac{\theta_B}{1-\theta_A-\theta_B} - \frac{\chi_B}{kT} + \frac{5}{2}\log T = \log\frac{c_B}{c_B{}^\circ} = \log c_B' \tag{18}$$

We can calculate adsorption isotherms from Eqs. (17) and (18), calculating c_A' and c_B' as functions of θ_A and θ_B; it is more convenient to calculate c_A' and θ_B as functions of θ_A and c_B'. We solve Eq. (18) for θ_B, obtaining

$$\theta_B = bc_B' \frac{(1-\theta_A)}{(1+bc_B')}$$
$$b = T^{-5/2} \exp\frac{\chi_B}{kT} \tag{19}$$

Some typical isotherms are plotted in Fig. 1. We see that unstable phases may occur [where $(\partial\mu_A/\partial\theta_A)_{c_B} = kT(\partial \log c_A'/\partial\theta_A)_{c_B}$ is negative], so that the system splits into two stable phases. We next determine the values of θ_A for these stable phases; again we follow Fowler and Guggenheim. If θ_{X1} and θ_{X2} represent the values of θ_X for the two surface phases in equilibrium with each other (X = A, B), then we must have

$$\lambda_{A1} \equiv \lambda_A(\theta_{A1}, \theta_{B1}) = \lambda_A(\theta_{A2}, \theta_{B2}) \tag{20}$$

$$\lambda_{B1} \equiv \lambda_B(\theta_{A1}, \theta_{B1}) = \lambda_B(\theta_{A2}, \theta_{B2}) \tag{21}$$

and

$$\phi(\theta_{A1}, \theta_{B1}) = \phi(\theta_{A2}, \theta_{B2}) \tag{22}$$

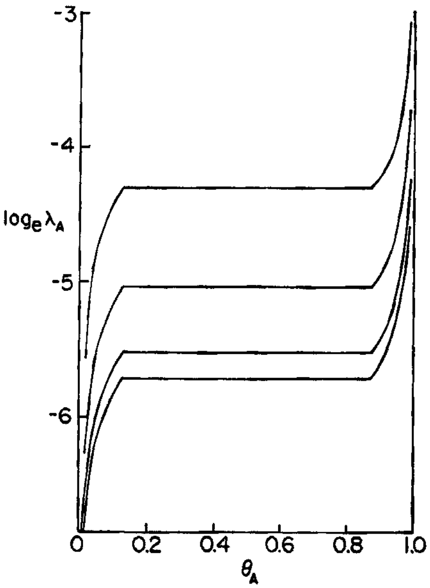

FIG. 1. Effect of competing salt concentration (c_B') on the adsorption isotherm. $T = 298$°K, $\chi_A = 1.2 \times 10^{-13}$, $\chi_B = 1.2 \times 10^{-13}$, $w = -1.234 \times 10^{-13}$ erg, $z = 6$, $c_B' = 30, 10, 3$, and 1×10^5 (top to bottom).

where ϕ is the spreading pressure of the surface phase.

We generalize Fowler and Guggenheim's Formula (1008,5) for $d\phi$ (*19*) to get

$$d\phi = \frac{N_S kT}{\text{area}}(\theta_A d\log\lambda_A + \theta_B d\log\lambda_B) \tag{23}$$

and note that Eq. (22) can be written as

$$\int_1^2 d\phi = 0 \tag{24}$$

We regard c_B' as fixed, θ_B as a function of c_B' and θ_A (through Eq. 19), and θ_A as the independent variable in Eq. (23); $\log\lambda_A$ is given by Eq. (14), and $\log\lambda_B$ is given by

$$\frac{\mu_B}{kT} \equiv \log\lambda_B = \log\frac{\theta_B}{1-\theta_A-\theta_B} - \log a_B{}^\circ(T) \tag{25}$$

Then Eq. (24) becomes

$$0 = \int_{\theta_{A1}}^{\theta_{A2}} \left\{\theta_A\left[\frac{\partial\log\lambda_A}{\partial\theta_A} + \frac{\partial\log\lambda_A}{\partial\theta_B}\frac{\partial\theta_B}{\partial\theta_A}\right] + \theta_B\left[\frac{\partial\log\lambda_B}{\partial\theta_A} + \frac{\partial\log\lambda_B}{\partial\theta_B}\frac{\partial\theta_B}{\partial\theta_A}\right]\right\} d\theta_A \tag{26}$$

