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Soil Clean Up by *in-situ* Surfactant Flushing. II. Theory of Micellar Solubilization

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Abstract

Mathematical models for describing the solubilization of various types of contaminants in micelles of ionic and nonionic surfactants are described. Contaminants which are purely hydrophobic compounds and those which are amphipathic are handled, and electrical effects are described by means of a Debye-Huckel theory approach. It is found that the concentration of contaminant solubilized is a linear function of the total surfactant concentration provided that this is above the critical micelle concentration of the surfactant, in agreement with experimental results.

INTRODUCTION

The contamination of aquifers with organic chemicals from waste disposal, underground storage tanks, and spills is now recognized as a major national problem. Present remediation methods are often costly and slow, and may not result in a permanent solution to the problem. Cheaper, more efficient techniques for soil and ground water clean up would result in reduced costs and reduced environmental impact.

In-situ methods, which manage the contaminated material in place, are attractive candidates. When applicable, they are relatively low in cost, often result in the destruction or removal of the toxic contaminants, rather than merely their containment, and are generally low in environmental impact. Two such techniques which have been found effective in certain site specific applications are *in-situ* biodegradation of hydrocarbons [Brubaker and Crockett (*2*)] and *in-situ* soil vapor stripping [Anastos et al. (*1*), Clarke (*3*), Crow et al. (*4*), Wilson et al. (*5–7*), Woodward-Clyde (*8*), Wootan and Voynick (*9*)]. Clarke and Mutch (*10*) have reviewed the general field of *in-situ* methods of clean up.

Ellis, Payne, and McNabb (*11*) investigated the use of aqueous nonionic surfactants for flushing PCBs, chlorinated phenols, and petroleum hydrocarbons from soils; removal efficiencies were over 90%, orders of magnitude greater than those obtained by flushing with water alone. They noted difficulties in working out treatment techniques for the contaminant-laden surfactant solutions, and regarded the development of a scheme for separating the surfactant solution from the contaminants so that it could be recycled as a vital future step in the development of surfactant flushing.

Nash (*12*) carried out a small-scale field trial of surfactant flushing at Volk Air National Guard Base, Wisconsin. Soil heavily contaminated with oil and other hydrocarbons at a fire pit used in training was treated in laboratory columns and *in situ*. The lab studies were quite encouraging. The field studies were plagued by clogging and heavy rains, and hydrocarbon removal was not statistically significant. Nash commented that the extremely high levels of oil and grease which were present in the soil may have led to severe channeling, as well as to the clogging of several of the test holes. We feel that Nash's negative findings merely establish that surfactant solutions are not effective in cleaning soil if they cannot penetrate it, and note that his lab column results were very encouraging.

In our first paper on surfactant flushing [Wilson (*13*), referred to henceforth as I], we presented a mathematical model for simulating surfactant flushing of a contaminated region in an acquifer by means of an injection well and a recovery well, either operating in an unconfined two-dimensional domain or operating surrounded by a slurry wall barrier. A mathematical model of the same type was constructed for simulating surfactant flushing of contaminated soils in laboratory columns. It is hoped that these will prove to be useful tools for engineers attempting to assess the technique for use in specific sites and for the design of surfactant flushing operations. That paper also gives a qualitative discussion of micellar solubilization and a number of references on the topic. Needless to say, micellar solubilization plays a crucial role in the functioning of the surfactant flushing technique. In the present paper we therefore present a simple theory of micellar solubilization. In this work we are particularly indebted to Vold and Vold (*14*) for a very lucid discussion of the micellization process, and to Israelashvili (*15*) for an equally clear discussion of a thermodynamic approach to micellization which has been very helpful.

We first discuss two models for the formation of micelles in surfactant solutions containing only a single surfactant (no solubilizate). The first model is quite realistic, but mathematically somewhat complex, in that it involves calculation of equilibrium constants and ultimately concentrations for an order of a hundred or so different micellar species. The second model is very much simpler; it specifies one micellar species which may reasonably be expected to be present at particularly high concentrations, and ignores the rest. We shall see that the two models, somewhat surprisingly, give rather similar results for plots of aggregation number versus surfactant concentration; this will give us confidence in using the approximate approach.

Next, the solubilization of hydrophobic compounds in surfactant micelles is discussed and modeled. Consideration of all possible micellar species would involve an order of 50,000 or so different species and is obviously intractable. We therefore use an extension of the second model mentioned above, in which a subset of roughly 200 micellar species is identified as being present at especially high concentrations; this limited set is then used to represent the micellization/solubilization process. The model is then used to calculate total solubilizate concentrations in solutions of known surfactant concentration which are in equilibrium with neat solubilizate.

Last, the solubilization of amphipathic contaminants (such as long-chain alcohols or fatty acids) is considered. Again a subset of micellar species of particularly high probability of occurrence is assumed to adequately represent the micellization/solubilization process. This model is also used to calculate total solubilizate concentrations in solutions containing surfactant at specified concentrations.

ANALYSIS

(a) First Model for Micelle Formation

Intuitively, a reasonable model for micelle formation in surfactant solutions which are relatively dilute is

$$\begin{aligned} &A + A \rightleftharpoons A_2 \\ &A + A_2 \rightleftharpoons A_3 \\ &\quad \cdots \\ &A + A_n \rightleftharpoons A_{n+1} \\ &\quad \cdots \end{aligned} \tag{1}$$

Thermodynamically (although certainly not kinetically) this mechanism is equivalent to

$$\begin{aligned} &2A \rightleftharpoons A_2 \\ &3A \rightleftharpoons A_3 \\ &\quad \cdots \\ &(n + 1)A \rightleftharpoons A_{n+1} \\ &\quad \cdots \end{aligned} \tag{2}$$

If one is calculating concentrations of the various micellar species at equilibrium, these mechanisms must give the same results. It is more convenient for our purposes to use the second set of reactions.

Let v_A = molecular volume of surfactant (molecule or iron)
S_A = cross-sectional area of ionic (or polar) head of surfactant
h_A = hydrophobic area of surfactant, assuming a roughly spherical coiled chain conformation with the ionic head on the outside
γ_A = surface free energy of the hydrophobic surface of the surfactant that is in contact with water, erg/cm^2

We wish to calculate the free energy $\Delta G^0 \equiv \Delta G_n^0$ for the process

$$nA \rightleftharpoons A_n$$

Assume that this consists of a surface free energy portion, a translational entropy contribution, and an electrical portion. The surface free energy contribution is calculated as follows. The radius of the (spherical) micelle is given by

$$\tfrac{4}{3}\pi r_n^3 = n v_A \tag{3}$$

so

$$r_n = \left(\frac{3\upsilon_A}{4\pi}\right)^{1/3} n^{1/3} \tag{4}$$

and the total area of the micelle is given by

$$S_n = 4\pi\left(\frac{3\upsilon_A}{4\pi}\right)^{2/3} n^{2/3} \tag{5}$$

The hydrophobic surface area of this micelle is then given by

$$h_n = 4\pi\left(\frac{3\upsilon_A}{4\pi}\right)^{2/3} n^{2/3} - S_A n \tag{6}$$

The hydrophobic area of n A monomers is just nh_A, so the change in surface free energy during micelle formation is given by

$$\Delta G_{\text{surface}} = \gamma_A\left[4\pi\left(\frac{3\upsilon_A}{4\pi}\right)^{2/3} n^{2/3} - S_A n - h_A n\right] \tag{7}$$

$$= \gamma_A\left[4\pi\left(\frac{3\upsilon_A}{4\pi}\right)^{2/3} n^{2/3} - (S_A + h_A)n\right] \tag{8}$$

The maximum value of n is obtained when the hydrophobic surface h_n is zero; this is given by

$$n_{\max} = 36\pi \frac{\upsilon_A^2}{S_A^3} \tag{9}$$

This gives an upper bound to the size of the micelles, given that they are constrained to be spherical.

The electrical free energy change is calculated within the framework of Debye-Huckel theory; more sophisticated and accurate methods could be used, but would add greatly to the difficulty of the computations and little to the insight into the process of micelle formation. See Levine (*17*).

