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Electrical Aspects of Adsorbing Colloid Flotation. VII. Cooperative Phenomena

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Abstract

Flotation is assumed to occur when a condensed film of surfactant forms on the particles to be floated, making their surfaces hydrophobic and permitting bubble attachment. This hemi-micelle formation is a cooperative phenomenon resulting from van der Waals forces between the hydrocarbon tails of the surfactant ions. The effects of temperature, ionic strength, and particle surface potential are examined by means of a statistical mechanical approach described by Fowler and Guggenheim. The effect of hemi-micelle formation at the air–water interface on the efficiency of flotation by a coulombic mechanism is also examined. Increasing temperature increases the surfactant concentration necessary for flotation; increasing ionic strength decreases this critical surfactant concentration, but also decreases the magnitude of the air–water surface potential, which decreases flotation efficiency.

INTRODUCTION

Foam flotation techniques are of considerable interest in connection with the removal of trace metals and other pollutants from wastewaters; much of this work has been recently reviewed (*1*, *2*). Zeitlin's group has demonstrated the exceptional effectiveness of adsorbing colloid flotation in a number of bench studies (*3–6*), which encouraged us to investigate its application to the treatment of a number of industrial wastes (*7*). We have also been interested in accounting for the dependence of these separations on ionic strength, as reported by Sheiham and Pinfold (*8*) and others, and in explaining the effects of other system variables. Heretofore, we have relied on a Gouy-Chapman model of the electric double layer (*9*, *10*) in which the air–water interface was charged by adsorbed ionic surfactant, and the oppositely charged floc particle was then attracted by coulombic forces to the air–water interface (*11–15*). This model appears to give results in agreement with the available experimental data.

It was therefore with considerable interest that we recently read an article by Fuerstenau and Healy on ore flotation (*16*) in which a rather different picture was assumed, and which has been able to account for a rather broad range of effects in mineral flotation (*17–21*). In this model the polar heads of the surfactant ions are adsorbed directly to the solid surface; the hydrocarbon chain tails of these ions then, at sufficiently high surface concentrations, present a hydrophobic surface to the aqueous phase. The surface free energies are thereby changed such that the contact angle of air bubbles on the solid surface is no longer zero, bubbles are able to attach, and flotation occurs.

Of particular interest is the formation of condensed phase (hemimicelles) on the solid surface at sufficiently high concentrations of surfactant in the bulk solution. This is a cooperative phenomenon, resulting from the van der Waals stabilization energy of the hydrocarbon tails when they are able to pack closely together, and it was found by Fuerstenau et al. that, as one would expect, it occurred at lower surfactant concentrations as the chain length of the surfactant was increased. This cooperative phenomenon is used to explain the very rapid and large increase of flotation efficiency which is observed with increasing surfactant concentration at intermediate surfactant concentrations. And the competition of surface-inactive ions with surfactant ions for space in the vicinity of the charged solid surface is used to account for the effects of varying ionic strength.

We present below a procedure based on a method described by Fowler and Guggenheim (*22*) which permits one to deal with cooperative phenomena such as that mentioned above. We note that the treatment is approximate—exact treatments of even the simplest two-dimensional cooperative phenomena have proven to be complex, sophisticated, and difficult (*23*). We calculate the adsorption isotherm of surfactant on the solid by means of Fowler and Guggenheim's prescription, estimating the binding energy of an isolated surfactant molecule to the solid by calculating the electric potential in the vicinity of the solid surface by means of a modified Poisson-Boltzmann equation. Fuerstenau and Healy (*16*) estimate the free energy for removal of hydrocarbon chains from water as approximately −0.6

kcal/mole of CH_2 groups; this information is needed in connection with the cooperative formation of hemi-micelles on the solid surface.

ANALYSIS

We take as our starting point the following adsorption isotherm, the derivation of which is given in Fowler and Guggenheim's book (*22*).

$$c(\theta) = \frac{c^\circ\theta}{1-\theta}\left(\frac{2-2\theta}{\beta+1-2\theta}\right)^z \tag{1}$$

$$\beta = [1 - 4\theta(1-\theta)\{1-\exp(-2w/zkT)\}]^{1/2} \tag{2}$$

$$c^\circ = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} kT\frac{j^S(T)}{j^A(T)}\exp(-\chi_0/kT) \tag{3}$$

Here θ = fraction of surface sites on the solid which are occupied by surfactant ions

