Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Electrical Aspects of Adsorbing Colloid Flotation. IX. Effects of Surfactant Overdosing

David J. Wilson[a]; R. Moffatt Kennedy[a]
[a] DEPARTMENTS OF CHEMISTRY, ENVIRONMENTAL ENGINEERING VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

To cite this Article Wilson, David J. and Kennedy, R. Moffatt(1979) 'Electrical Aspects of Adsorbing Colloid Flotation. IX. Effects of Surfactant Overdosing', Separation Science and Technology, 14: 4, 319 — 332
To link to this Article: DOI: 10.1080/01496397908057150
URL: http://dx.doi.org/10.1080/01496397908057150

SEPARATION SCIENCE AND TECHNOLOGY, 14(4), pp. 319–332, 1979

Electrical Aspects of Adsorbing Colloid Flotation. IX. Effects of Surfactant Overdosing

DAVID J. WILSON and R. MOFFATT KENNEDY

DEPARTMENTS OF CHEMISTRY AND ENVIRONMENTAL ENGINEERING
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

The effect on flotation of excessively high surfactant concentrations is examined within the framework of the Fuerstenau-Somasundaran-Healy model. Statistical mechanical methods are used to calculate the adsorption isotherm of a second hemimicelle of surfactant on top of the hemimicelle in the primary adsorption layer. The resulting structure presents the charged ends of the surfactant ions to the water, making the coated surface hydrophilic. The effects of temperature, surfactant chain length and cross-sectional area, ionic strength, and ionic size are studied.

INTRODUCTION

Foam flotation separation methods have been of considerable interest in recent years in connection with the removal of metal ions and other contaminants from industrial wastewaters. A number of recent extensive reviews exist (*1–6*, for example). The success of Zeitlin's group in developing a large number of bench-scale adsorbing colloid flotation methods for trace elements in seawater (*7–11*, for example) encouraged us to employ this variant to the treatment of a number of industrial wastes (*12*) and to examine in some detail two models for the attachment of floc particles to bubbles (*13–17*).

We here examine the effect of excessively high surfactant concentrations on precipitate and adsorbing colloid flotation within the framework of the Fuerstenau-Somasundaran-Healy model (*18–24*). In this model, flotation results when a condensed layer of surfactant (a hemimicelle) is formed on the solid surface, ionic heads on the solid, and hydrocarbon tails to the solution; this makes the solid surface hydrophobic, permitting bubble attachment and flotation. In earlier papers we used statistical mechanics to analyze the adsorption isotherms of surfactant on the solid surface (*15*) and the effects of added salts on these adsorption isotherms (*17*). We here investigate the adsorption of surfactant from more concentrated solutions; under these conditions one would anticipate the formation of a second hemimicelle on top of the hemimicelle in the primary adsorption layer. The resulting micellar structure (shown in Fig. 1) presents ionic heads to the liquid solution, presumably yielding a hydrophilic surface and inhibiting bubble attachment and foam flotation. Our method of attack is an approximate approach discussed by Fowler and Guggenheim (*25*). This model has been proposed by Grieves and his co-workers who noted the interference of excess surfactant with the precipitate flotation of sulfite (*29*).

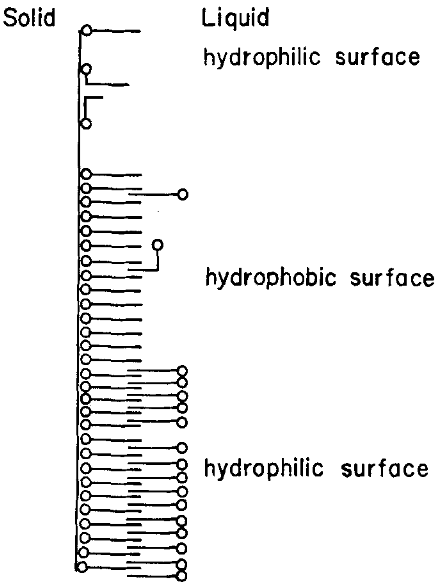

FIG. 1. Surface phases present at various surfactant concentrations in the bulk phase.