From Eq. (19) we find that

$$\frac{\partial\theta_B}{\partial\theta_A} = \frac{bc_B'}{1+bc_B'} \tag{27}$$

From Eq. (25) we have

$$\frac{\partial\log\lambda_B}{\partial\theta_A} = \frac{1}{1-\theta_A-\theta_B} \tag{28}$$

and

$$\frac{\partial\log\lambda_B}{\partial\theta_B} = \frac{1-\theta_A}{\theta_B(1-\theta_A-\theta_B)} \tag{29}$$

From Eq. (14) we have

$$\frac{\partial\log\lambda_A}{\partial\theta_B} = \frac{1}{1-\theta_A-\theta_B} \tag{30}$$

and

$$\frac{\partial \log \lambda_A}{\partial \theta_A} = \frac{1-\theta_B}{\theta_A(1-\theta_A-\theta_B)} + \frac{z}{2}\left[\frac{2+\dfrac{\partial\beta}{\partial\theta_A}}{\beta-1+2\theta_A} + \frac{2-\dfrac{\partial\beta}{\partial\theta_A}}{\beta+1-2\theta_A} - \frac{1}{\theta_A(1-\theta_A)}\right] \tag{31}$$

$$\frac{\partial\beta}{\partial\theta_A} = \frac{2(1-D)(2\theta_A-1)}{\beta} \tag{32}$$

where β is defined by Eq. (13).

We now wish to find values θ_{A1} and θ_{A2} such that Eqs. (20) and (26) are satisfied. (Use of Eq. 19 in Eq. 25 guarantees that Eq. 21 is satisfied.) We proceed as follows. For fixed c_B' we calculate a table of $\log \lambda_A$ as a function of $\theta_A = n\Delta\theta$, $n = 1, 2, \ldots, N$ (θ_B is determined by Eq. 19). Then we find those values of $n\Delta\theta$ for which $\log \lambda_A[(n+1)\Delta\theta] - \log \lambda_A[n\Delta\theta]$ change sign. If there are none, our table and Eq. (16) give us the adsorption isotherm, $\log c_A'$ as a function of θ_A. If there are two, we have a loop in our isotherm, and a phase transition occurs. In this case let the two values of n be n_l and n_r, and calculate $\log \lambda_A((n_l + n_r)/2)(\Delta\theta)$. Then increment n above $(n_l + n_r)/2$ until $\log \lambda_A(n\Delta\theta) - \log \lambda_a((n_l + n_r)/2)(\Delta\theta)$ changes sign; call the value of $n\Delta\theta$ for which this occurs θ_2. Similarly, decrement n below $(n_l + n_r)/2$ until $\log \lambda_A(n\Delta\theta) - \log \lambda_A((n_l + n_r)/2)(\Delta\theta)$ changes sign; call this value of $n\Delta\theta$ θ_1.

We use θ_1 and θ_2 as trial limits for the integral Eq. (26), which we evaluate numerically with the aid of Eqs. (27) to (32). If the integral is greater than (less than) zero, we replace θ_1 by $\theta_1 + \Delta\theta(\theta_1 - \Delta\theta)$, determine the new value of $\log \lambda_A(\theta_1)$ from the table, and we then increase (decrease) θ_A from θ_2 until $\log \lambda_A(\theta_A) - \log \lambda_A(\theta_1)$ changes sign; this value of θ_A is our new upper limit. We use the new values of θ_1 and θ_2 as trial limits for the integral, Eq. (26), and continue this process until the integral changes sign. The values of θ_1 and θ_2 for which this occurs are our desired θ_{A1} and θ_{A2}, which specify the fractions of surface coverage by surfactant in the two phases in equilibrium with each other.