$c(\theta)$ = concentration of surfactant in bulk solution in equilibrium with solid surface having a fraction θ of its sites occupied by surfactant

z = maximum number of nearest neighbors of a surfactant ion on the surface, taken here as 6

$2w/z$ = increase in energy when a new pair of nearest neighbors is formed

χ_0 = increase in energy when a surfactant ion is adsorbed on an isolated site on the solid surface

m = mass of surfactant ion

k = Boltzmann's constant

h = Planck's constant

T = absolute temperature

$j^S(T)$ = partition function for the internal degrees of freedom of a surfactant ion in solution

$j^A(T)$ = partition function for the internal degrees of freedom of an adsorbed surfactant ion

Let us assume that j^S/j^A is essentially independent of the inert salt concentration, and that χ_0 can be calculated by multiplying the charge on an adsorbed surfactant ion by the electric potential at that point. We write $c^0 = c'\exp(-\chi_0/kT)$, where c' is assumed to be independent of ionic strength and no more than weakly temperature-dependent. For dodecyl sulfate at room temperature, $c' \cong 2.85 \times 10^{-4}$ mole/l. We define a reduced concentration, σ, as

$$\sigma(\theta) = \frac{c(\theta)}{c'} = \exp(-\chi_0/kT)\frac{\theta}{1-\theta}\left(\frac{2-2\theta}{\beta+1-2\theta}\right)^z \tag{4}$$

As noted above, the free energy for the removal of hydrocarbon chains from water has been estimated as -0.6 kcal/mole of CH_2 groups. This yields Eq. (5) for w, where n is the number of CH_2 groups in the surfactant tail plus 1. We note that roughly six new pairs of nearest neighbors are formed when a surfactant ion goes into the condensed surface phase.

$$w = -n \times 2.070 \times 10^{-14}\ \text{ergs} \tag{5}$$

We previously showed (*13*) how the method of Macdonald and Brachman (*24*) could be used to calculate electric potentials in the electric double layer for solutions in which the finite volume of the electrolyte ions was taken into account. The Poisson-Boltzmann equation for the case of planar geometry is

$$\frac{d^2\psi(x)}{dx^2} = \frac{A\sinh(z'e\psi/kT)}{1+B\cosh(z'e\psi/kT)} \tag{6}$$

where $\psi(x)$ = electric potential a distance x from the solid–liquid interface
$|z'e|$ = magnitude of the charge of the ions of z'–z' electrolyte
$A = 8\pi z'ec_\infty/(1 - 2c_\infty/c_{\max})D$
$B = 2c_\infty/(c_{\max} - 2c_\infty)$
c_∞ = anion (or cation) concentration in bulk solution, ions/cm^3
$c_{\max}$ = maximum possible concentration of ions in solution, ions/cm^3
D = dielectric constant

The solution to Eq. (6) is given by

$$x = \frac{-\psi_0}{|\psi_0|}\int_{\psi_0}^{\psi(x)} \frac{d\psi}{\left\{\dfrac{2AkT}{Bz'e}\log\left[\dfrac{1+B\cosh z'ec/kT}{1+B}\right]\right\}^{1/2}} \tag{7}$$

where ψ_0 is the potential at the solid–liquid interface. We assume that the center of charge of the surfactant ion is at a distance l from the charged floc surface; $\psi(l)$ is then obtained from Eq. (7). The binding energy of an isolated surfactant ion on the solid surface is given by

$$\chi_0 = z_s e\psi(l) \tag{8}$$

where $z_S e$ is the charge of the surfactant ion. (This estimate neglects the contribution of the ionic atmosphere of the surfactant ion.)

The isotherms obtained from Eq. (1) exhibit a critical temperature given by *(22)*

$$T_c = -w/kz \log(z/z - 2) \tag{9}$$

Below this temperature, values of θ in the vicinity of one-half are unstable, and the system breaks up into two stable phases. It has been shown *(22)* that the values of θ for these phases are the two roots of the equation

$$\sigma(1/2) \equiv \exp[(w - \chi_0)/kT] = \exp(-\chi_0/kT)\frac{\theta}{1-\theta}\left(\frac{2-2\theta}{\beta(\theta)+1-2\theta}\right)^z \tag{10}$$

other than $\theta = \frac{1}{2}$. Thus, if on calculating $\sigma(\theta)$ we find $\sigma(\theta) > \sigma(\frac{1}{2})$ for $\theta < \frac{1}{2}$, we set $\sigma(\theta) = \sigma(\frac{1}{2})$; if $\sigma(\theta) < \sigma(\frac{1}{2})$, $\theta > \frac{1}{2}$, we set $\sigma(\theta) = \sigma(\frac{1}{2})$. The situation is essentially identical to that arising with van der Waals isotherms for nonideal gases below the critical temperature *(25)*.