ANALYSIS

In order to examine this second phase change on the surface (hemimicelle → micelle), we must first estimate the binding energy, χ_0, of an isolated surfactant ion in the second layer, and the net stabilizing energy, w, associated with van der Waals attraction and coulombic repulsion between adjacent surfactant ions in the second layer. We estimate χ_0 roughly from Fuerstenau and Healy's statement that the standard free energy of removal of 1 mole of CH_2 groups from water is in the range -0.6 to -0.7 kcal (*26*). In the process of putting 1 mole of surfactant in the second layer of the surface phase, we in essence remove 2 moles of CH_3 groups from contact with the water—the terminal CH_3 groups of the hemimicelle and those of the surfactant ions in the second layer. We therefore roughly estimate χ_0 as between -1.2 and -1.4 kcal/mole, or about -9.03×10^{-14} erg/ion.

We estimate w as follows. The van der Waals interactions between the hydrocarbon chains give a contribution

$$w(\text{van der Waals}) = -n(CH_2) \times u \tag{1}$$

where $u = 4.51 \times 10^{-14}$ erg and $n(CH_2)$ = number of CH_2 groups in the surfactant chain. There is a destabilizing contribution associated with the coulombic repulsion of the ionic heads; this we calculate by a Güntelberg charging process, following Stigter (*27*),

$$w(\text{Coulomb}) = z_s \int_0^1 \psi'_0 e \, d\lambda \tag{2}$$

in which we calculate the work required to reversibly charge the surfactant ions in the second layer while all other ions are fully charged. ψ'_0 is the electric potential at the ionic heads of these ions when their ionic charge is $z_s e\lambda$.

In the diffuse double layer beyond this plane we calculate the electric potential from

$$\frac{d^2\psi}{dx^2} = \frac{A \sinh(z'e\psi/kT)}{1 + B\cosh(z'e\psi/kT)} \tag{3}$$

where $A = 8\pi z'ec_\infty/[D(1 - 2c_\infty/c_{\max})]$
$B = 2c_\infty/(c_{\max} - 2c_\infty)$
$z'e$ = |charge| of ions in the ionic atmosphere, assuming a 1–1 electrolyte

c_∞ = salt concentration in bulk solution, cations/cm^3
$c_{\max}$ = maximum possible concentration of ions/cm^3
D = dielectric constant of water
ψ = electric potential at a distance x from the ionic heads in the second layer of adsorbed surfactant
k = Boltzmann's constant
T = temperature

We let $y = z'e\psi/kT$ to get

$$\frac{d^2y}{dx^2} = \frac{(z'eA/kT)\sinh y}{1 + B\cosh y} \tag{4}$$

Then

$$\frac{dy}{dx}\frac{d^2y}{dx^2} = (z'eA/kT)\frac{\sinh y}{1 + B\cosh y}\frac{dy}{dx} \tag{5}$$

which integrates to give

$$\tfrac{1}{2}\left(\frac{dy}{dx}\right)^2\Bigg|_{y=0}^{y=y(x)} = \int_0^{y(x)} \frac{(z'eA/kT)\sinh y\, dy}{1 + B\cosh y} \tag{6}$$

Note that when $y = 0$, $x \to \infty$ and $y' = 0$. This yields

$$\tfrac{1}{2}\left[\frac{dy(x)}{dx}\right]^2 = (z'eA/kTB)\log_e\frac{1 + B\cosh y(x)}{1 + B} \tag{7}$$

Recall

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\rho}{D} \tag{8}$$

so

$$\frac{d\psi}{dx}\bigg|_{x=\infty} - \frac{d\psi}{dx}\bigg|_{x=0} = -\frac{4\pi}{D}\int_0^\infty \rho\, dx \tag{9}$$

The first term vanishes and the integral must be $-\sigma_c$, where σ_c is the surface charge density from electrical neutrality. This gives

$$\frac{d\psi_0}{dx} = -4\rho\sigma_c/D \tag{10}$$

and

$$\frac{dy(0)}{dx} = -\frac{4\pi z'e\sigma_c}{DkT} \tag{11}$$

Substituting Eq. (11) into Eq. (7) evaluated at $x = 0$ then yields

$$\tfrac{1}{2}\left(\frac{4\pi z'e\sigma_c}{DkT}\right)^2 = \frac{z'eA}{BkT}\log_e\frac{1 + B\cosh y_0}{1 + B} \tag{12}$$

From this we find, after some manipulation,

$$\psi_0 = \frac{z_s}{|z_s|}\frac{kT}{z'e}\operatorname{argcosh}\left\{(1 + B^{-1})\exp\left[\frac{8z'eB}{AkT}\left(\frac{\pi\sigma_c}{D}\right)^2\right] - B^{-1}\right\} \tag{13}$$

Next, we need to estimate σ_c, which is done by

$$\sigma_c = z_s e/S \tag{14}$$

where S is the area per surfactant ion, certainly no less than 20 to 25 Å^2; quite possibly substantially larger if the surfactant hydrocarbon chains are permitted to be crimped or tangled.

