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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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To cite this Article Wilson, David J.(1978) 'A Noncoulombic Model for Adsorbing Colloid Flotation', Separation Science and Technology, 13: 2, 107 — 116

To link to this Article: DOI: 10.1080/01496397808057093

URL: http://dx.doi.org/10.1080/01496397808057093

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SEPARATION SCIENCE AND TECHNOLOGY, 13(2), pp. 107–116, 1978

A Noncoulombic Model for Adsorbing Colloid Flotation

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Abstract

A model for floc foam flotation is examined in which the driving force for bubble attachment to a floc particle derives from a nonzero contact angle of the air–water interface with the solid surface. Binding energies are calculated and found to be sufficient to overcome random thermal forces and also the viscous drag forces occurring in wet foams in stripping columns. Adsorption isotherms of floc particles at the air–water interface are calculated; a Langmuir isotherm is found to be an excellent approximation in most cases.

INTRODUCTION

Adsorbing colloid flotation methods have been demonstrated by Zeitlin and his co-workers to be extremely effective in the removal of traces of metal ions from aqueous solution (*1–4*); this work led us to investigate the utility of the technique in the treatment of industrial wastes (*5–8*). We have accounted for the dependence of these separations on ionic strength and other variables by means of an electric double layer model in which ionic surfactant charges the air–water interface which then attracts oppositely charged floc particles by coulombic forces (*9–11*).

An alternative model has been employed by Fuerstenau, Somasundaran, and their co-workers to describe ore flotation, and it accounts satisfactorily for quite a number of effects (*12–17*). In this model the ionic heads of the surfactant are adsorbed to the surfaces of the solid particles, and the hydrocarbon chains of the surfactant may then present a hydrophobic surface to the aqueous phase. The interfacial free energies are thereby modified, resulting in bubble contact angles on the solid which are different from zero; bubbles attach, and flotation occurs.

We recently applied statistical mechanical methods to Fuerstenau's model, examining the formation of hemimicelles of surfactant on the floc particles (*18*). A sharp onset of surface condensation of surfactant with increasing surfactant concentration in the bulk liquid was found, consistent with Fuerstenau's experimental results, and the effects of ionic strength and surfactant chain length in the model were found to be consistent with experiment. In the present work we estimate the magnitude of the floc–bubble binding energy and calculate the adsorption isotherms of floc particles on the air–water interface within the framework of Fuerstenau's model. Floc–bubble binding forces are also compared to the viscous drag forces in wet foams in stripping columns.

ANALYSIS, FIRST MODEL

We assume that the binding energy between the air–water interface and a floc particle is due solely to differences in the interfacial free energies γ_{aw} (air–water), γ_{as} (air–solid), and γ_{sw} (solid–liquid). We assume with some temerity that our floc particles may be approximated as spheres, and that the process of attachment of a floc particle to the air–water interface is as diagramed in Fig. 1. We assume the radius of the air bubble to be much larger than that of the floc particle.

We let θ be the contact angle at the meeting of air–water, air–solid, and solid–water interfaces, as indicated in Fig. 1; *r* is the radius of the floc particle. As the particle attaches, the loss in air–water interface is given

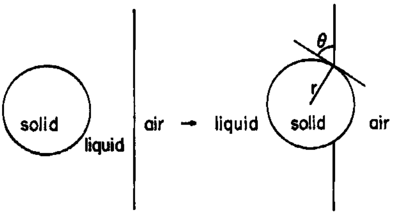

Fig. 1. First model of floc-bubble attachment.

by

$$L_{aw} = \pi r^2 \sin^2 \theta \tag{1}$$

The loss in solid–water interface is given by

$$L_{sw} = 2\pi r^2(1 - \cos \theta) \tag{2}$$

and this is also the gain in air–solid interface. The free energy change during attachment is therefore given by

$$\Delta G = -\gamma_{aw}\pi r^2 \sin^2 \theta + (\gamma_{as} - \gamma_{sw})2\pi r^2(1 - \cos \theta) \tag{3}$$

At equilibrium the contact angle is given by (*19*)

$$\cos \theta = (\gamma_{as} - \gamma_{sw})/\gamma_{aw} \tag{4}$$

so that Eq. (3) can be written as

$$\Delta G = -\gamma_{aw}\pi r^2(1 - 2\cos \theta + \cos^2 \theta) \tag{5}$$

The free energy change takes on its maximum value, zero, when $\theta = 0$.