RESULTS

Adsorption isotherms were calculated by the procedure outlined above on an XDS Sigma 7 computer; about 3 sec of machine time was required

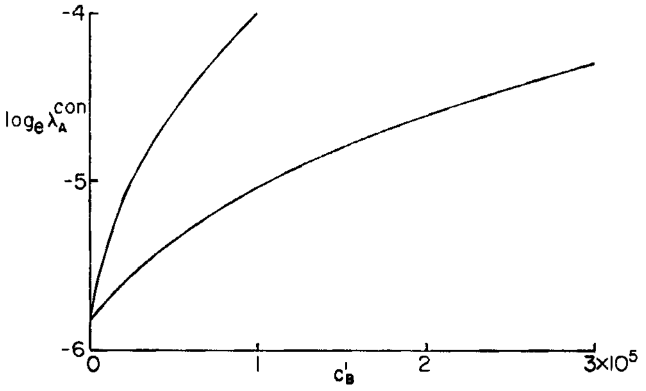

FIG. 2. Effect of c_B' on surfactant condensation concentration. $T = 298\,°K$, $\chi_A = 1.2 \times 10^{-13}$, $w = -1.2 \times 10^{-13}$ erg, $z = 6$. $\chi_B = 1.2 \times 10^{-13}$ (lower) and 1.8×10^{-13} (upper) erg.

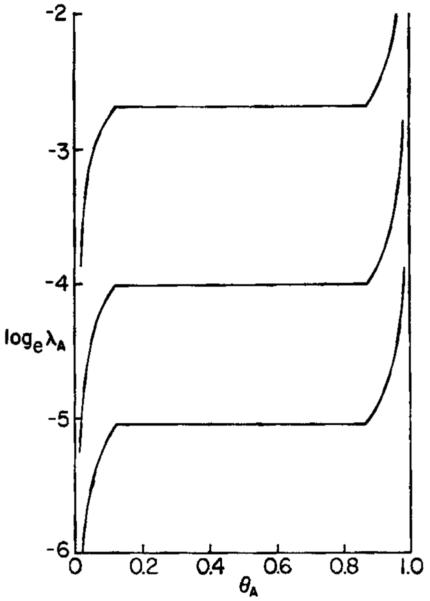

FIG. 3. Effect of χ_B on the adsorption isotherm. $c_B' = 10^5$; $\chi_B = 2.4$, 1.8, and 1.2×10^{-13} erg (top to bottom); other parameters as in Fig. 1.

per isotherm. The results are plotted as $\log_e \lambda_A$ vs θ_A for various values of the parameters.

In Fig. 1 we see the effect of increasing the reduced concentration of salt, c_B'. As the salt concentration increases, the activity of surfactant required to bring about condensation of the surfactant on the floc surface (λ_A^{con}) increases, too, although the shape of the isotherm is unaffected. The dependence of $\log_e \lambda_A^{\text{con}}$ on c_B' is shown in Fig. 2. The larger the binding energy of the salt ion to the floc, χ_B, the more effective it is in preventing condensation of the surfactant on the floc, or (equivalently) in displacing sorbed surfactant from the floc; this is shown in Figs. 2 and 3.

Thus, with positively charged ferric hydroxide flocs, one would expect that univalent anions would be fairly effective in displacing anionic surfactants such as the alkyl sulfates, but that divalent anions would be comparably effective at substantially lower concentrations. One would also anticipate that complexing or chelating ions would be especially effective in displacing surfactant.

The effect of the magnitude of w, the energy of interaction between the surfactant ions, is shown in Fig. 4, and is in agreement with our earlier

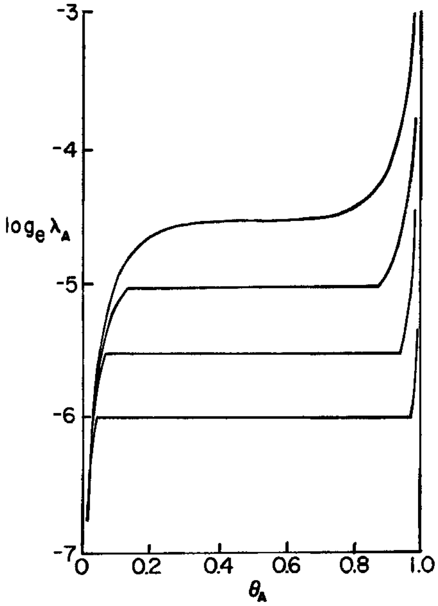

FIG. 4. Effect of w on the adsorption isotherm. $w = -1.0$, -1.2, -1.4, and -1.6×10^{-13} erg (top to bottom); $c_B' = 10^5$; other parameters as in Fig. 1.

calculations on a similar but simpler model (*10*). The effect of the binding energy holding an isolated surfactant ion to the floc surface, χ_A, is shown in Fig. 5, and is also similar to our earlier results (*10*). The results of varying temperature are shown in Fig. 6; the bulk concentration of surfactant required to produce a condensed surface phase increases with temperature, as one would expect.