We recall from the Debye-Huckel theory that the electric potential around a spherical charge distribution in an electrolyte solution is given by

$$\psi(r) = \frac{\alpha \exp(-\kappa r)}{r} \tag{10}$$

The Debye length, $1/\kappa$, is given by

$$\kappa = \left[\frac{8\pi c_s e^2}{DkT}\right] \tag{11}$$

where c_s = inert 1-1 electrolyte concentration, cations (or anions)/mL
e = magnitude of electronic charge, 4.803×10^{-10} esu
k = Boltzmann's constant, 1.381×10^{-16} erg/K
D = dielectric constant of water, given by $D = 78.54 - 0.3612(t - 25) + 0.00690(t - 25)^2$
t = temperature, °C
T = temperature, K

The electrical neutrality requirement for the system (micelle plus ionic atmosphere) can be shown to yield

$$\left.\frac{d\psi}{dr}\right|_{r=r_n} = -\frac{4\pi\sigma}{D} \tag{12}$$

where σ, the micelle's surface charge density, is given by

$$\sigma = -\frac{ne}{4\pi r_n^2} \tag{13}$$

if we have a singly-charged anionic surfactant. Here r_n is the radius of a micelle containing n surfactant ions. So

$$\left.\frac{d\psi}{dr}\right|_{r=r_n} = \frac{ne}{Dr_n^2} \tag{14}$$

From Eq. (10) we have

$$\left.\frac{d\psi}{dr}\right|_{r=r_n} = -\alpha\left[\frac{1}{r_n^2} + \frac{\kappa}{r_n}\right]\exp(-\kappa r_n) \tag{15}$$

which, together with Eq. (14), yields

$$\alpha = -\frac{ne\exp(\kappa r_n)}{D(1 + \kappa r_n)}$$

so that

$$\psi(r) = -\frac{ne\exp[-\kappa(r - r_n)]}{D(1 + \kappa r_n)r} \tag{16}$$

and

$$\psi(r_n) = -\frac{ne}{D(1 + \kappa r_n)r_n} \tag{17}$$

We next use a Guntelberg charging process to calculate the electrical free energies of the *n* surfactant ions 1) in the micelle and 2) isolated. For the micelle,

$$\Delta G_{\text{elec}}(n) = \int_0^1 \frac{-ne\lambda}{D(1 + \kappa r_n)r_n}(-ned\lambda) \tag{18}$$

which gives

$$\Delta G_{\text{elec}}(n) = \frac{n^2e^2}{2D(1 + \kappa r_n)r_n} \tag{19}$$

For a single surfactant ion in a roughly spherical conformation and undergoing rapid tumbling from molecular collisions with the solvent,

$$\Delta G_{\text{elec}}(1) = \frac{e^2}{2D(1 + \kappa r_1)r_1} \tag{20}$$

where r_1 is estimated by

$$r_1 = \left(\frac{3v_{\text{A}}}{4\pi}\right)^{1/3} \tag{21}$$

Then

$$\Delta G^0_{\text{elec}} = \frac{n^2e^2}{2D(1 + \kappa r_n)r_n} - \frac{ne^2}{2D(1 + \kappa r_1)r_1} \tag{22}$$

As the surfactant ions become micellized, they undergo a loss of translational degrees of freedom which leads to a decrease in translational entropy. Let us assume that the standard translational entropy change per surfactant ion is ΔS_1^0. Then this gives a contribution to the free energy of micelle formation by n surfactant ions of $\Delta G_{\text{trans}}^0 = -(n-1)T\Delta S_1^0$.

On combining the three terms contributing to the standard free energy change of micelle formation, we obtain

$$\begin{aligned}\Delta G_n^0 &= \Delta G_{\text{surface}}^0(n) + \Delta G_{\text{elec}}^0(n) + \Delta G_{\text{trans}}^0(n)\\ &= \gamma_A[4\pi r_1^{2/3} n^{2/3} - (S_A + h_A)n]\\ &\quad + \frac{e^2}{2D}\left[\frac{n^2}{(1+\kappa r_1 n^{1/3}) r_1 n^{1/3}} - \frac{n}{(1+\kappa r_1) r_1}\right]\\ &\quad - (n-1)T\Delta S_1^0, \qquad n = 2, 3, \ldots, n_{\max}\end{aligned} \tag{23}$$

The equilibrium constant for the reaction

$$nA \rightleftharpoons A_n$$

is given by

$$\begin{aligned}K_n &= \exp(-\Delta G_n^0/kT)\\ &= \frac{[A_n]}{[A]^n}, \qquad n = 2, 3, \ldots, n_{\max}\end{aligned} \tag{24}$$

A mass balance gives

$$A_{\text{total}} = [A] + \sum_{n=2}^{n_{\max}} n[A_n] \tag{25}$$

$$= [A] + \sum_{n=2}^{n_{\max}} nK_n[A]^n \tag{26}$$

This equation for [A] is solved by a simple search technique; since the right-hand side monotonically increasing with increasing [A] and since 0 and A_{total} provide lower and upper bounds to [A], this is not difficult. Because of the very high powers of [A] which occur in Eq. (26), Newton's method or other more sophisticated algorithms run into stability problems which do not arise with a binary search.

With such a model one should be able to calculate mean aggregation numbers and, from these, critical micelle concentrations (cmc). The (mean) aggregation number is the average number of surfactant ions in the clusters in which a surfactant ion is associated. If one were to conduct a poll of the surfactant ions in the solution, asking each how many ions (counting itself) it was associated with, the average of the answers would be the aggregation number. From this it is readily seen that $\bar{n}$, the aggregation number, is given by

$$\bar{n} = \sum_{n=1}^{n_{\max}} n \frac{n[A_n]}{A_{total}} \tag{27}$$

$$= \frac{[A] + \sum_{n=2}^{n_{\max}} n^2 K_n [A]^n}{A_{total}} \tag{28}$$

Thus, once the value of [A] has been determined, the aggregation number can readily be calculated.

A plot of $\bar{n}$ versus the nominal surfactant concentration for sodium dodecylsulfate is shown in Fig. 1. The surfactant concentration at which $\bar{n}$ starts to increase is the critical micelle concentration, below which micelle formation is negligible and above which [A[is essentially unchanged as A_{total} increases, with virtually all of the added surfactant going to form micelles. The parameters used in the calculation are given in Table 1.

Added salt decreases the Coulombic repulsions between the surfactant ionic heads, increasing micellar stability and decreasing critical micelle concentrations, again in agreement with experimental data. See Fig. 2. The effect of chain length of the surfactant on the cmc is shown in Fig. 3. Increasing the length of the surfactant hydrocarbon chain (the hydrophobic part of the ion) from 10 through 12 to 14 results in quite substantial reductions in the cmc, as observed experimentally. It is apparent that one can recover the salient features of micelle formation by means of this relatively simple model. For experimental data on aggregation numbers and the effects of salt concentration and surfactant

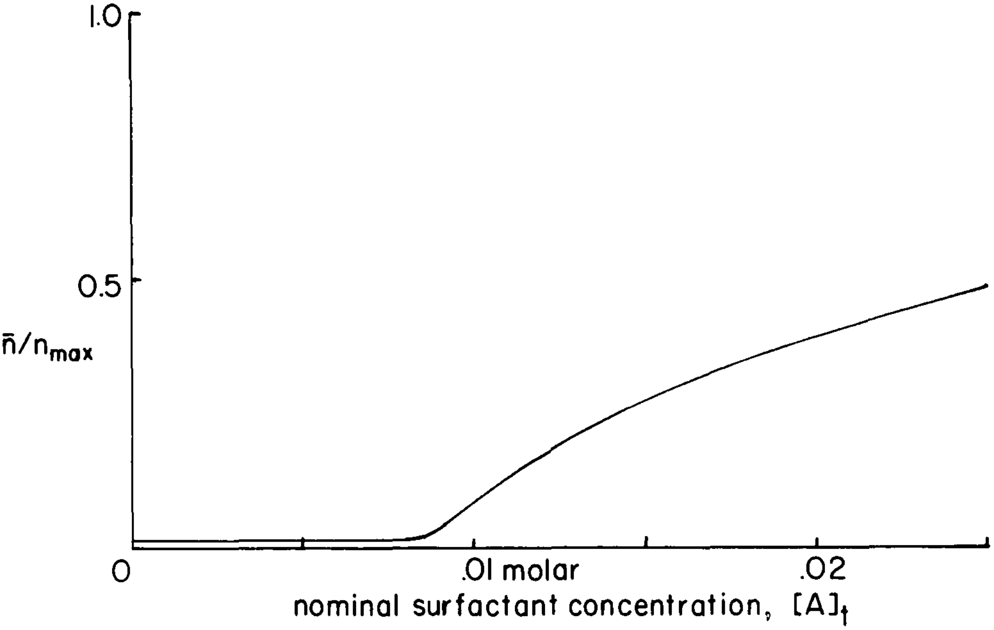

FIG. 1. Plot of aggregation number, n, versus nominal surfactant concentration, $[A]_t$, calculated with the first (elaborate) model for micelle formation. $n_{max} = 71$. The surfactant being simulated is sodium dodecylsulfate (SDS). Added salt concentration = 0. The other parameters for this run are given in Table 1.