Let us next calculate the adsorption isotherm of floc particles on the air–water interface; we use a method described by Hill (*20*) which employs the grand partition function. We earlier used this approach in calculating adsorption isotherms for adsorbing colloid flotation within the framework of a Gouy-Chapman model (*9*). We consider an area of the air–water interface capable of accommodating one particle, $6r^2/\sqrt{3}$, and a column of liquid based on this area and capable of containing a maximum of m floc particles. This constitutes one site, which contains m cells; we assume that the sites are independent of each other.

The grand partition function for a site is then given by

$$\xi = \prod_{i=1}^{m} \{1 + q\lambda \exp[-\beta V(i)]\} \tag{6}$$

where $\beta = 1/kT$

λ = absolute activity of the floc particles, $\exp(\mu/kT)$, where μ is the chemical potential of a floc particle

q = partition function for the internal degrees of freedom of a floc particle, assumed independent of the cell in which the particle is located

$V(i)$ = potential energy of a floc particle in cell i. $V(1) = \Delta G$, given by Eq. (5); $V(i) = 0$, $i > 1$

The average number of floc particles per site is then given by

$$\bar{s} = \sum_{i=1}^{m} \frac{\lambda q \exp[-\beta V(i)]}{1 + \lambda q \exp[-\beta V(i)]} \tag{7}$$

$$= \frac{\lambda q \exp(-\beta \Delta G)}{1 + \lambda q \exp(-\beta \Delta G)} + \frac{(m-1)\lambda q}{1 + \lambda q} \tag{8}$$

In the absence of the interface,

$$\bar{s} + m\sigma = \frac{m\lambda q}{1 + \lambda q} \tag{9}$$

which we obtain from Eq. (8) by setting $\Delta G = 0$. Here σ is the average concentration of floc particles per cell. Equation (9) yields

$$\lambda q = \frac{\sigma}{1 - \sigma} \tag{10}$$

and substitution of this result in Eq. (8) yields

$$\bar{s} = \frac{1}{1 + \dfrac{1-\sigma}{\sigma} \exp(\beta \Delta G)} + (m-1)\sigma \tag{11}$$

We are actually interested in the excess of floc particles in the site as compared to a similar volume of bulk solution,

$$\bar{s}_{\text{excess}} = \bar{s} - m\sigma \tag{12}$$

From Eq. (11) we obtain for this quantity

$$\bar{s}_{\text{excess}} = \frac{\sigma(1-\sigma)[1 - \exp(\beta \Delta G)]}{\sigma + (1-\sigma)\exp(\beta \Delta G)} \tag{13}$$

For the typical case, as we shall see, $\exp(\beta \Delta G)$ is much less than unity, and Eq. (13) can be accurately approximated by

$$\bar{s}_{\text{excess}} = \frac{1}{1 + \exp(\beta \Delta G)/\sigma}, \qquad \sigma \ll 1 \tag{14}$$

The basal area of a site is $2\sqrt{3}r^2$ (we assume hexagonal close-packing in the plane), and the volume of a cell is therefore given by

$$V = 4\sqrt{3}r^3 \tag{15}$$

The concentration of floc particles in the bulk solution is therefore given by

$$c_b = \sigma/(4\sqrt{3}r^3) \tag{16}$$

and the excess surface concentration by

$$c_s = \bar{s}_{\text{excess}}/(2\sqrt{3}r^2) \tag{17}$$

From Eqs. (13) and (16) we find that the bulk floc particle concentration at which $\bar{s}_{\text{excess}}$ has risen to 1/2 is given by

$$\begin{aligned} c_b' &= \left[1 - \left(1 - \frac{8\exp(\beta\Delta G)}{1 - \exp(\beta\Delta G)}\right)^{1/2}\right]\Big/ 16\sqrt{3}r^3 \\ &\cong \exp(\beta\Delta G)/(4\sqrt{3}r^3) \end{aligned} \tag{18}$$

RESULTS

Let us now examine the magnitudes of the floc particle–air bubble interaction energies for representative values of the parameters. We choose 40 dynes/cm for λ_{aw}; this corresponds to the surface tension of solutions of sodium lauryl sulfate (NLS) at roughly the critical micelle concentration. λ_{aw} at lower NLS concentrations may increase up to about 72 dynes/cm at room temperature. Let us assume floc particles 1000 Å in radius. The floc–bubble binding energy as a function of contact angle is then given in Table 1.