The economics of adsorbing colloid flotation depend on the extent to which the relatively expensive surfactant can be separated from the sludge in the collapsed foamate and recycled. We have noticed during the operation of a foam flotation pilot plant that relatively large amounts of surfactant (sodium laurylsulfate, NLS) were missing, appearing in neither the column effluent nor in the clarified foamate; this surfactant was presumed to be in the ferric hydroxide sludge which floated in the clarifier.

To determine the extent to which laurylsulfate ion could be displaced from ferric hydroxide sludge by added salt, a run was made in a con-

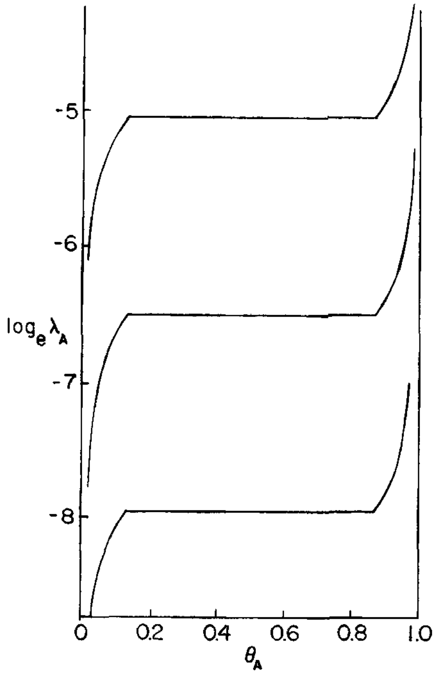

FIG. 5. Effect of χ_A on the adsorption isotherm. $c_B' = 10^5$; $\chi_A = 1.2$, 1.8, and 2.4×10^{-13} erg (top to bottom); other parameters as in Fig. 1.

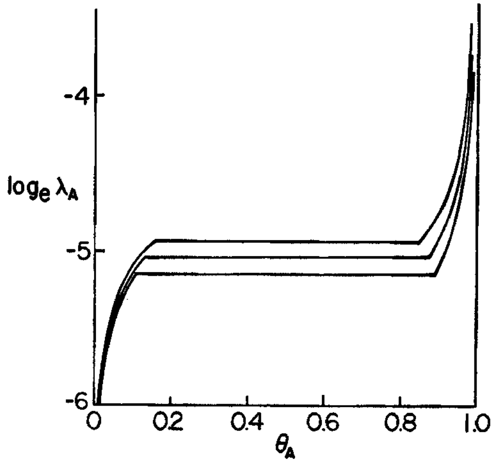

FIG. 6. Effect of temperature on the adsorption isotherm, $c_B' = 10^5$, $T = 308$, 298, and 288°K (top to bottom); other parameters as in Fig. 1.

TABLE 1

Effect of Added Na_2CO_3 on Filtrate NLS Concentration

Nominal Na_2CO_3 concentration		NLS concentration
ppm	mole/liter	(ppm)
0.0	0	44
440	4.15×10^{-3}	94
1,260	1.19×10^{-2}	2,700
10,900	0.102	3,700

tinuous flow apparatus. The NLS concentration was 50 ppm, that of ferric ion was 100 ppm, and the ionic strength was approximately 0.01 *M*. The collapsed foamate volume was 4.2% of the initial total volume treated during the run. Fifty-milliliter aliquots of foamate were treated with various amounts of sodium carbonate; the foamate was then filtered and the filtrate analyzed for NLS. The results are shown in Table 1.

These preliminary results clearly indicate the possibility of displacing surfactant by addition of salts, and appear to be consistent with the theory presented above. A more complete study is in progress.

VISCOUS DRAG EFFECTS

In an earlier paper (*11*) we examined the effects of viscous drag in dislodging floc particles from air–water interfaces in the very wet foams which occur in continuous flow stripping columns. We here present a similar analysis of the viscous forces on floc particles attached to bubbles rising through the liquid pool at the bottom of a batch foam flotation column. We first examine the situation where the bubbles are sufficiently small that creeping flow is occurring and Stokes' law is applicable. The geometry is indicated in Fig. 7.

