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Soil Cleanup by In-Situ Surfactant Flushing. IX. Electrical Effects in Micelle Formation

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ABSTRACT

BASIC computer programs were written to model the tendency of ionic surfactants to form micelles at various concentrations. A mass-action, multispecies approach involved the use of the hydrophobic effect and the electrical repulsion of the ionic heads. The Poisson–Boltzmann equation was used to model the electrical effects in both planar and spherical coordinates and with and without linearization of the charge density term. In the most elaborate model a modified Boltzmann charge density expression took into account the finite sizes of the ions surrounding the micelle. A "zero surface tension" approach allowed the calculation of the maximum size of the micelle. Calculations focused on the behavior of sodium dodecylsulfate. Micelle formation as a function of ionic strength and surfactant size were satisfactorily modeled. Temperature dependence was not good, and a fitted nonsurface energy term remains unresolved.

INTRODUCTION

Contamination of soils and aquifers with organic chemicals from improper waste disposal, leaking underground storage tanks, and spills is a major problem in the United States, and there is a good deal of interest

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in cleanup techniques which are effective, economical, and of modest environmental impact. The Superfund amendments have spurred interest in technologies which detoxify the contaminated material or drastically reduce the potential loading to the environment should a release occur. In-situ surfactant washing and (ex-situ) soil surfactant washing are of interest in this connection since they have potential for removing organic compounds of low water solubility from both the vadose zone and the zone of saturation. As indicated in a recent EPA bulletin (1), these and other soil-flushing technologies are still in the developmental stage, but they do show promise for the remediation of soils and aquifers contaminated with PCBs, polynuclear aromatic hydrocarbons, and other hydrophobic organics of low volatility.

Surfactants are effective in removing hydrophobic organics of low water solubility by means of micellar solubilization, by which the solubilities of these compounds in aqueous systems are greatly enhanced if surfactants are present at concentrations above the critical micelle concentration (cmc), so that surfactant micelles are formed. The interiors of the micelles are hydrocarbonlike in character, providing a medium in which nonpolar or slightly polar hydrophobic organics are quite soluble. McBain and Hutchinson's book (2) and Klevens's review article (3) provide excellent background on micellar solubilization.

In two papers on soil surfactant flushing and washing we reviewed the literature on (in-situ) surfactant flushing and (ex-situ) surfactant washing (4, 5); the interested reader is referred to those papers for references.

As indicated above, micellar solubilization plays a crucial role in surfactant-based remediation techniques, so an understanding of micelle formation and micellar solubilization is essential in the design and optimization of these methods. The text by Vold and Vold provides a good foundation for this (6), and Israelachvili has provided a somewhat more advanced thermodynamic treatment (7).

Three general approaches to micelle formation have been advanced: the mass-action model, the phase separation model, and the small system thermodynamic approach. The law of mass action has been applied to micelle formation by many workers, among these being McBain (8), Jones and Bury (9), Murray and Hartley (10), Vold (11), Mysels (12), Corkill (13), and Mukerjee (14). These approaches regard micellization either as the formation of *n*-mer which is in equilibrium with monomer or as a stepwise process with many species of micelles.

In the phase separation model, the formation of the micelle is described as a phase change with the calculation of the thermodynamic chemical potential for each species providing the starting point. Stainsby and Alexander (15), Shinoda (16, 17), McBain and Hutchinson (2), and Matijevic

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and Pethica (18) were among those pioneering this approach. More recently, sophisticated pseudophase separation models have been constructed; see for example the work of Holland and Rubingh (19) and especially Israelachvili et al. (20), who also include geometric constraints. A related approach is the more recent "zero surface tension" theory of Sorensen (21, 22) which uses the thermodynamic theory of droplet nucleation to predict micellar growth and behavior.

Perhaps the most rigorous treatment of the thermodynamics of micelle formation has been the application of Hill's small system thermodynamics (23). Hall and Pethica (24) have given an excellent treatment of this. Due to its complexity, it has received limited use.

With respect to our present knowledge of micelles, the following quote from Sorensen (22) is appropriate; "In spite of an overwhelming literature about micelles, the theories proposed seem to be of an ad-hoc nature and to lack real predictive power." The field is evidently still ripe for study. Since the general approach that will be taken here is the mass action, multispecies approach, a short outline of its features will be presented, following the treatment by Vold and Vold of the equilibria and thermodynamic relations involved in the formation of micelles (6).

For the stepwise formation of a micelle from its monomers one can write for each step

$$\mathrm{M} + \mathrm{M}_n \rightarrow \mathrm{M}_{n+1} \tag{1}$$

where M denotes the monomer and n denotes the number of monomers in the aggregate (from 2 to n_{max}). Applying the law of mass action gives a value for each equilibrium constant,

$$K_{n+1} = \frac{[\mathrm{M}_{n+1}]}{[\mathrm{M}][\mathrm{M}_n]} \tag{2}$$

where the brackets indicate the concentration of the species in mole fraction units and we have assumed ideal behavior. If we define the standard state for the monomer to be infinite dilution, then the free energy change for incorporating 1 mole of monomer into a mole of micelles of size n is

$$\Delta G^\circ = -RT \log_e K_{n+1} \tag{3}$$

from which we obtain

$$\Delta G^\circ = -RT \log_e\left(\frac{[\mathrm{M}_{n+1}]}{[\mathrm{M}_n]}\right) + RT \log_e[\mathrm{M}] \tag{4}$$