RESULTS

Some representative adsorption isotherms are shown in Fig. 1, which

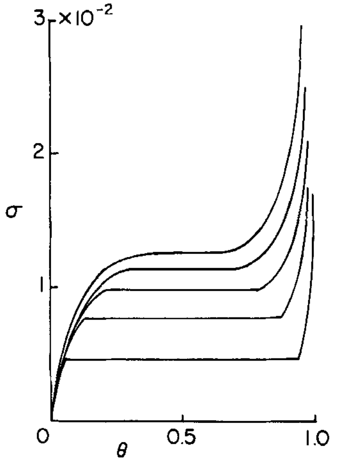

FIG. 1. Adsorption isotherms of surfactant on floc with condensation. For all plots $T = 298\,^\circ K$, $\chi_0 = 8.0 \times 10^{-14}$ erg. From the top down: $-w = 1.0, 1.04, 1.1, 1.2$, and 1.4×10^{-13} erg.

exhibits the effects of varying w, the surfactant–surfactant interaction energy. The values of w used here are somewhat smaller than would be used, say, for sodium lauryl sulfate (2.48×10^{-17} erg) in order to make the features of the plots clearer. The reduced concentration at which hemimicelle formation occurs, σ_{crit}, is seen to decrease rather rapidly with increasing values of w (and of the hydrocarbon chain length), as noted by Fuerstenau and co-workers (*16*), and the critical temperature increases as indicated by Eq. (9).

The dependence of σ_{crit} on w is indicated over a much wider range of w in Fig. 2. On noting that $\sigma_{\text{crit}} = \sigma(\frac{1}{2})$ and using Eqs. (5) and (10), we obtain

$$\begin{aligned} \frac{-\partial \log \sigma_{\text{crit}}}{\partial n} &= \frac{1}{kT} \times 2.070 \times 10^{-14} \\ \frac{-\partial \log_{10} \sigma_{\text{crit}}}{\partial n} &= 65.2/T = 0.219 \end{aligned} \tag{11}$$

at 298°K. The value of this derivative, which we obtain from the results

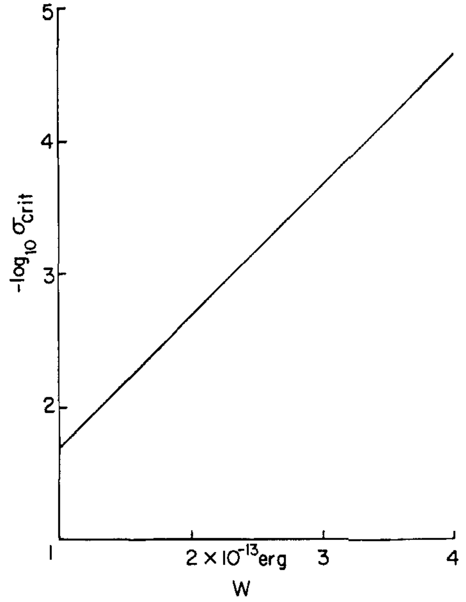

FIG. 2. Dependence of σ_{crit} on w. $\psi_0 = 50$ mV, $T = 320$°K, $l = 10^{-7}$ cm, $c_\infty = 10^{-3}$ mole/l, $z_s = -1$, $c_{\text{max}} = 1.0$ mole/l.

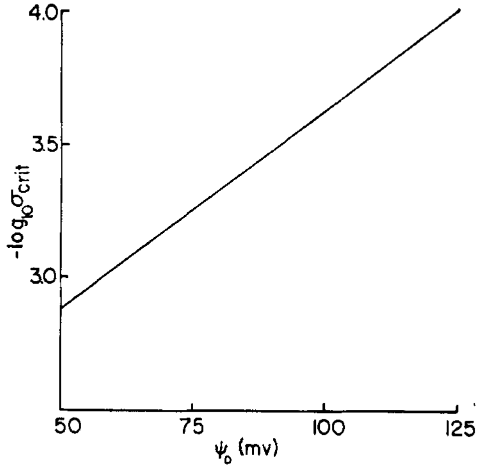

FIG. 3. Dependence of σ_{crit} on ψ_0. $T = 298\,°K$, $l = 10^{-7}$ cm, $c_\infty = 10^{-3}$ mole/l, $c_{max} = 1.0$ mole/l, $w = -2 \times 10^{-13}$ erg.

of Fuerstenau, Somasundaran, and co-workers (*16*), is approximately 0.32. Increasing the magnitude of the interaction energy of the hydrocarbon chains from 0.6 to 0.88 kcal/mole of CH_2 groups eliminates the discrepancy; in view of uncertainty in the figure of 0.6 and the approximations inherent in the theory, the agreement is better than one might expect.