We let

r = bubble radius

a = floc particle radius

ρ = liquid density–air density

η = liquid viscosity

v = rise velocity of bubble

The buoyancy force on the bubble is then given by

$$F_B = \frac{4}{3}\pi r^3 \rho g \tag{33}$$

Stokes' law gives the viscous drag force on the bubble as

$$F_D = 6\pi r\eta v \tag{34}$$

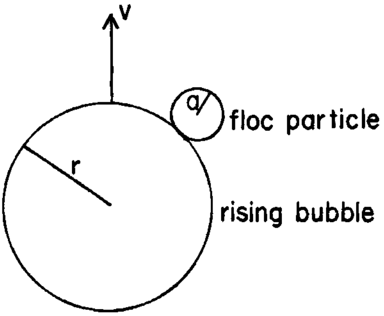

FIG. 7. Physical definition of drag force problem.

so that

$$v = \frac{2\rho g r^2}{9\eta} = 2.18 \text{ cm/sec for a bubble of radius 0.01 cm} \tag{35}$$

We wish to estimate a boundary layer thickness δ within which the viscous drag occurs; we do so by setting

$$F_D = 4\pi r^2 \eta \frac{\bar{v}}{\delta} \tag{36}$$

where $\bar{v} = (\pi/2)v$, since as the bubble rises a distance $2r$, the boundary layer moves a (curved) distance πr with respect to the bubble. We set F_D (Eq. 36) equal to F_B and substitute in our expressions for $\bar{v}$ and v to find, on rearrangement,

$$\delta = \frac{\pi}{3} r \tag{37}$$

We then calculate the viscous drag force on the floc particle by using Stokes' law again on (hopefully) spherical floc particles. The average relative velocity of the liquid in the boundary layer which streams past the floc particle we assume to be given by $a \cdot (\bar{v}/\delta)$, so the floc drag force is given by

$$\begin{aligned} F_f &= 6\pi a\eta \cdot \frac{\delta}{a\bar{v}} \\ &= 2\pi\rho g a^2 r \\ &= 6.16 \times 10^3 r a^2 \end{aligned} \tag{38}$$

If r is 0.01 cm and a is 10^{-5} cm, this gives a floc drag force of 6.2×10^{-9} dynes. In our earlier work (*11*) we estimated the floc binding force for such particles to be of the order of 10^{-5} dynes, so we see that viscous drag forces are far too small to detach the floc particles from the rising bubbles in this regime. Actually, the Reynolds number for this bubble is 4.36, substantially greater than unity, the upper limit of our Stokes' law treatment, which has been pushed beyond its range of applicability even for these quite small bubbles. Bubbles of radius 0.006 cm have a Reynolds number of 0.94, which is very close to our upper limit; in this case the viscous drag force on our floc particle ($a = 10^{-5}$ cm) is 3.7×10^{-9} dynes.

For larger, more rapidly rising bubbles we must refine our Stokes' law treatment. We do so as follows. The drag force on a rising spherical bubble is

$$F_D = \frac{1}{2}\rho v^2 \pi r^2 C_D \tag{39}$$

where F_D = viscous drag force
ρ = density of liquid through which the bubble is rising
v = rise velocity of the bubble
πr^2 = area of the bubble normal to the direction of motion
C_D = drag coefficient, a function of the Reynolds number

The Reynolds number is the ratio of the inertial to viscous forces and for this case is defined as

$$R = \frac{2rv\rho}{\eta} \tag{40}$$

where η = absolute viscosity of the liquid. In the case where the viscous forces are dominant; i.e., $R \rightarrow 0$, the drag coefficient can be calculated from Oseen's improvement to Stokes' law, i.e.,

$$C_D = \frac{24}{R}\left(1 + \frac{3}{16}R\right) \tag{41}$$

Equation (41) is valid for all cases such that $R < 5$. Substituting Eq. (41) in Eq. (39) yields

$$F_D = 6v\pi r\eta + \frac{9}{4}\rho v^2 \pi r^2 \tag{42}$$

The first term on the right-hand side of Eq. (42) is Stokes' law and the second term is Oseen's improvement.