TABLE 1

Parameters Used in the First Model for Micelle Formation

Effective area of ionic head (sulfate) = 64.3 Å^2
Surface free energy of water–hydrocarbon tail interface = 50 erg/cm^2
Molar translational entropy change per ion or molecule on micellization = −27 cal/mol · degree
Temperature = 298 K
Dielectric constant of water = 78.54

	Sodium decylsulfate	Sodium dodecylsulfate	Sodium tetradecylsulfate
Molecular weight	260.35 g/mol	288.35	316.35
Density	1.225 g/mL	1.170	1.186
Molar volume	228.0 mL/mol	246.45	266.74

chain length on the cmc, see Rosen (*18*) and Lucassen-Reynders (*19*). Actually, as we shall see in the next section, the model can be simplified still further and still provide a quite adequate description of micelle formation. We shall need this further simplification when we turn to systems containing two surfactants or a surfactant and a solubilizate.

(b) Second Model for Micelle Formation

We note that the standard free energy change per surfactant ion on micellization is given by

$$\frac{\Delta G_n^0}{n} = \gamma_A\left[\frac{4\pi r_1^2}{n^{1/3}} - (S_A + h_A)\right] + \frac{e^2}{2D}\left[\frac{n^{2/3}}{(1 + \kappa r_1 n^{1/3})r_1} - \frac{1}{(1 + \kappa r_1)r_1}\right] - (n - 1)T\Delta S_1^0 \tag{29}$$

This passes through a minimum at the value of n for which

$$\frac{d}{dn}\left(\frac{\Delta G_n^0}{n}\right) = 0 \tag{30}$$

The value of n so determined should correspond to the most probable micellar structure. This requirement leads to the following recursive equation for n_{mp}, the most probable value of n:

$$n_{mp} = \frac{8\pi D r_1^3 \gamma_A}{e^2}\left[\frac{(1 + \kappa r_1 n_{mp}^{1/3})^2}{2 + \kappa r_1 n_{mp}^{1/3}}\right] \tag{31}$$

Unless κ is extremely small (very low ionic strengths), we find that insertion of physically reasonable parameters into Eq. (31) yields values of n_{mp} that are greater than $n_{\max}$ calculated from Eq. (9). This is not physically possible, from which we arrive at the conclusion that micelles containing $n_{\max}$ surfactant ions are generally the most stable and will therefore predominate in the solution.

This result then suggests that we consider a model for micelle formation of the following form:

$$n_{\max}A \rightleftharpoons A_{n\max} \tag{32}$$

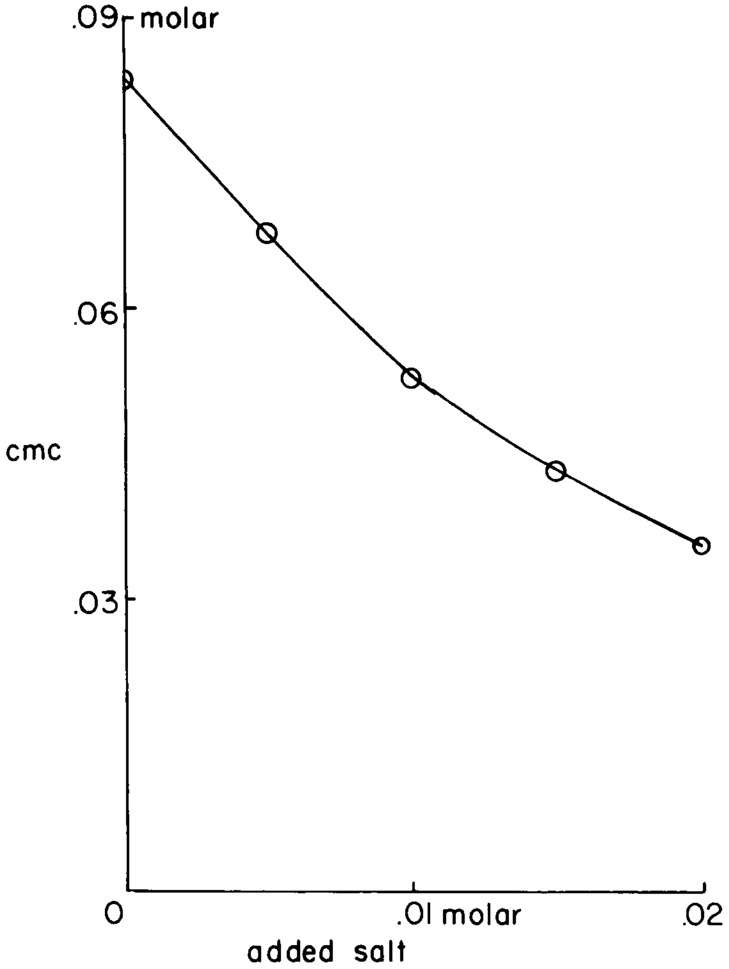

FIG. 2. Plot of critical micelle concentration (cmc) versus added 1-1 salt concentration, calculated with the first model for micelle formation. The surfactant is SDS. The parameters for these are given in Table 1.

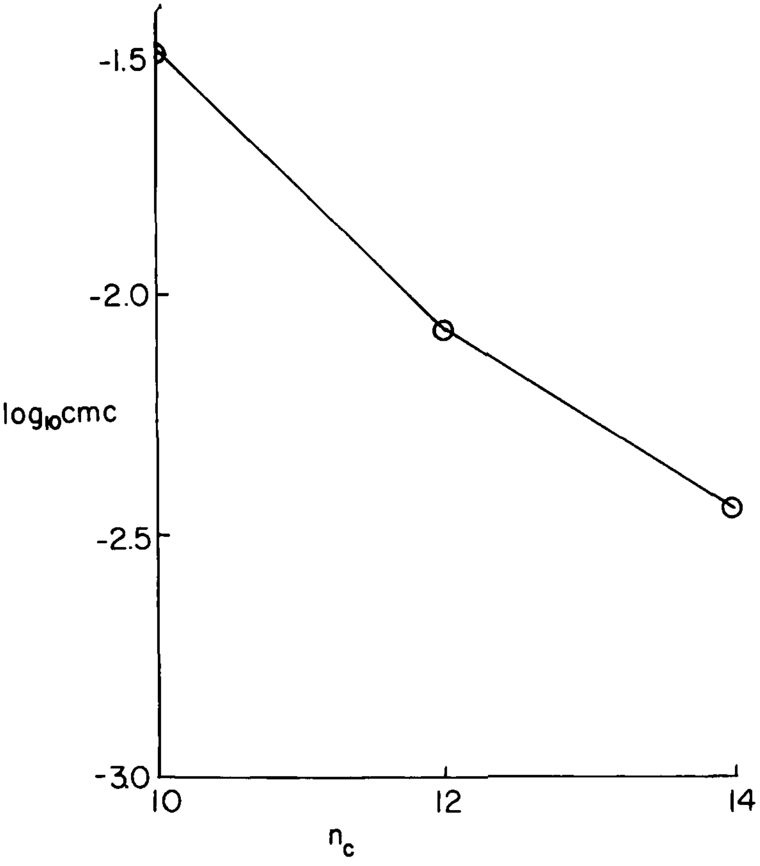

FIG. 3. Plot of $\log_{10}$ (cmc) versus number of carbon atoms in the chain for sodium decylsulfate, SDS, and sodium tetradecylsulfate. These calculations were made with the first model. The parameters for these runs are given in Table 1.