The effects of surface potential ψ_0 on the value of σ_{crit} are shown in Fig. 3, and the dramatic decrease in σ_{crit} with increasing surface potential is what one would intuitively anticipate. Ionic strength also exhibits a marked effect upon σ_{crit}, as shown in Fig. 4, and is well established experimentally. We note that our analysis here is predicated upon the assumption that the concentration of surfactant in the bulk solution is at all times sufficiently low that the surfactant is an ideal solute; in particular, we have ignored the possibility of micelle formation in the bulk solution. This surely leads to spurious results at the upper end of the curve in Fig. 3, where one would expect σ_{crit} to be a very rapidly increasing function of $\log_{10} c_\infty$. The binding energy of the surfactant to the solid, χ_0, is reduced to values less than kT with increasing c_∞, and the formation of micelles then should become competitive with the formation of hemi-micelles on the solid surface. At this point, between roughly $c_\infty = 0.1$ and 1.0 in Fig. 4, foam flotation should cease.

Experimentally, we did observe that foam flotation is less efficient at

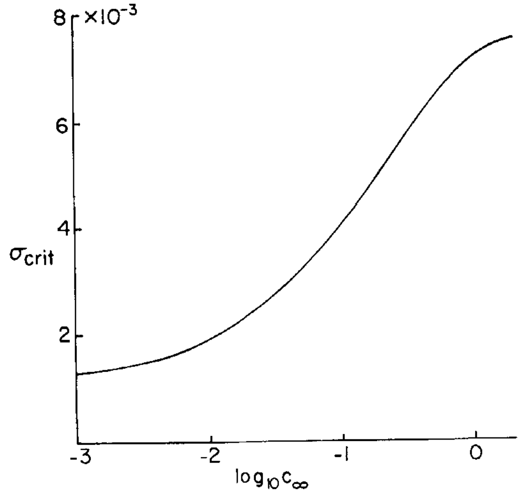

FIG. 4. Dependence of σ_{crit} on c_∞. $T = 298\,°\text{K}$, $l = 10^{-7}$ cm, $c_{\text{max}} = 10$ moles/l, $\psi_0 = 50$ mV, $w = -2 \times 10^{-13}$ erg.

TABLE 1[a]

Effect of Temperature on σ_{crit}

T	σ_{crit}
298	1.33×10^{-3}
320	2.08×10^{-3}
340	2.99×10^{-3}

[a] In these runs, $l = 10^{-7}$ cm, $c_\infty = 10^{-3}$ mole/l, $\psi_0 = 50$ mV, $z_s = -1$, and $z' = 1$.

higher salt concentrations and that increasing the surfactant concentration above the levels which are effective at lower ionic strengths is of little or no help. The ionic strength at which failure occurs depends somewhat on pH, and therefore upon ψ_0, as one would anticipate (*15*).

The effect of temperature on σ_{crit} is shown in Table 1. We note that σ_{crit} increases with increasing temperature rather rapidly; as long as σ_{crit} does not approach the reduced critical micelle concentration and as long as the reduced surfactant concentration exceeds σ_{crit}, flotation should take place. However, these results indicate that the high-temperature cutoff of foam flotation should depend markedly on surfactant concentration. This type of temperature dependence does not appear in our earlier approach (*11–15*), and an experimental study of the interaction of temperature and surfactant concentration at relatively low surfactant levels may provide a means of distinguishing between the two models. This result also suggests the importance of investigating the temperature dependence of the air–water surface potential within the framework of our other model. We discuss this in the following section.