The velocity of rise of the bubble is determined by setting the net buoyant force acting on the bubble equal to the viscous drag force. The net buoyant force on the bubble is

$$F_B = \frac{4}{3}\pi r^3 g\rho \tag{43}$$

where F_B = buoyant force
$(4/3)\pi r^3$ = bubble volume
g = gravitational constant

Then

$$\frac{9}{4}\rho\pi r^2 v^2 + 6\pi r\eta v = \frac{4}{3}\pi r^3 \rho g \tag{44}$$

and

$$v = \frac{-6\pi r\eta + [36\pi^2 r^2 \eta^2 + 12\rho^2 g\pi^2 r^5]^{1/2}}{\frac{9}{2}\rho\pi r^2}$$

$$= \frac{4\eta}{3\rho r}\left[-1 + \left(1 + \frac{\rho^2 g r^3}{3\eta^2}\right)^{1/2}\right] \tag{45}$$

It is assumed that the drag force on a small, spherical floc particle of radius a attached to the rising bubble can be approximated by Stokes' law. The problem is defined schematically in Fig. 6. The occurrence of "corners" and the fact that the floc particle is not in a uniform flow field account for the approximate nature of the solution. To compute the drag force on the floc particle, the average velocity on the particle must be estimated. Schlichting (*20*) states that the thickness of the boundary layer surrounding the rising bubble may be estimated as the diameter of the bubble; i.e., each point on the surface of the bubble moves with velocity v, and one diameter removed from the bubble the fluid velocity is zero. If the boundary layer thickness is δ, then

$$\delta \simeq 2r \tag{46}$$

If one assumes that the velocity varies linearly within the boundary layer, the average velocity acting on the floc particle, $\bar{v}_f$, could be estimated as

$$\bar{v}_f = \frac{av}{\delta} \tag{47}$$

Then the drag on the particle is

$$F_f = 6\pi a\eta\left(\frac{av}{\delta}\right) = \frac{3\pi a^2 \eta v}{r} \tag{48}$$

If $r = 0.01$ cm, $a = 10^{-5}$ cm, $\rho \cong 1.0$ g/cm^3, and $\eta = 0.01$ P, then

$v = 1.421$ cm/sec (compare with 2.178 cm/sec from above treatment)

R (bubble) $= 2.84$

$\bar{v}_f = 7.1 \times 10^{-4}$ cm/sec

R (particle) $= 1.42 \times 10^{-6}$

$F_f = 1.34 \times 10^{-9}$ dynes (compare with 6.2×10^{-9} dynes from simple treatment)

In Ref. *11* the binding force for such particles was estimated to be of the order of 10^{-5} dynes and thus in the fluid regime of $R \to 0$ the viscous forces are much too small to detach the floc particle.

As the size of the rising bubble increases, both the Reynolds number and the rate of rise increase. When $R > 5$ the Stokes-Oseen formulation is rendered invalid and alternative methods of solution must be sought. Batchelor (*21*) has noted that if $r > 0.05$ cm the air bubble can no longer remain spherical; hence this size will constitute an upper limit for this work. Below this limiting size but above the limits of the Stokes-Oseen analysis, two methods exist for computing the drag force. For a pure gas bubble rising in a liquid free of impurities, Batchelor (*21*) states

$$C_D = \frac{48}{R}\left(1 - \frac{2.2}{R^{1/2}}\right) \tag{49}$$

In this case the boundary layer does not separate and there is no wake. Moore (*22*) states that bubbles rising in a fluid containing surface-active impurities, as is the case here, behave as small solid spheres and the drag coefficient approaches that of a solid sphere. Hence Eq. (49) seems to be of very little practical importance.

The solution for a laminar boundary layer for a solid sphere in a uniform flow field of velocity v can be found in Schlichting (*23*). Schlichting further states that boundary layer separation occurs at $\theta = \theta_s = 109.6°$; see Fig. 7 for definition. It should be noted that the value of θ_s is not a constant, but rather a value which is dependent on the method of solution. It is assumed here that any floc particle which came into contact with the rising bubble behind θ_s could not become attached.