where $n_{\max}$ is given by Eq. (9), $K_{n_{\max}}$ is given by setting $n = n_{\max}$ in Eq. (23) and substituting the resulting $\Delta G^0_{n_{\max}}$ into Eq. (24). The mass balance equation is

$$A_{\text{total}} = [A] + n_{\max} K_{n_{\max}} [A]^{n_{\max}} \tag{33}$$

and the aggregation number is given by

$$\bar{n} = \frac{[A] + n^2_{\max} K_{n_{\max}} [A]^{n_{\max}}}{A_{\text{total}}} \tag{34}$$

A plot of $\bar{n}$ versus A_{total} is shown in Fig. 4. The surfactant being modeled is sodium dodecylsulfate; the parameters used are given in Table 2. Hardly surprisingly, this model yields cmc's which are affected by ionic strength and by surfactant alkyl group chain length, as seen in Figs. 5 and

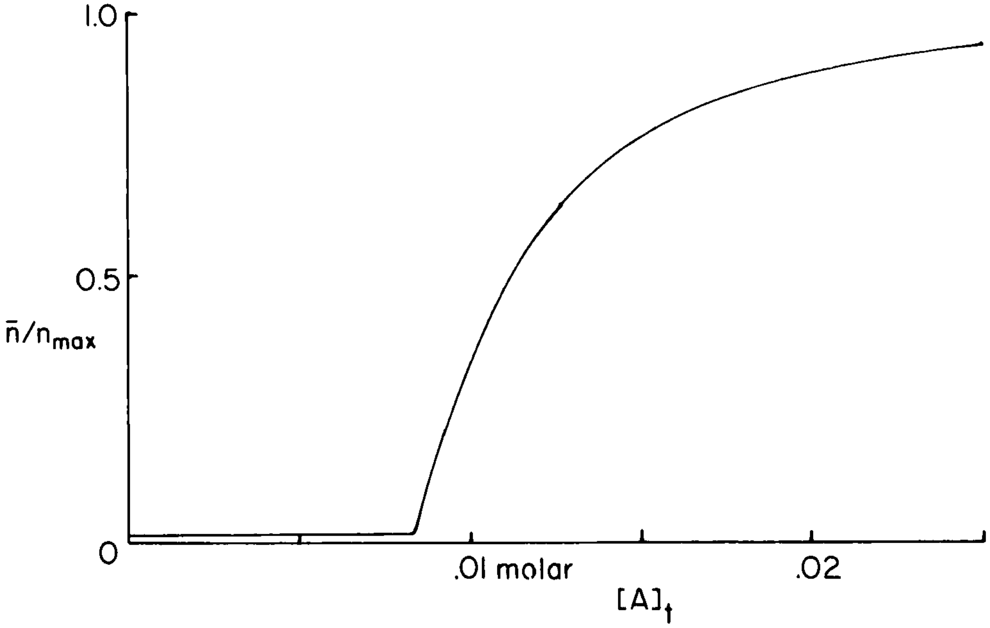

FIG. 4. Plot of aggregation number, n, versus nominal surfactant concentration, $[A]_t$, calculated with the second (simple) model for micelle formation. $n_{\max} = 71$. SDS is the surfactant being simulated. Added salt concentration = 0. The other parameters are given in Table 2. Compare with Fig. 1.

TABLE 2
Parameters Used in the Second Model for Micelle Formation

Effective area of ionic head = 64.3 Å^2

Surface free energy of water–hydrocarbon tail interface = 50 erg/cm^2

Molar translational entropy change per ion or molecule on micellization = −24.27 cal/mol · degree

Temperature = 298 K

Surfactant molecular weights, densities, and molar volumes as in Table 1

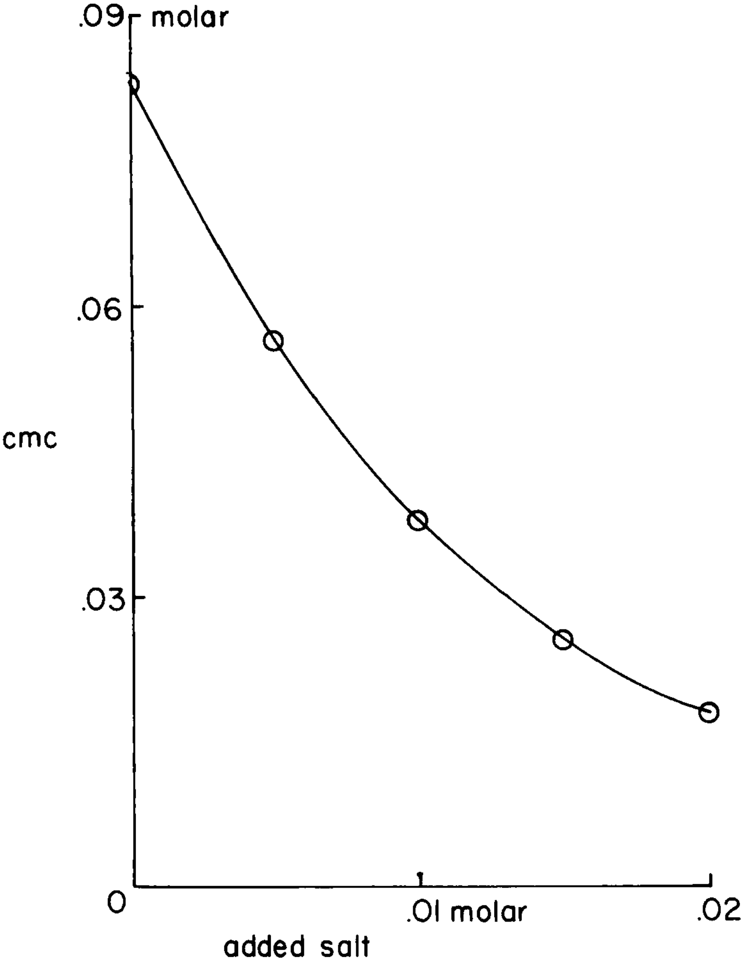

FIG. 5. Plot of cmc versus added 1-1 salt concentration, calculated with the second model for micelle formation. SDS was simulated. The parameters are given in Table 2. Compare with Fig. 2.

6; the effects are rather similar to those seen with our first, more complex model.

The rather good agreement between these two models for micelle formation gives us hope that simplifications analogous to those used in the second model might permit the development of mathematically tractable models for micellar solubilization of hydrophobic compounds and the formation of mixed micelles containing two amphipathic species. We address these problems in the next two sections.

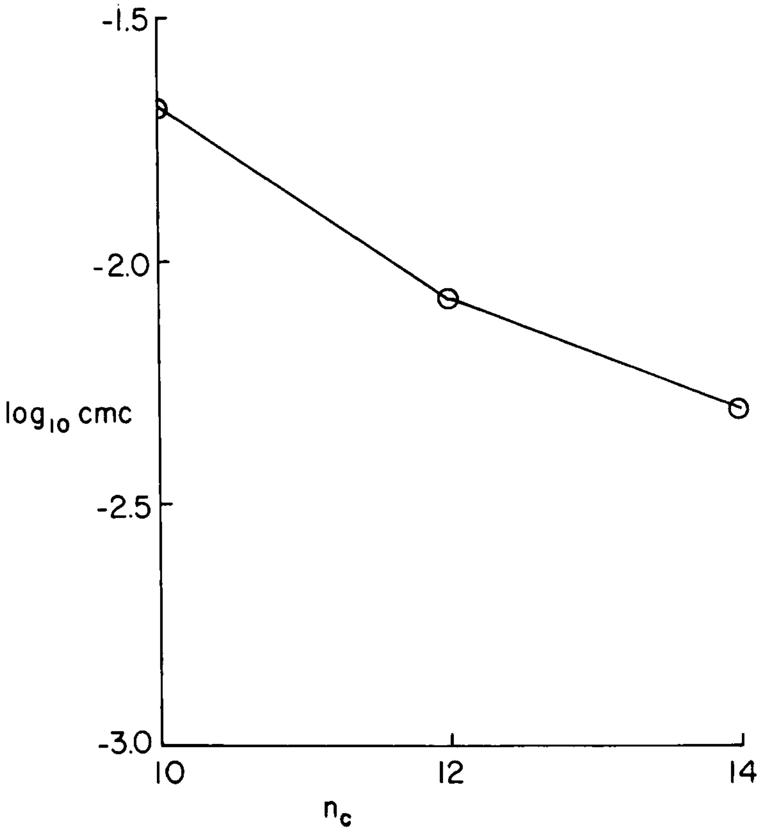

FIG. 6. Plot of $\log_{10}$ (cmc) versus number of carbon atoms in the chain for sodium decylsulfate, SDS, and sodium tetradecylsulfate. The second model was used to make these calculations. The run parameters are given in Table 2. Compare with Fig. 3.