We are now in position to calculate w(Coulomb) by carrying out the charging process described by Eq. (2). ψ_0' is obtained from Eq. (13) by writing

$$\sigma_c'(\lambda) = \sigma_c\lambda = z_s e\lambda/S \tag{15}$$

This yields

$$w(\text{Coulomb}) = kT\frac{|z_s|}{z'}\int_0^1 \operatorname{argcosh} \times\left\{(1 + B^{-1})\exp\left[\frac{8z'eB}{AkT}\left(\frac{\pi\sigma_c}{D}\right)^2\lambda^2\right] - B^{-1}\right\}d\lambda \tag{16}$$

We take the dielectric constant of water as given by

$$D(T) = 78.54 - 0.361187(T - 25) + 0.689621 \times 10^{-3}(T - 25)^2 \tag{17}$$

which is obtained by a least squares fit to data between 0 and 100°C (*28*). Here only temperature is in degrees Centigrade.

The adsorption isotherm of the surfactant in the second layer is then given by (*25*)

$$\frac{c(\theta)}{c'} = \sigma(\theta) = \exp\left(\frac{-\chi_0}{kT}\right)\frac{\theta}{1 - \theta}\left(\frac{2 - 2\theta}{\beta + 1 - 2\theta}\right)^2 \tag{18}$$

$$\beta = \{1 - 4\theta(1 - \theta)[1 - \exp(-2w/zkT)]\}^{1/2} \tag{19}$$

where θ = fraction of surface sites occupied by surfactant ions
z = number of nearest neighbors of a surfactant ion in the condensed surface phase, taken here as 6

$c(\theta)$ = concentration of surfactant ions in the bulk solution, ions/cm^3
c' = $(2\pi mkT/h^2)^{3/2}kT\,(j^S(T)/j^A(T))$; we neglect the dependence of c' on T and ionic strength
m = mass of a surfactant ion
k = Boltzmann's constant
h = Planck's constant
$j^S(T)$ = partition function for the internal motions of a surfactant ion in solution
$j^A(T)$ = partition function for the internal motions of an adsorbed surfactant ion
w = w(van der Waals) + w(Coulomb)
$2w/z$ = increase in energy when a new pair of surfactant nearest neighbors is formed

The critical temperature above which a surface phase change does not occur is given by (*25*)

$$T_c = -w/[kz \log_e (z/z - 2)] \tag{20}$$

Below this temperature the system may break up into two surface phases; if it does, the values of θ for these phases are the two roots of the equation

$$\begin{aligned}\sigma(\tfrac{1}{2}) &\equiv \exp[(w - \chi_0)/kT] \\ &= \exp(-\chi_0/kT)\frac{\theta}{1-\theta}\left(\frac{2 - 2\theta}{\beta(\theta) + 1 - 2\theta}\right)^z\end{aligned} \tag{21}$$

other than $\theta = 1/2$. (See Ref. *25*.)

THEORETICAL RESULTS

We now examine the adsorption isotherms of the second layer of surfactant. We note that if this layer is fairly sparsely occupied, the surface presented to the solution is mainly the ends of the hydrocarbon chains from the first layer of adsorbed surfactant, so that the surface should be hydrophobic and flotation should occur, provided that the surfactant concentration is high enough to form a condensed hemimicelle (*15*, *17*). If the second layer is densely occupied, the surface presented to the solution is mainly the ionic heads of the surfactant in the second layer; the surface should then be hydrophilic, and flotation should not occur.