ANOTHER COOPERATIVE EFFECT

We were very much interested to see if the dependence of foam flotation efficiency on surfactant chain length, demonstrated experimentally, could be grafted onto our earlier model (*12–14*) in a convincing way. Somasundaran (*26*) and Somasundaran and Fuerstenau (*27*) had previously commented on the importance of surfactant adsorbed at the air–water interface in bringing about flotation, and we could see no reason why this surfactant should not be subject to the same type of cooperative interactions as surfactant adsorbed at a solid–liquid interface. Such interactions, resulting in the abrupt condensation of hemi-micelles on the air–water interface, would lead to an abrupt change in the surface potential of this interface, and this, in turn, to an abrupt increase in flotation efficiency (as shown in our earlier calculations). We here calculate the effect of bulk surfactant concentration on the potential of the air–water interface.

Integration of Poisson's equation

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi}{D}\rho \tag{12}$$

and the electrical neutrality requirement yield in the usual way

$$S = \frac{-D}{4\pi e z_s}\frac{d\psi(0)}{dx} \tag{13}$$

where ρ = charge density
S = surface concentration of surfactant, ions/cm^2
$z_s e$ = charge of surfactant ion

For semi-infinite geometry, the first integral to Eq. (6), the Poisson-Boltzmann equation, which satisfies the appropriate boundary conditions, yields

$$\frac{d\psi(0)}{dx} = \frac{-|\psi_0|}{\psi_0}\frac{2A}{\beta e B}\log_e\left[\frac{1 + B\cosh(\beta e\psi_0)}{1 + B}\right]^{1/2} \tag{14}$$

On substituting Eq. (14) into Eq. (13) and solving for ψ_0, we obtain

$$\psi_0 = \pm \frac{1}{\beta e} \operatorname{argcosh} \left[\frac{(1 + B) \exp \left\{ \frac{\beta e B}{2A} \left(\frac{4\pi e |z_s| S}{D} \right)^2 \right\} - 1}{B} \right] \tag{15}$$

Thus, from the surface concentration of the surfactant, we can calculate the surface potential of the air–water interface for use in obtaining adsorption isotherms.

From the assumed surface concentration of surfactant, S, we can also calculate the fraction of surface sites occupied, θ, from

$$\theta = S/S_1 \tag{16}$$

where S_1 is the number of sites available per cm^2. We assume the area occupied per surfactant ion to be roughly 0.4 nm^2, which yields for S_1 a value of 2.5×10^{14} cm^{-2}.

We then calculate a reduced bulk surfactant concentration $\sigma(\theta)$ by means of Eq. (4), exactly as before, except that the prescription for calculating χ_0 is changed. We calculate χ_0 from

$$\chi_0 = n(\mathrm{CH_2})c_1 \tag{17}$$

where $n(\mathrm{CH_2})$ is the number of $\mathrm{CH_2}$ and $\mathrm{CH_3}$ groups in the chain, and c_1 is estimated as about 4.417×10^{-14} ergs. Thus the binding energy of an isolated surfactant ion to the air–water interface is assumed to be determined only by the hydrophobic hydrocarbon chain. We calculate w from

$$w = -n(\mathrm{CH_2})c_2 + z_s e \psi_0(1) \tag{18}$$

where c_2 estimates the cooperative van der Waals stabilizing energy per $\mathrm{CH_2}$ group (estimated as 3.50×10^{-14} ergs), and $\psi_0(1)$ is the value for ψ_0 obtained from Eq. (15) when S is set equal to S_1—i.e., $\theta = 1$. This takes into account the mutual electrostatic repulsion of the surfactant ions in the condensed surface phase by approximating it as if the surface were completely covered; we neglect the much weaker repulsion of the surfactant ions in the dilute surface phase in our estimation of w.

Thus, from Eqs. (5) and (15)–(18) it is possible to calculate ψ_0 as a function of the reduced bulk surfactant concentration σ. The results are illustrated in Fig. 5 for various ionic strengths. We see that the magnitude of the surface potential remains low up to the value of σ at which condensation of the surfactant film occurs, and then it jumps by roughly 100 mV. In our previous work we had found for all models examined that an increase in $|\psi_0|$ from 50 mV to a value of 100 mV resulted in a spec-