(c) Model for Micellar Solubilization

In the surfactant flushing of hydrophobic compounds from contaminated soils the solubilization of the hydrophobic contaminants within surfactant micelles is crucial. This mechanism can increase the apparent solubilities of hydrophobics in aqeuous systems by a couple orders of magnitude or so, thereby increasing removal rates of contaminants by a comparable amount. [See McBain and Hutchinson's monograph (*16*).]

We here develop a simple thermodynamic theory for solubilization. Our fundamental chemical processes can be taken as

$$nA + mB \rightleftharpoons A_nB_m; \qquad n, m = 1, 2, \ldots \tag{35}$$

without loss of generality, where A is the surfactant ion and B is the hydrophobic solubilizate. We write the chemical potential of the species A_nB_m as

$$\mu_{nm} = \mu_{nm}^0 + kT \log_e [A_nB_m] \tag{36}$$

where $[A_nB_m]$ is the molar concentration of the species. Similarly we take

$$\mu_A = \mu_A^0 + kT \log_e [A] \tag{37}$$

$$\mu_B = \mu_B^0 + kT \log_e [B] \tag{38}$$

The free energy change of the process of forming A_nB_m is then given by

$$\Delta G = \mu_{nm}^0 + kT \log_e [A_nB_m] - n(\mu_A^0 + kT \log_e [A]) - m(\mu_B^0 + kT \log_e [B]) \tag{39}$$

At equilibrium $\Delta G = 0$, which yields in the usual way

$$\frac{[A_nB_m]}{[A]^n[B]^m} = \exp\left(-\frac{\mu_{nm}^0 - n\mu_A^0 - m\mu_B^0}{kT}\right) = \exp(-\Delta G_{nm}^0/kT) = K_{nm} \tag{40}$$

If we can calculate the ΔG_{nm}^0, we can in principle calculate all the equilibrium constants and, from these and material balance equations, the concentrations of all the various micellar species. In fact, if n and m are allowed to range independently from 0 to, say, 100, we would have 10^4 equilibrium constants to calculate and 10^4 species concentrations to compute. This formidable task can be drastically simplified by the following argument.

Let us assume that μ^0_{nm} is minimized for micelles which do not have a hydrophobic surface exposed to the water. It is then reasonable to focus our attention on only those species A_nB_m having no exposed hydrophobic surface, since these species will have equilibrium constants much larger than those of the species having an exposed hydrophobic surface. This restriction then allows us to calculate m as a single-valued function of n; we proceed as follows: Let

v_A = molecular volume of A
v_B = molecular volume of B
S_A = cross-sectional area of the polar/ionic head of A, the surfactant
r_{nm} = radius of spherical micelle containing nA's and mB's

Then to have no hydrophobic surface the condition

$$4\pi r_{nm}^2 = nS_A \tag{41}$$

must be satisfied, so that

$$r_{nm} = \left(\frac{nS_A}{4\pi}\right)^{1/2} \tag{42}$$

Now the volume of an A_nB_m micelle is given by

$$\tfrac{4}{3}\pi r_{nm}^3 = nv_A + mv_B \tag{43}$$

So

$$m = \frac{1}{v_B}\left(\frac{4}{3}\pi r_{nm}^3 - nv_A\right) \tag{44}$$

or

$$m = \frac{1}{v_B}\left[\frac{4}{3}\pi\left(\frac{S_A}{4\pi}\right)^{3/2} n^{3/2} - v_A n\right] \tag{45}$$

The lowest possible value for n occurs when $m = 0$, which yields

$$\frac{4}{3}\pi\left(\frac{nS_A}{4\pi}\right)^{3/2} - nv_A = 0 \tag{46}$$

from which

$$n = n_{\min} = 36\pi v_A^2/S_A^3 \tag{47}$$

This result and Eq. (45) then allow us to determine the subset of significant micelles having n and m values as follows:

n	m
$n_{\min}$	0
$n_{\min} + 1$	$m(n_{\min} + 1)$
$n_{\min} + 2$	$m(n_{\min} + 2)$
. . .	. . .

where the m values are calculated from Eq. (45).

Next it is necessary to get an estimate for

$$\mu_{nm}^0 - n\mu_A^0 - m\mu_B^0$$

given that the micelles under consideration have no exposed hydrophobic surface. Contributions to this free energy difference are as follows.

(a) There is a decrease in the hydrophobic area exposed to the water when micelle formation occurs. If we let

h_A = hydrophobic area of monomeric A

h_B = hydrophobic area of monomeric B

then this results in a change in free energy of

$$\Delta G_{\text{hydrophobic}} = -nh_A\gamma_A - mh_B\gamma_B \tag{48}$$

where γ_A = surface free energy per unit area of the interface between the hydrophobic portion of A and water
γ_B = surface free energy per unit area of the B–water interface

(b) There is a configurational entropy term which we estimate as an entropy of mixing,

$$\Delta S_{\text{config}} = -k\left[n \log_e \frac{n}{n+m} + m \log_e \frac{m}{m+n}\right] \tag{49}$$

This contributes a term to ΔG^0 of

$$\Delta G_{\text{config}} = kT\left[n \log_e \frac{n}{n+m} + m \log_e \frac{m}{m+n}\right] \tag{50}$$

(c) If the surfactant is ionic, there is an electrical contribution to the free energy change which we estimate by means of the Debye-Huckel theory. This is done exactly as in our model for micelle formation; see section (a). The result is

$$\Delta G^0_{\text{elec}}(n,m) = \frac{n^2e^2}{2D(1+\kappa r_{nm})r_{nm}} - \frac{ne^2}{2D(1+\kappa r_1)r_1} \tag{51}$$

where we recall that $r_{nm} = (nS_A/4\pi)^{1/2}$.

(d) Both A and B lose translational degrees of freedom when they are incorporated into micelles, with a corresponding loss in translational entropy. We assume that the standard translational entropy change on forming A_nB_m is given by $(n + m - 1)\Delta S_1$, which contributes a term $-(n + m - 1)T\Delta S_1$ to the standard free energy change of micellization.

Combining the four sets of terms contributing to ΔG^0_{nm} then yields

$$\begin{aligned}\Delta G^0_{nm} = {} & -nh_A\gamma_A - mh_B\gamma_B + kT\left(n \log_e \frac{n}{n+m} + m \log_e \frac{m}{n+m}\right) \\ & + \frac{e^2}{2D}\left\{\frac{n^2}{\left[1+\kappa\left(\frac{S_A}{4\pi}\right)^{1/2} n^{1/2}\right]\left(\frac{S_A}{4\pi}\right)^{1/2} n^{1/2}} - \frac{n}{(1+\kappa r_1 r_1)}\right\} \\ & - (n+m-1)T\Delta S^0_1\end{aligned} \tag{52}$$

Then

$$K_{nm} = \exp\left(-\frac{\Delta G^0_{nm}}{kT}\right) \tag{53}$$

and we are ready to proceed with the solution to the equilibrium calculations.