In Fig. 2 we see the effect of ionic strength. Increasing ionic strength increases the shielding of the surfactant ions, thereby decreasing their

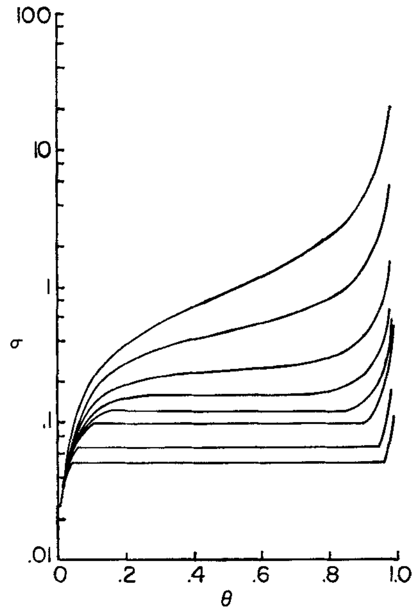

FIG. 2. Adsorption isotherms of the second surfactant layer. Effect of ionic strength. $T = 293°K$; $c_{\max} = 10\ M$; $D = 80.36$; $u = 3.0 \times 10^{-14}$ erg; $S = 30\ Å^2$; $z' = 1$; $z_s = 1$; $n(CH_2) = 14$; $c_\infty = 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.075$, and $0.10\ M$, top to bottom.

coulombic repulsion energy in the condensed second layer. This permits the formation of the condensed second layer, providing another mechanism for the interference of added salts with foam flotation in addition to those previously discussed (*13–17*).

The effect of increasing hydrocarbon chain length is shown in Fig. 3. As one would expect, increasing the number of CH_2 groups which can undergo van der Waals interaction decreases the concentration of surfactant at which a condensed second layer may form, thereby rendering the surface hydrophilic. The results suggest that one must be careful to avoid excessive surfactant concentrations, particularly if the number of CH_2 groups in the chain is fairly large.

Figure 4 shows the expected dependence of the adsorption isotherms on the magnitude of the van der Waals interactions. The effect of temperature is exhibited in Fig. 5; a 30° temperature increase is seen to result in a roughly 3- to 4-fold increase in the surfactant concentration at which a densely occupied second layer is formed.

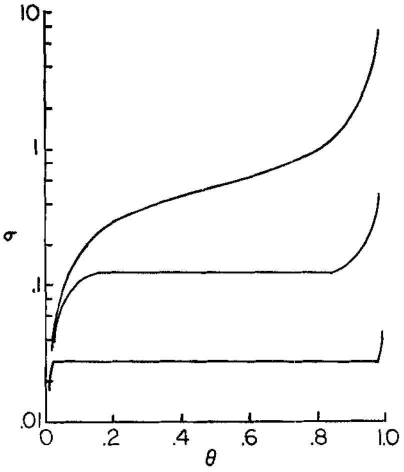

FIG. 3. Adsorption isotherms of the second surfactant layer. Effect of $n(CH_2)$. $c_\infty = 0.04\ M$; $n(CH_2) = 12$, 14, and 16 from top to bottom; other parameters as in Fig. 2.

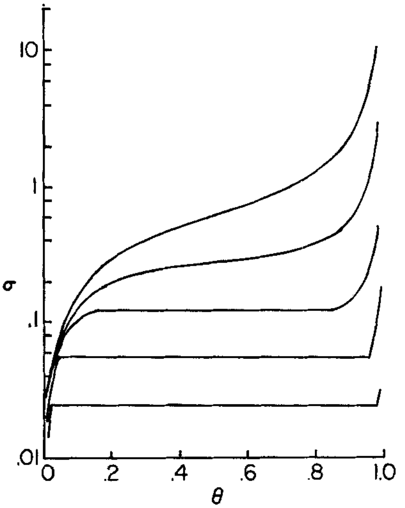

FIG. 4. Adsorption isotherms of the second surfactant layer. Effect of u. $c_\infty = 0.04\ M$; $u = 2.50$, 2.75, 3.00, 3.25, and 3.50×10^{-14} erg, top to bottom; other parameters as in Fig. 2.