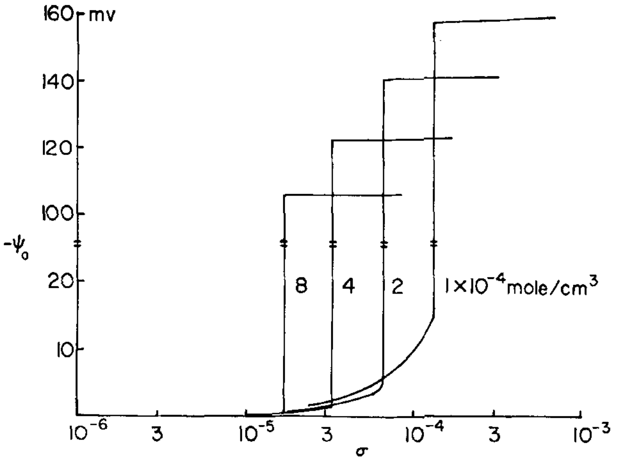

FIG. 5. Effect of c_∞ on the dependence of ψ_0 on σ. $T = 298\,°\mathrm{K}$, $z_S = -1$, $c_{\max} = 1.0\ \mathrm{mole/cm^3}$, $z_e = 1$, $n(\mathrm{CH_2}) = 12$, $c_1 = 4.417 \times 10^{-14}\ \mathrm{erg^{-1}}$, $c_2 = 3.500 \times 10^{-14}\ \mathrm{erg^{-1}}$. Note break in the scale of the ordinate. From left to right, $c_\infty = 8, 4, 2,$ and $1 \times 10^{-4}\ \mathrm{mole/cm^3}$.

tacular increase in the adsorption isotherms. Our results here indicate that foam flotation should be negligible until the bulk concentration of surfactant exceeds the point at which hemi-micelle formation takes place at the air–water interface, at which point there should be a rather sudden onset of flotation. Increasing ionic strength decreases the minimum surfactant concentration at which foam flotation should occur, but it also decreases the value of $|\psi_0|$ and the Debye length, both of which effects decrease the floc adsorption isotherm in the region of surfactant concentration above the point where hemi-micelles form.

The effects of changing temperature on the dependence of ψ_0 on reduced surfactant concentration are shown in Fig. 6. Evidently increasing the temperature very markedly increases the surfactant concentration needed to form hemi-micelles; one would be well-advised to conduct floc foam flotation separations at the lowest practical temperature to reduce surfactant requirements.

Increasing the length of the hydrocarbon chain has the effect shown in Fig. 7. Increased chain length shifts the reduced surfactant concentration at which hemi-micelle formation takes place to substantially lower values, in agreement with experimental findings.

In summary, in both models examined here cooperative phenomena

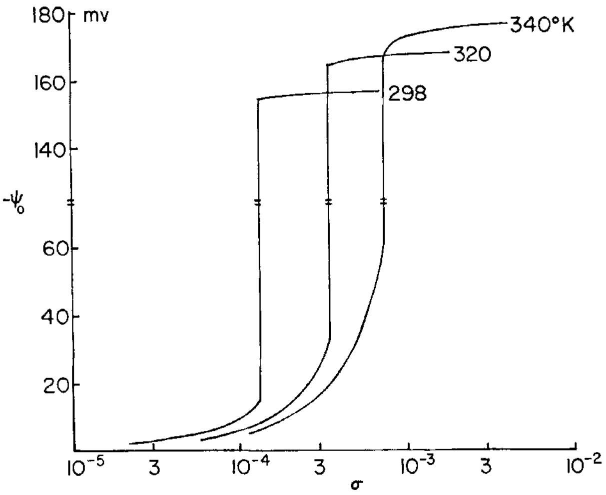

FIG. 6. Effect of T on the dependence of ψ_0 on σ. T = 298, 320, and 340°K (left to right); $c_\infty = 10^{-4}$ mole/cm^3. Other parameters as in Fig. 5.

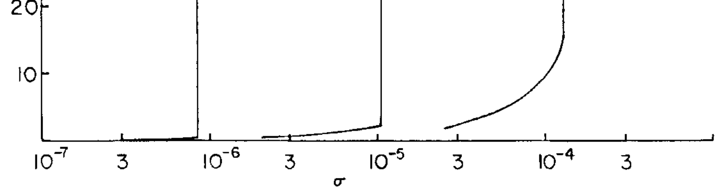

FIG. 7. Effect of surfactant chain length on the dependence of ψ_0 on σ. $n(CH_2)$ = 12, 14, and 16; $c_\infty = 10^{-4}$ mole/cm^3. Other parameters as in Fig. 5.

lead to the formation of hemi-micelles of surfactant. The sharpness of the onset of this phase transition with increasing surfactant concentration results in a correspondingly sharp onset of floc foam flotation. The phase transition occurs at lower bulk surfactant concentrations as the length of the surfactant hydrocarbon chain is increased. Higher temperatures raise the surfactant concentration at which the phase transition occurs.

Acknowledgment

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