Recall

$$nA + mB \rightleftharpoons A_nB_m \tag{35}$$

and

$$K_{nm} = \frac{[A_nB_m]}{[A]^n[B]^m} \tag{40}$$

Also,

$$A_{\text{total}} = [A] + \sum_{n=n_{\text{min}}}^{\infty} n[A_nB_m] \tag{54}$$

and

$$B_{\text{total}} = [B] + \sum_{n=n_{\text{min}}}^{\infty} m(n)[A_nB_m] \tag{55}$$

from stoichiometry. Now

$$[A_nB_m] = K_{nm}[A]^n[B]^m$$

so

$$A_{\text{total}} = [A] + \sum_{n=n_{\text{min}}}^{\infty} nK_{nm}[A]^n[B]^m \tag{56}$$

and

$$B_{total} = [B] + \sum_{n=n_{min}}^{\infty} m(n)K_{nm}[A]^n[B]^m \qquad (57)$$

Typically we are given A_{total} (the total nominal surfactant concentration). If neat B is present, [B] can be taken as the saturation concentration of B in water, also known. One then substitutes this value of [B] into Eq. (56) and solves the resulting equation for [A]. The search technique mentioned previously is used. The value of [A] obtained is then put into Eq. (57) and the total amount of B in solution, B_{total}, is calculated. Thus, the model allows us to calculate the saturation concentration of solubilizate B in a surfactant solution of any specified surfactant concentration.

Some results obtained with this model are shown in Figs. 7, 8, and 9. The parameters used in the calculations are given in Table 3. The figures are plots of the total solubilizate concentration versus total surfactant concentration. In Fig. 7 the solubilizate is *p*-dichlorobenzene; in Fig. 8, naphthalene; in Fig. 9, biphenyl. The surfactant simulated is sodium

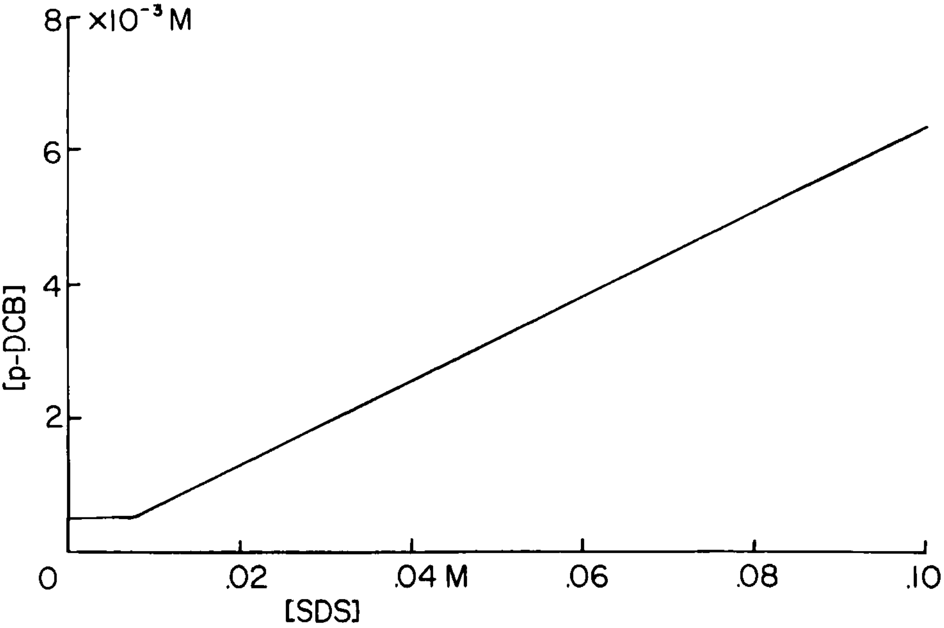

FIG. 7. Simulation of the solubilization of *p*-dichlorobenzene (*p*-DCB) by SDS. The parameters for this run are given in Table 3.

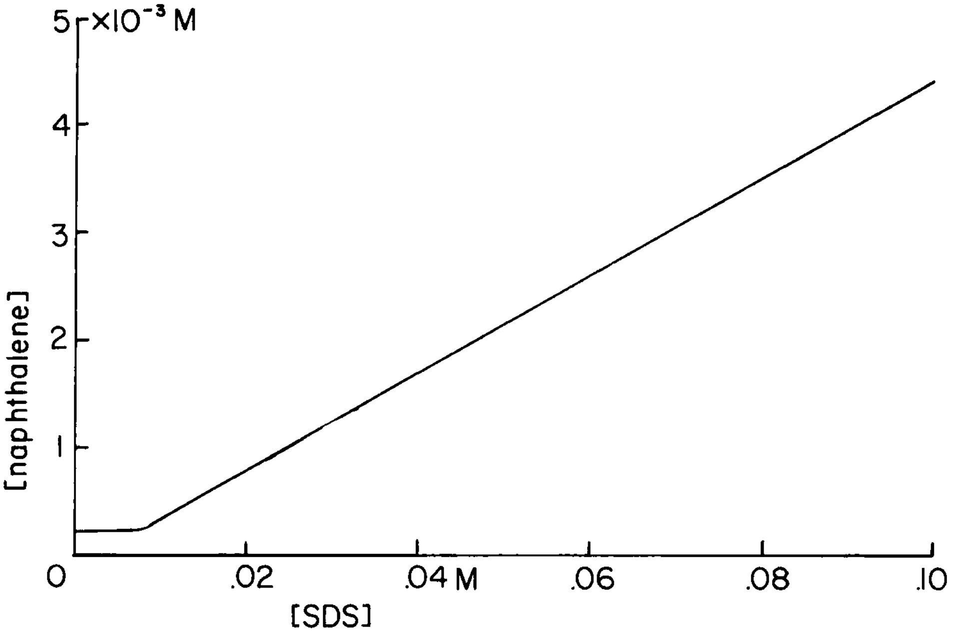

FIG. 8. Simulation of the solubilization of naphthalene by SDS. The parameters for this run are given in Table 3.

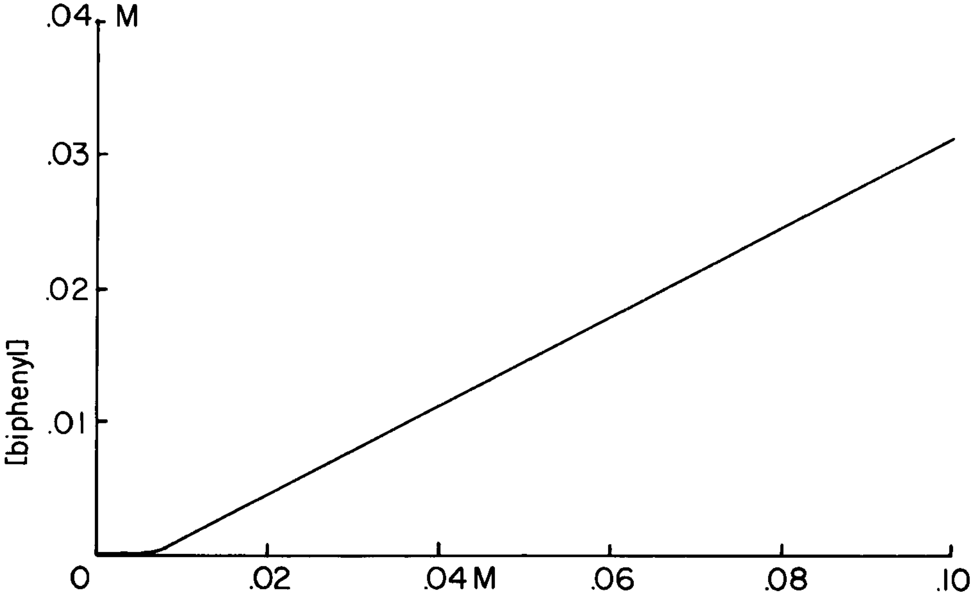

FIG. 9. Simulation of the solubilization of biphenyl by SDS. Run parameters are given in Table 3.