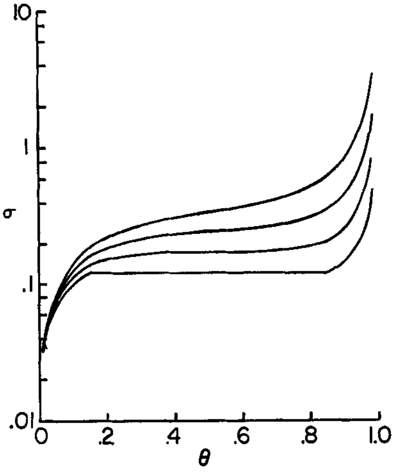

FIG. 5. Adsorption isotherms of the second surfactant layer. Effect of temperature. $c_\infty = 0.04\,M$; $T = 50$, 40, 30, and 20°C; $D = 69.94$, 73.28, 76.75, and 80.36, top to bottom; other parameters as in Fig. 2.

The surface area occupied by a surfactant ion in the condensed second layer has a very marked influence on the adsorption isotherms as seen in Fig. 6. The smaller the surface area per ion, the higher the surfactant concentration required to form a densely occupied second layer. The effect is rather large and is due to the markedly increased coulombic repulsions of the surfactant ions for each other as these ions are crowded more closely together. (We also see that σ_c, the surface charge density, increases with decreasing S, area per ion, according to Eq. 14, and that ψ_0, the electric potential at the plane of the ionic heads in the second layer, increases with increasing σ_c according to Eq. 13.)

The impact of the effective size of the nonsurfactant ions in the solution is surprisingly large, as seen in Fig. 7. This effective size is inversely proportional to $c_{\max}$. As the hydrated ions increase in size, they must be less effective in forming a thin, highly charged, strongly screening diffuse double layer, so the coulombic repulsions of the surfactant ions in the second adsorbed layer increase. This, in turn, makes the formation of a condensed phase second layer more difficult, and so higher surfactant concentrations are required.

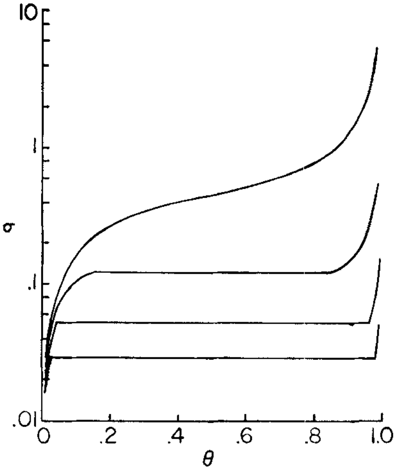

FIG. 6. Adsorption isotherms of the second surfactant layer. Effect of area/ion, S. $c_\infty = 0.04\ M$; $S = 25$, 30, 35, and 40 Å, top to bottom; other parameters as in Fig. 2.

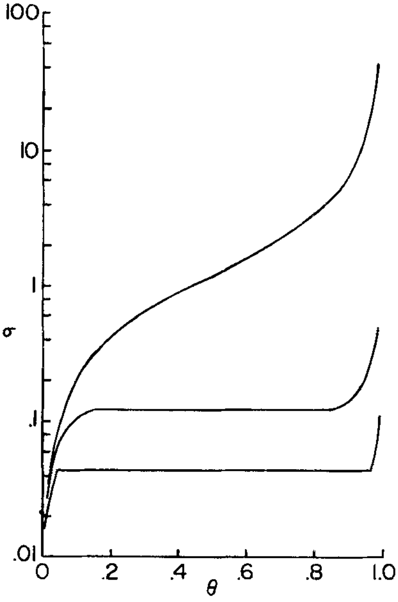

FIG. 7. Adsorption isotherms of the second surfactant layer. Effect of $c_{\max}$. $c_\infty = 0.04\ M$; $c_{\max} = 5$, 10, and 20 M, top to bottom; other parameters as in Fig. 2.

EXPERIMENTAL RESULTS

We here report data on the reduction of efficiency of the precipitate flotation of freshly precipitated ferric hydroxide by the addition of excessive amounts of sodium decyl sulfate, sodium lauryl sulfate (NLS), or sodium tetradecyl sulfate. A batch-type flotation column described previously (*30*) was used; the air flow rate was approximately 60 ml/min, batch volume was 200 ml, initial Fe(III) concentrations were 100 mg/l (as reagent grade ferric nitrate), and pH adjustments were made with 1.0 and 0.1 *N* solutions of sodium hydroxide and 0.1 *N* nitric acid, both reagent grade. Fisher laboratory grade NLS was used; the other surfactants were Eastman yellow label. In some runs the ionic strength of the solution was increased by the addition of reagent grade sodium nitrate. The time required for essentially complete removal of the ferric hydroxide (observed visually) was measured with a stopwatch. In all cases the pH of the solution was kept at 6.0 ± 0.2.