We find that for even these rather small particles the floc–bubble binding energy is roughly a thousand times larger than kT; $|\Delta G|$ remains much larger than kT for contact angles of any appreciable size for particles of radius 100 Å. Evidently unless the contact angle is essentially zero, floc–bubble attachment is an interaction which overwhelms the effects of random thermal motions, and floc foam flotation should be an extremely efficient process provided that conditions are such that the floc is hydro-

TABLE 1

Floc-Bubble Binding Energy as a Function of Contact Angle[a]

$\cos\theta$	$-\Delta G$ (erg)
1.0	0
0.9	1.257×10^{-10}
0.8	5.027
0.6	20.11
0.4	45.24
0.2	80.42
0	125.66
−1.0	502.64

[a] $kT = 4.14 \times 10^{-14}$ erg at 298°K.

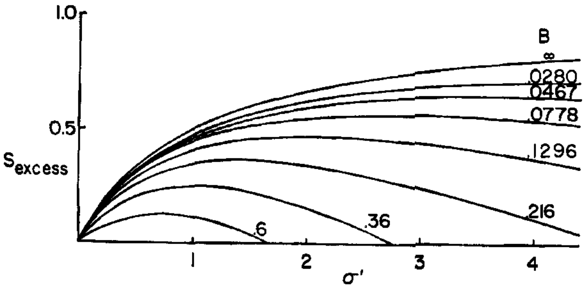

FIG. 2. Floc adsorption isotherms; plot of s_{excess} vs σ' [$= \sigma \exp(-\beta\Delta G)$] calculated from Eq. (13). $B = \exp(\beta\Delta G)$.

phobic. This requires that the surfactant concentration and the surface potential of the floc be such that the surfactant is able to form a condensed surface phase (hemimicelle) with the hydrophobic tails of the surfactant ions presented to the liquid phase; conditions for this to occur were explored in our earlier paper (*18*).

Estimation of contact angles in this model is likely to prove difficult. The flocs are generally hydrous oxides, highly and probably irreproducibly hydrated, and their characteristics can be expected to change with time. Contact angle measurements on well-characterized crystalline samples are probably not very helpful in estimating contact angles on these fresh, unaged flocs.

In Fig. 2 we see plots of s_{excess} versus $\sigma' = \sigma \exp(-\beta\Delta G)$ calculated from Eq. (13) for various values of $\exp(\beta\Delta G)$ as indicated. Given the results of Table 1, it is evident that use of the approximate isotherm, Eq. (14), is generally warranted.

ALTERNATIVE MODEL

We next consider the case of small bubbles interacting with plane solid surfaces. As with our previous model, this is rather idealized; if, however, the two models yield similar results, this suggests that geometrical variations are of relatively minor importance in floc–bubble attachment. The model is sketched in Fig. 3.

We let

V_b = bubble volume
r = initial bubble radius

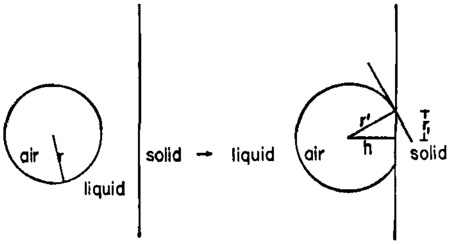

FIG. 3. Second model of floc-bubble attachment.

r' = radius of attached bubble
θ = contact angle
$A_{sw}{}^i$ = initial area of solid–water interface
$A_{aw}{}^i$ = initial area of air–water interface
$A_{sw}{}^f$ = final area of solid–water interface
$A_{aw}{}^f$ = final area of air–water interface
$A_{as}{}^f$ = final area of air–solid interface
$\gamma_{aw}, \gamma_{sw}, \gamma_{sa}$ are interfacial free energies, as before