TABLE 3

Parameters for Micellar Solubilization of *p*-Dichlorobenzene, Naphthalene, and Biphenyl

Surfactant (SDS) properties: see Table 1
Temperature = 298 K
Molar translational entropy change per ion or molecule on micellization = −27.8 cal/mol · degree
Added salt concentration = 0.0 *M*

	p-Dichlorobenzene	Naphthalene	Biphenyl
Molar volume (mL/mol)	100.82	111.93	130.68
Effective molecular area (Å^2)	230	240	290
Hydrophobe-water interfacial free energy (erg/cm^2)	35	35	35
Solubility in water (*M*)	0.000537	0.00023	0.000049

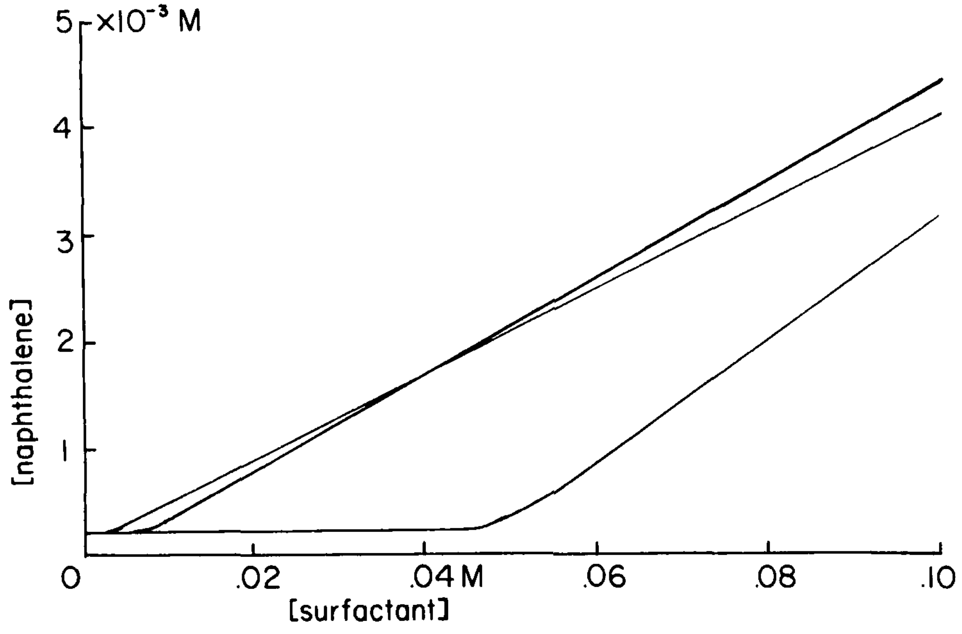

FIG. 10. Comparison of the solubilization of naphthalene by sodium decylsulfate, SDS, and sodium tetradecylsulfate, going from right to left on the lower portions of the curves. Run parameters are given in Table 3.

dodecylsulfate. Comparing values of B_{total} with A_{total} shows that, as expected, solubilizate concentration is found to be a linear function of the surfactant concentration when this is above the cmc. Also as found experimentally, enhancements in total hydrophobe concentration above the saturation concentration are quite large; with dichlorobenzene, naphthalene, and biphenyl increases by factors of as much as two orders of magnitude are found by the model for surfactant solutions which are no more than 0.1 *M* in total surfactant.

A comparison of simulated solubilization curves for naphthalene with sodium decylsulfate, sodium dodecylsulfate, and sodium tetradecylsulfate is made in Fig. 10. The slopes of the plots are relatively similar, and we see that the onset of the linear increase in total naphthalene concentration occurs at approximately the cmc of the surfactant, in agreement with experimental results. [For a review of solubilization by surfactant solutions, see Rosen (*18*). See also Hall and Tiddy's article (*19*).]

It is hoped that this model, with parameters which can be estimated from data generally available, and with comparatively modest computational requirements, will be useful in helping the environmental engineer optimize the selection of surfactant and surfactant concentration for use in surfactant flushing operations. We note that the model is not designed to be a high-precision tool to predict the effects of small and subtle differences in molecular structure.

(d) Model for the Formation of Mixed Micelles

The model for micellar solubilization must be modified somewhat if the solubilizate is itself amphipathic (a long-chain alcohol or amine, for instance) or if we wish to describe micelle formation when two surfactants are present. In this model, as in the last, we shall introduce the simplification of considering only the most significant micelles—that is, those which present no hydrophobic area to the aqueous phase. Again without loss of generality, we can take the mechanism of mixed micelle formation to be

$$mA + nB \rightleftharpoons A_mB_n; \qquad m, n = 0, 1, 2, \ldots \tag{58}$$

Let S_A = cross-sectional area of the hydrophilic head of A
S_B = cross-sectional area of the hydrophilic head of B
v_A = molecular volume of A
v_A = molecular volume of B

$r_A = (3v_B/4\pi)^{1/3}$ = effective radius of A, assuming a spherical molecular conformation
$r_B = (3v_B/4\pi)^{1/3}$ = effective radius of B, assuming a spherical molecular conformation

The equilibrium constants for Eq. (58) are

$$K_{mn} = \frac{[A_mB_n]}{[A]^m[B]^n} \tag{59}$$

We focus our attention on that subset of micelles having virtually no hydrophobic surface exposed to the aqueous phase, since the free energies of formation per ion of these will be lower than those of the micelles having hydrophobic surface exposed. The radius of the micelle A_mB_n is given by

$$\frac{4\pi}{3} r_{mn}^3 = mv_A + nv_B \tag{60}$$

The requirement that the micelle have no exposed hydrophobic surface yields

$$4\pi r_{mn}^2 = mS_A + nS_B \tag{61}$$

The maximum value for m (obtained when $n = 0$) is

$$m_{\max} = 36\pi v_B^2/S_A^3 \tag{62}$$

Similarly,

$$n_{\max} = 36\pi v_A^2/S_B^3 \tag{63}$$

(These are rounded off to the nearest integers.)

Eliminating r_{mn} between Eqs. (60) and (61) and rearranging gives

$$3(4\pi)^{1/2}(mv_A + nv_B) - (mS_A + nS_B)^{3/2} = 0 = f(m,n) \tag{64}$$

We wish to calculate $n(m)$ for values of m ranging from 0 to $m_{\max}$. To do this, for a specified value of m we evaluate $f(m,n)$, $n = 0, 1, 2, \ldots$ up to a maximum value of $n_{\max}$. Let n' be the value of n such that $f(m,n')$ and $f(m,n' + 1)$ are of opposite sign. If $|f(m,n')| < |f(m,n' + 1)|$, then set

$n'' = n'$; otherwise set $n'' = n' + 1$. Then the desired value of $n(m)$ is n''. This procedure then gives the compositions $[m,n(m)]$ of all the significant micelles.

The free energy change ΔG^0_{mn} associated with mixed micelle formation is

$$\Delta G^0_{mn} = \mu^0_{mn} - m\mu^0_A - n\mu^0_B \tag{65}$$

as before. Again, this has four components—surface free energy, configurational, translational entropy, and electrical. These are calculated as follows.

(a) Surface Free Energy

Let h_A = hydrophobic surface of monomeric A in a spherical conformation, $= 4\pi r_A^2 - S_A$

h_B = hydrophobic surface of monomeric B in a spherical conformation, $= 4\pi r_B^2 - S_B$

γ_A = surface free energy of the hydrophobic surface of A, erg/cm^2

γ_B = surface free energy of the hydrophobic surface of B, erg/cm^2

Then

$$\Delta G^0_{\text{surface}} = -(mh_A\gamma_A + nh_B\gamma_B) \tag{66}$$

(b) Configurational Free Energy

This is calculated exactly as in the previous model; the result is

$$\Delta G^0_{\text{config}} = kT\left(m \log_e \frac{m}{m+n} + n \log_e \frac{n}{m+n}\right) \tag{67}$$

(c) Electrical

The electrical component of the free energy change is calculated by essentially the same procedure as before. If A is anionic and B is electrically neutral, the result is

$$\Delta G^0_{\text{elec}} = \frac{m^2e^2}{2D(1+\kappa r_{mn})r_{mn}} - \frac{me^2}{2D(1+\kappa r_{\text{A}})r_{\text{A}}} \tag{68}$$

where

$$r_{mn} = \left(\frac{mS_{\text{A}} + nS_{\text{B}}}{4\pi}\right)^{1/2} \tag{69}$$

If both A and B are anionic, we obtain

$$\Delta G^0_{\text{elec}} = \frac{(m+n)^2e^2}{2D(1+\kappa r_{mn})r_{mn}} - \frac{me^2}{2D(1+\kappa r_{\text{A}})r_{\text{A}}} - \frac{ne^2}{2D(1+\kappa r_{\text{B}})r_{\text{B}}} \tag{70}$$

The translational entropy contribution to the free energy change on micelle formation is given by

$$\Delta G^0_{\text{trans}} = -(n + m - 1)T\Delta S^0_1$$

as before.