The velocity of bubble rise is again determined by equating the net buoyant force to the drag force; however, the fact that the boundary layer separates precludes the use of an explicit formula for C_D. Equation (50) must be solved by trial and error using a graph of C_D versus the Reynold's number; e.g., Schlichting (*24*).

$$\frac{1}{2}\rho v^2 \pi r^2 C_D = \frac{4}{3}\pi r^3 \rho g \tag{50}$$

Then the velocity distribution within the boundary layer on the sphere is given by Schlichting (*25*)

$$\begin{aligned}\frac{v-u}{v} &= 1.5f_1' - 0.5\theta^3(g_3' + h_3') \\ &\quad + 0.0375\theta^5[g_5' + h_5' + 3.33k_5' + 3.33j_5' + 3.33q_5'] + \cdots\end{aligned} \tag{51}$$

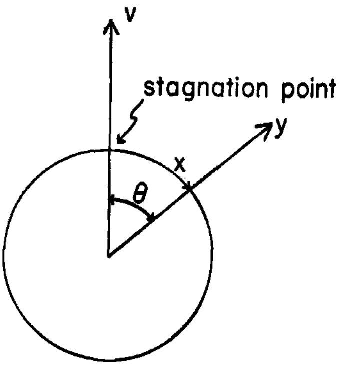

FIG. 8. Coordinates used in drag force problem. x is measured along the circumference; y, perpendicular to the circumference.

where the primed variables are tabulated in terms of the dimensionless variable

$$= \frac{y}{r}\left[\frac{\eta}{3vr\rho}\right]^{1/2} \tag{52}$$

and u is the velocity within the boundary layer. Figure 8 defines the notation.

Investigation of Eq. (51) shows that for a sphere of radius $r = 0.05$ cm, the maximum velocity occurs near $\theta = 60° = 1.05$ radians. On using Stokes' law and $r = 0.05$ cm, $\eta = 0.01$ P:

$$v = 11.1 \text{ cm/sec}$$

$$R\text{(bubble)} = 111$$

$$R\text{(floc)} = 0.5$$

$$\bar{v}_f = 0.03 \text{ cm/sec}$$

$$F_f = 5.7 \times 10^{-8} \text{ dynes}$$

At small bubble sizes the viscous forces are much too small to separate the bubble and the floc particle; however, as the bubble size increases the viscous forces become large, so that it may be impossible to attach floc to the bubble. Although these results are approximate, they are indicative of the optimum sizes of bubbles in such processes. Certainly floc particles should readily attach to bubbles as large as a millimeter in diameter.

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REFERENCES

1. R. Lemlich (ed.), *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972.
2. R. B. Grieves, *Chem. Eng. J.*, *9*, 93 (1975).
3. P. Somasundaran, *Sep. Sci.*, *10*, 93 (1975).
4. Y. S. Kim and H. Zeitlin, *Ibid.*, *7*, 1 (1972).
5. C. Matsuzaki and H. Zeitlin, *Ibid.*, *8*, 185 (1973).
6. F. Chaine and H. Zeitlin, *Ibid.*, *9*, 1 (1974).
7. D. Voyce and H. Zeitlin, *Anal. Chim. Acta*, *69*, 27 (1974).
8. D. J. Wilson, *Foam Flotation Treatment of Heavy Metals and Fluoride-Bearing Industrial Wastewaters*, Environmental Protection Technology Series, EPA-600/2-77-072, April 1977.
9. D. J. Wilson, *Sep. Sci.*, *12*, 321 (1977).
10. D. J. Wilson, *Ibid.*, *12*, 447 (1977).
11. D. J. Wilson, *Ibid.*, *13*, 107 (1978).
12. D. W. Fuerstenau and T. W. Healy, in Ref. *1*, p. 91.
13. D. W. Fuerstenau, T. W. Healy, and P. Somasundaran, *Trans. AIME*, *229*, 321 (1964).
14. P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *J. Phys. Chem.*, *68*, 3562 (1964).
15. P. Somasundaran and D. W. Fuerstenau, *Ibid.*, *70*, 90 (1966).
16. T. Wakamatsu and D. W. Fuerstenau, *Adv. Chem. Ser.*, *79*, 161 (1968).
17. P. Somasundaran, *Trans. AIME*, *241*, 105 (1968).
18. P. Somasundaran and D. W. Fuerstenau, *Ibid.*, *241*, 102 (1968).
19. R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, 1952, pp. 429–443.
20. H. Schlichting, *Boundary Layer Theory*, McGraw-Hill, New York, 1968, p. 107.
21. G. K. Batchelor, *An Introduction to Fluid Dynamics*, Cambridge University Press, 1970, p. 368.
22. D. W. Moore, *J. Fluid Mech.*, *23*, 749 (1965).
23. Ref. *20*, pp. 227–229.
24. Ref. *20*, p. 17.
25. Ref. *20*, p. 226.

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