Initially we have

$$r = \left(\frac{3V_b}{4\pi}\right)^{1/3} \tag{19}$$

$$A_{aw}{}^i = 4\pi\left(\frac{3V_b}{4\pi}\right)^{2/3} \tag{20}$$

After bubble attachment has occurred, we find

$$V_b = \frac{4}{3}\pi(r')^3 - \int_0^{2\pi}\int_0^{\theta}\int_0^{r'} r^2\,dr \sin\theta'\,d\theta'\,d\phi + \frac{1}{3}\pi r_1{}^2 h \tag{21}$$

where r', h, and r_1 are defined in Fig. 3. This yields

$$V_b = \frac{\pi(r')^3}{3}(2 + 2\cos\theta + \sin^2\theta\cos\theta) \tag{22}$$

$$r' = \left[\frac{3V_b}{\pi(2 + 2\cos\theta + \sin^2\theta c s\theta)}\right]^{1/3} \tag{23}$$

$$r_1 = \sin\theta r' \tag{24}$$

The air–water interfacial area is given by

$$A_{aw}^{f} = \int_{\theta}^{\pi}\int_{0}^{2\pi} (r')^2 \sin\theta' \, d\phi \, d\theta'$$

$$= 2\pi(1 + \cos\theta)\left[\frac{3V_b}{(2 + 2\cos\theta + \sin^2\theta\cos\theta)}\right]^{2/3} \tag{25}$$

The air–solid surface area is

$$A_{as}^{f} = \pi r_1^{\,2} = \pi \sin^2\theta\left[\frac{3V_b}{(2 + 2\cos\theta + \sin^2\theta\cos\theta)}\right]^{2/3} \tag{26}$$

The solid–water surface area is

$$A_{sw}^{f} = A_{sw}^{i} - A_{as}^{f} \tag{27}$$

The change in free energy resulting from bubble attachment is given by

$$\Delta G = \gamma_{aw}[A_{aw}^{f} - A_{aw}^{i}] + (\gamma_{sa} - \gamma_{sw})A_{as}^{f} \tag{28}$$

Substituting Eqs. (4), (25), (26), and (27) in Eq. (28) then yields

$$\Delta G = -\gamma_{aw}\pi^{1/3}(3V_b)^{2/3}[-(2 + 2\cos\theta + \sin^2\theta\cos\theta)^{1/3} + 4^{1/3}] \tag{29}$$

or, in terms of the initial bubble radius,

$$\Delta G = -\gamma_{aw}\pi 4^{2/3} r^2[-(2 + 2\cos\theta + \sin^2\theta\cos\theta)^{1/3} + 4^{1/3}] \tag{30}$$

Let us consider a bubble of 1000 Å radius, and, as before, let $\gamma_{aw} = 40$ ergs/cm^2. The free energy of attachment is then given in Table 2 as a function of contact angle.

We find that for contact angles of any appreciable size the floc particle–bubble binding energy is orders of magnitude larger than kT for bubbles having a radius of 100 Å or greater. Thus, with either of the two models

TABLE 2

Floc-Bubble Binding Energy as a Function of Contact Angle, Second Model

$\cos\theta$	$-\Delta G$ (erg)
1.0	0
0.9	1.22×10^{-10}
0.8	4.73
0.6	18.07
0.4	39.16
0.2	67.68
0	103.70
−1.0	502.65

examined here, the binding energy is ample to produce extremely efficient separations despite the presence of random thermal motions.

VISCOUS DRAG FORCES

In stripping columns there is a countercurrent flow of liquid downward between rising air–water interfaces. We next examine the magnitude of the viscous drag forces resulting from this countercurrent flow to show that they are insufficient to tear loose floc particles bound to the air–water interface.