The standard free energy change for the formation of A_mB_n is then

$$\Delta G^0_{mn} = \Delta G^0_{\text{surface}} + \Delta G^0_{\text{config}} + \Delta G^0_{\text{elec}} + \Delta G^0_{\text{trans}} \tag{71}$$

and the equilibrium constants are given by

$$K_{mn} = \exp(-\Delta G^0_{mn}/kT) \tag{72}$$

Almost as before, our mass balance equations are

$$\text{A}_{\text{total}} = [\text{A}] + \sum_{m=0}^{m_{\max}} mK_{mn}[\text{A}]^m[\text{B}]^{n(m)} \tag{73}$$

and

$$\text{B}_{\text{total}} = [\text{B}] + \sum_{m=0}^{m_{\max}} n(m)K_{mn}[\text{A}]^m[\text{B}]^{n(m)} \tag{74}$$

At this point we are confronted by two cases. In the first case, Component B is a contaminant, present in neat form; then [B] is just the saturation concentration of B in pure water. This value of [B] is inserted in Eq. (73), which becomes a polynomial equation in [A] which is solved by a binary search technique as in the model for the solubilization of hydrophobics. The resulting value for [A] is then substituted into Eq. (74), along with the known value of [B], to obtain the total concentration of B, both free and solubilized, in the solution.

In the second case, both A and B are surfactants, with A_{total} and B_{total} specified. Then both [A] and [B] are unknown, so Eqs. (73) and (74) must be solved simultaneously. This requires a two-dimensional search procedure, and is computationally somewhat more time consuming than the one-dimensional searches required in the previous calculations.

Aggregation numbers can then defined in a number of different ways.

(1) Aggregation Number of A with A. This is the average response to the question, asked of all A ions, "How many A ions, counting yourself, are you associated with?" It is given by

$$\bar{n}_{A/A} = \frac{[A] + \sum_{m=0}^{m_{max}} m(m[A_m B_n])}{A_{total}} \tag{75}$$

$$= \frac{[A] + \sum_{m=0}^{m_{max}} m^2 K_{mn}[A]^m[B]^{n(m)}}{A_{total}} \tag{76}$$

(2) Aggregation Number of A with A and B. This is the average response to the question, asked of all A ions, "How many ions, both A and B and counting yourself, are you associated with?" It is given by

$$\bar{n}_{A/A+B} = \frac{[A] + \sum_{m=0}^{m_{max}} [m + n(m)]mK_{mn}[A]^m[B]^n}{A_{total}} \tag{77}$$

(3) Total Aggregation Number. This is the average response to the question, asked of all A and B ions, "How many ions, both A and B and counting yourself, are you associated with?" It is given by

$$\bar{n}_{\mathrm{A+B/A+B}} = \frac{[\mathrm{A}] + [\mathrm{B}] + \sum_{m=0}^{m_{\max}} [m + n(m)]^2 K_{mn}[\mathrm{A}]^m[\mathrm{B}]^n}{\mathrm{A}_{\mathrm{total}} + \mathrm{B}_{\mathrm{total}}} \tag{78}$$

(4) Aggregation Number of A with B. This is the average answer to the question, asked of all A ions, "How many B ions are you associated with?" It is given by

$$\bar{n}_{\mathrm{A/B}} = \frac{\sum_{m=0}^{m_{\max}} n(m) m K_{mn}[\mathrm{A}]^m[\mathrm{B}]^n}{\mathrm{A}_{\mathrm{total}}} \tag{79}$$

Other aggregation numbers ($\bar{n}_{\mathrm{B/B}}$, $\bar{n}_{\mathrm{B/A+B}}$, $\bar{n}_{\mathrm{B/A}}$) can be defined similarly. Here we are particularly interested in the first case, in which we wish to calculate the maximum concentrations of a polar contaminant which can be solubilized by surfactant solutions of various strengths. In Fig. 11

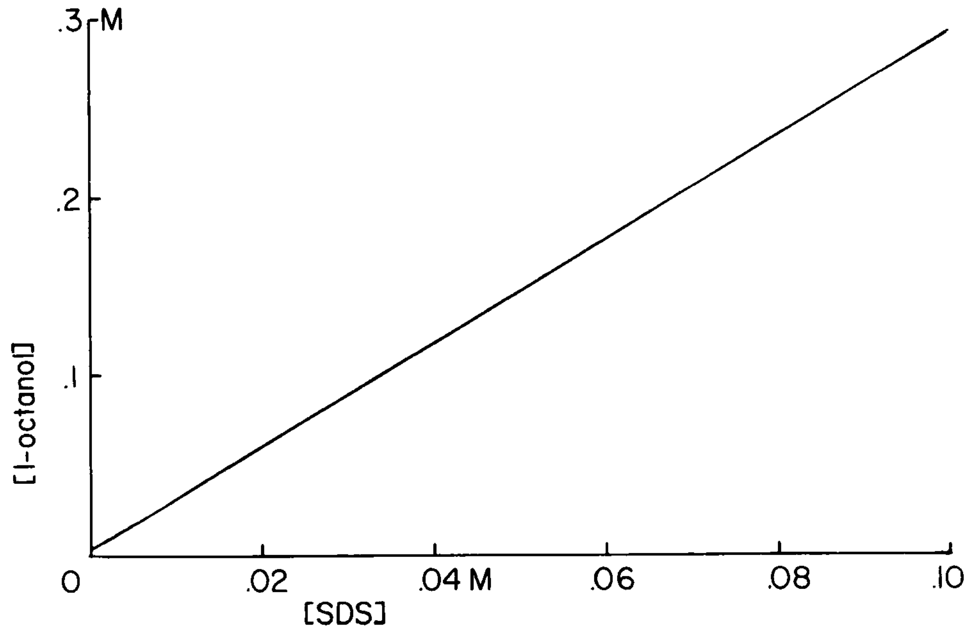

FIG. 11. Simulation of the solubilization of 1-octanol by SDS. Run parameters are given in Table 4.

TABLE 4
Parameters for Micellar Solubilization of 1-Octanol with SDS

Surfactant properties: see Table 1
Temperature = 298 K
Molar translational entropy change per ion or molecular on micellization = −28 cal/mol · degree
Added salt concentration = 0.0 *M*
Properties of 1-octanol:
  Molar volume = 157.93 mL/mol
  Cross-sectional area of hydrophilic head = 46.36 $Å^2$
  Hydrophobic area of molecule = 151.58 $Å^2$
  Surface free energy of water–hydrocarbon tail interface = 50 erg/cm^2
  Solubility in water = 0.0045 *M*

we see the simulated solubilization curve for 1-octanol in sodium dodecylsulfate. Parameters for this run are given in Table 4. The amphipathic contaminant (1-octanol) shows a roughly 30-fold increase in effective solubility as the surfactant concentration increases from 0 to 0.1 *M*. We find, in agreement with experiment, that 1-octanol very markedly decreases the cmc of the surfactant; see, for example, Shinoda (*20*). The plots of total contaminant concentration versus surfactant concentration are linear above the cmc, as was found previously with nonpolar solubilizates.

CONCLUSIONS

We conclude that these rather simple models for the solubilization of polar and nonpolar organic contaminants by surfactant solutions provide useful insight into the nature of the solubilization process. The linear dependence of solubilizate concentration on surfactant concentration is in agreement with experimental results. The theory predicts that enhancements of solubilities of such contaminants by approximately two orders of magnitude can be achieved at surfactant concentrations $\leqslant 0.1$ *M*. The models are capable of being run on readily-available microcomputers; each of the plots presented required only a few minutes of machine time.

We note that the models could be substantially improved by the use of a better method for calculating the electrical free energies; this would add greatly to the computer time required to run the models.

Acknowledgments

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