Measurements were made over a range of surfactant concentrations, and it was found that, above a certain concentration well below the critical micelle concentration (cmc), the flotation time required for ferric hydroxide removal increased very markedly with increasing surfactant concentration. Figure 8 shows the effect of added sodium nitrate on the dependence of removal time on NLS concentration. At low ionic strengths the removal time increases roughly tenfold as the NLS concentration is increased from 60 to approximately 200 mg/l. Preston (*31*) reported the cmc of NLS as in the range from 1800 to 2500 mg/l at room temperature, so this effect is not due to the binding of floc particles to preexisting micelles. The shift upward of the curves as ionic strength is increased is presumably due to (a) some competition between NO_3^- and lauryl sulfate ion for sites in the primary adsorption layer, and (b) a reduction in the coulombic repulsions of the surfactant ionic heads in the second layer due to increased screening by the ionic atmosphere; this would facilitate the formation of a second condensed layer, making the precipitate hydrophilic at lower surfactant concentrations.

Figure 9 compares removal times for NLS and sodium tetradecyl sulfate at various surfactant concentrations. The increased chain length in tetradecyl sulfate results in stronger van der Waals forces tending to stabilize the second layer. Therefore condensation of the second layer is able to take place at lower surfactant concentrations, and we find that the removal time increases more rapidly and at lower concentrations for tetradecyl sulfate than for lauryl sulfate. For tetradecyl sulfate the onset of the

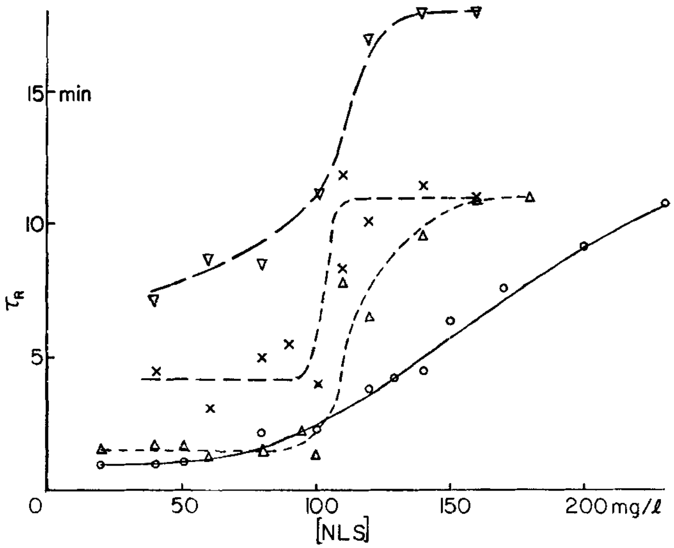

FIG. 8. Effect of ionic strength on the dependence of removal time on NLS concentration. $NaNO_3$ corresponding to 0, 0.01, 0.02, and 0.04 mole/liter, bottom to top, was added.

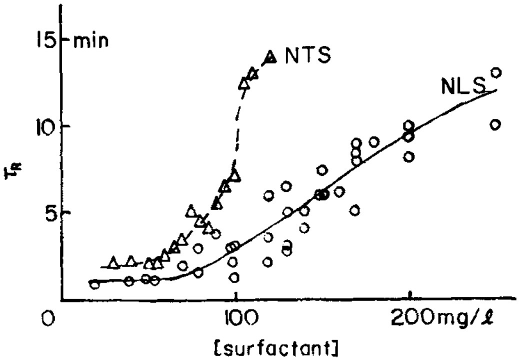

FIG. 9. The dependence of removal time on NLS (bottom) and sodium tetradecy sulfate top) concentration. pH = 6.0, no added $NaNO_3$.