Equating the gravitational pull down on an element of liquid 1 cm × 1 cm × thickness dx to the viscous drag in the opposite direction yields

$$\rho g = -\eta \frac{d^2v}{dx^2} \tag{31}$$

where ρ = liquid density
g = gravitational constant
η = viscosity
v = velocity in the downward direction

Integration of Eq. (31) and use of the boundary conditions $v(0) = v(l) = 0$ yields

$$v = \frac{\rho g}{2\eta}(lx - x^2) \tag{32}$$

We now estimate the viscous drag force on the floc particle. We assume the spherical particle is attached to the air–water interface and is moving with it, and that the relative velocity of the liquid streaming past it is given by $v(x)$. We let the particle radius be r, and estimate an upper limit on the viscous drag on the particle.

$$v(x = 2r) = \frac{\rho g}{2\eta}(2lr - 4r^2) \tag{33}$$

$$\text{Viscous force} = f_v = 6\pi\eta r v \tag{34}$$

$$f_v = 6\pi\rho g r^2(l - 2r) \tag{35}$$

If our particle has a radius of 10^{-5} cm and we assume that the film thickness l is 10^{-2} cm, we find that the viscous force is 1.84×10^{-8} dynes. We roughly estimate the binding force of the floc particle to the air–water interface as

$$f_b \cong \frac{\Delta G}{r} = \frac{10^{-10}\,\text{erg}}{10^{-5}\,\text{cm}} \geqq 10^{-5}\,\text{dynes} \tag{36}$$

at least three orders of magnitude larger than the viscous drag. We note that the binding force increases proportional to r, while the viscous force increases roughly proportional to r^2; thus viscous drag may interfere with floc foam flotation when particle radii are of the order of 10^{-2} cm or larger, or if the foams are extremely wet (large l).

We conclude that the change in contact angle resulting from the formation of a hemimicelle of ionic surfactant at the solid–liquid interface (with the hydrocarbon tails facing away from the solid) should provide an ample driving force for floc foam flotation. The energies involved are sufficient to overcome the disrupting effects of random thermal motions for all but the smallest particles. They are also sufficient to prevent detachment of floc particles for all but extremely large particles.

Acknowledgment

This work was supported by a grant from the National Science Foundation.

REFERENCES

1. Y. S. Kim and H. Zeitlin, *Sep. Sci.*, *7*, 1 (1972).
2. C. Matsuzaki and H. Zeitlin, *Ibid.*, *8*, 185 (1973).
3. W. F. Chaine and H. Zeitlin, *Ibid.*, *9*, 1 (1974).
4. D. Voyce and H. Zeitlin, *Anal. Chim. Acta*, *69*, 27 (1974).
5. A. N. Clarke and D. J. Wilson, *Sep. Sci.*, *10*, 417 (1975).
6. S. -D. Huang and D. J. Wilson, *Ibid.*, *11*, 215 (1976).
7. R. P. Robertson, D. J. Wilson, and C. S. Wilson, *Ibid.*, *11*, 569 (1976).
8. T. E. Chatman, S. -D. Huang, and D. J. Wilson, *Ibid.*, *12*, 461 (1977).
9. J. W. Wilson, D. J. Wilson, and J. H. Clarke, *Ibid.*, *11*, 223 (1976).
10. D. J. Wilson, *Ibid.*, *11*, 289 (1976).
11. D. J. Wilson, *Ibid.*, *12*, 231 (1977).
12. D. W. Fuerstenau and T. W. Healy, in *Adsorptive Bubble Separation Techniques* (R. Lemlich, ed.), Academic, New York, 1972, p. 91.
13. D. W. Fuerstenau, T. W. Healy, and P. Somasundaran, *Trans. AIME*, *229*, 321 (1964).
14. A. M. Gaudin and D. W. Fuerstenau, *Ibid.*, *202*, 958 (1955).
15. P. Somasundaran and D. W. Fuerstenau, *J. Phys. Chem.*, *70*, 90 (1966).
16. P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *Ibid.*, *68*, 3562 (1964).
17. T. Wakamatsu and D. W. Fuerstenau, *Adv. Chem. Ser.*, *79*, 161 (1968).
18. D. J. Wilson, *Sep. Sci.*, *12*, 447 (1977).
19. A. W. Adamson, *Physical Chemistry of Surfaces*, 2nd ed., Wiley-Interscience, New York, 1967, p. 353.
20. T. L. Hill, *Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, Massachusetts, 1960, pp. 130–132.

Received by editor May 3, 1977