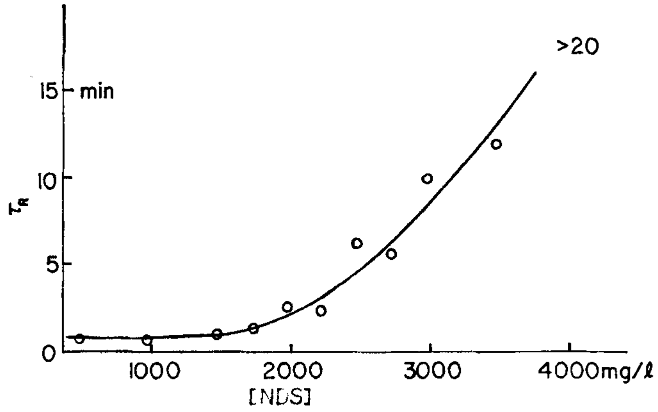

FIG. 10. The dependence of removal time on sodium decyl sulfate concentration. pH = 6.0, no added $NaNO_3$.

increase in removal time, about 60 mg/l, occurs at a concentration far below the cmc of this surfactant, about 700 mg/l according to Preston (*31*). The trend is confirmed by the data for sodium decyl sulfate shown in Fig. 10. The weaker van der Waals forces between the hydrocarbon tails do not lead to condensation of a second layer of surfactant until the surfactant concentration is about 1700 mg/l, much larger that that needed by NLS. The cmc of sodium decyl sulfate is given by Preston as in the range from 7,000 to 10,000 mg/l (*31*).

We conclude that these experimental findings lend support to the model for the interference of excessively high surfactant concentrations with precipitate flotation. The occurrence of the phenomenon at surfactant concentrations far below the cmc's of the surfactants studied establishes that it is not associated with the existence of free micelles of surfactant in the solution.

Acknowledgment

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

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. P. Richmond, *Chem. Ind.* (*London*), *19*, 792 (1977).
5. P. Somasundaran and K. P. Ananthapadmanabhan, to be published in *Recent Advances in Separation Science* (N. N. Li, ed.), CRC Press, West Palm Beach, Florida.
6. A. N. Clarke and D. J. Wilson, *Sep. Purif. Methods*, In Press.
7. M. Hagadone and H. Zeitlin, *Anal. Chim. Acta*, *86*, 289 (1976).
8. N. Rothstein and H. Zeitlin, *Anal. Lett.*, *9*, 461 (1976).
9. F. E. Chaine and H. Zeitlin, *Sep. Sci.*, *9*, 1 (1974).
10. D. Voyce and H. Zeitlin, *Anal. Chim. Acta*, *69*, 27 (1974).
11. Y. S. Kim and H. Zeitlin, *Sep. Sci.*, *7*, 1 (1972).
12. 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.
13. D. J. Wilson, *Sep. Sci.*, *11*, 391 (1976).
14. D. J. Wilson, *Ibid.*, *12*, 231 (1977).
15. D. J. Wilson, *Ibid.*, *12*, 447 (1977).
16. D. J. Wilson, *Sep. Sci. Technol.*, *13*, 107 (1978).
17. B. L. Currin, F. J. Potter, D. J. Wilson, and R. H. French, *Ibid.*, *13*, 285 (1978).
18. D. W. Fuerstenau and T. W. Healy, in Ref. *1*, p. 91.
19. D. W. Fuerstenau, T. W. Healy, and P. Somasundaran, *Trans. AIME*, *229*, 321 (1964).
20. P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *J. Phys. Chem.*, *68*, 3562 (1964).
21. P. Somasundaran and D. W. Fuerstenau, *Ibid.*, *70*, 90 (1966).
22. T. Wakamatsu and D. W. Fuerstenau, *Adv. Chem. Ser.*, *79*, 161 (1968).
23. P. Somasundaran and D. W. Fuerstenau, *Trans. AIME*, *241*, 102 (1968).
24. P. Somasundaran, *Ibid.*, *241*, 105 (1968).
25. R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, London, 1952, pp. 429–443.
26. D. W. Fuerstenau and T. W. Healy, in Ref. *1*, p. 115.
27. D. Stigter, *J. Colloid Interface Sci.*, *47*, 473 (1974).
28. C. D. Hodgman (ed.), *Handbook of Chemistry and Physics*, 42nd ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p. 2525.
29. R. B. Grieves, W. T. Strange, and D. Bhattacharya, *AIChE Symp. Ser. No. 150*, *71*, 40 (1975).
30. T. E. Chatman, S.-D. Huang, and D. J. Wilson, *Sep. Sci.*, *12*, 461 (1977).
31. W. C. Preston, *J. Phys. Colloid Chem.*, *52*, 84 (1948).

Received by editor September 13, 1978