Since the ratio $[\mathrm{M}_{n+1}]/[\mathrm{M}_n]$ will be close to unity, the first term of this expression will be much smaller than the second, and the free energy therefore becomes

$$\Delta G^\circ = RT \log_e[\mathrm{M}] \tag{5}$$

Experimentally, one finds that the monomer concentration [M] remains essentially equal to the critical micelle concentration after the cmc is reached, as additional surfactant goes into the formation of more micelles. This allows the substitution of the cmc for [M], so that

$$\Delta G^\circ = RT \log_e \mathrm{cmc} \tag{6}$$

Other thermodynamic parameters such as the enthalpy and entropy of micellization can then be obtained via the Gibbs–Helmholtz equation,

$$\frac{\partial(\Delta G/T)}{\partial T} = -\frac{\Delta H}{T^2} \tag{7}$$

Substituting Eq. (6) into Eq. (7) then gives

$$\frac{\partial(\log_e \mathrm{cmc})}{\partial T} = -\frac{\Delta H}{RT^2} \tag{8}$$

which allows computation of the enthalpy change using the variation of the cmc with temperature. The equation

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

can then be solved for the entropy change.

Experimental studies show that ΔH is very small for most surfactants and can be positive as well as negative. For example, the ΔH for sodium dodecylsulfate (SDS) in water is 0.6 kcal/mol from Eq. (8). Equation (6) gives a ΔG value of -5.23 kcal/mol for SDS (6), so we see from Eq. (9) that ΔS must be positive and relatively large, showing that micellization is an entropy-driven process.

This positive entropy change may not at first seem reasonable for taking surfactant out of the aqueous environment and "confining" it to a micelle. When the surfactant is dissolved in water, however, the hydrophobic part distorts the hydrogen bonding of the water molecules. Solubility studies of hydrocarbons dissolved in water show that the hydrogen bonds are not necessarily broken (as evidenced by the low enthalpy change values), but the restructuring of the water molecules to accommodate the hydrocarbon results in a more orderly arrangement (25). When the hydrocarbon is removed from the water environment and enters the micelle, the water molecules go back to their more disorderly and flexible structure, thereby increasing the entropy. Additionally, the environment of the micelle core itself may contribute to the entropy gain. Although there is no universal agreement as to its exact nature, a consensus exists that it is in a liquidlike

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hydrocarbon state. The increased freedom of the hydrophobic chain in this nonpolar interior may also give some contribution to the entropy (26).

An important parameter of the micellization process is the average aggregation number of the surfactant, the average number of monomer units per micelle. Since the distribution of micellar species is envisioned as being sharply spiked about a maximum after the cmc is reached, this number indicates how large the micelles can become. As an example, SDS has an aggregation number of about 65 at zero added ionic strength and 25°C. Shinoda (27) and Rosen (26) published tables of aggregation numbers for a wide selection of surfactants; these were obtained mainly by light scattering, diffusion-viscosity, and electrophoretic mobility.

A number of factors affect the aggregation number. It increases with the hydrophobic character of the surfactant—i.e., with increasing chain length for a homologous series of surfactants. It increases with the addition of electrolyte to the solution; the effect is more pronounced with ionic surfactants than with nonionics, and involves the neutralization of some of the coulombic repulsion between the ionic heads. This repulsion tends to oppose the micellization process. Solubilized organics also cause an increase in aggregation number. Temperature effects are small, random, and depend on the nature of the polar head group (26).

By far the most important parameter involving micellization is the cmc. Shinoda (27) and Rosen (26) published extensive cmc data, and Mukerjee and Mysels (28) discussed methods and tabulated values for 721 compounds. The conclusions which can be drawn are as follows. As the hydrophobic character of the surfactant (such as hydrocarbon chain length) increases, the cmc decreases. Ionic surfactants typically have larger cmc's than nonionic surfactants, attributed to the electrical repulsions between the ionic heads. Since added electrolytes tend to decrease this repulsion, they also decrease the cmc. Two competing factors seem to be involved in the effect of temperature. First, an increase in temperature causes decreased hydration of the hydrophilic head group, favoring micellization. In opposition, an increase in temperature causes disruption of the structured water environment, which disfavors micellization. Critical micelle concentrations seem to reach a minimum for ionic surfactants at about 25°C and at about 50°C for nonionics (26).

Earlier we developed some mathematical models for describing the solubilization of various types of contaminants in micelles of ionic and nonionic surfactants (29). Contaminants which are purely hydrophobic and those which are amphipathic were handled, and electrical effects were described by means of a Debye–Huckel theory type approach. The models indicated that the concentration of contaminant solubilized is a linear function of the total surfactant concentration provided that this is above the

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cmc of the surfactant, in agreement with experimental results. They predicted reasonable dependence of cmc on surfactant hydrocarbon chain length and on solution ionic strength (for ionic surfactants). However, the predicted temperature dependence of the cmc was much too large, and the Debye–Huckel theory approximations used in handling the electrical interactions were felt to be too crude.

Six mathematical models were therefore developed for predicting the cmc of an ionic surfactant in aqueous solution as a function of ionic strength, temperature, and surfactant dimensions. Parameters for SDS were used primarily, and the theoretical results were compared to experimental values from the literature. The models were based on a mass-action, multispecies approach to the formation of aggregates and involved the calculation of opposing energy terms. These involved the use of surface tension for the attractive hydrophobic effect and a Poisson–Boltzmann equation treatment for the electrical repulsion of the ionic heads. The Poisson–Boltzmann equation was solved in both planar and spherical coordinates with and without linearization of the charge density term. Additional refinements included in some of the models were 1) the use of a modified charge density expression which takes into account the finite sizes of the ions surrounding the micelle, and 2) the incorporation of a "zero surface tension" approach which allows ready calculation of the maximum size of the micelle. Table 1 describes each model.

Of these six models, the best results were obtained for that which used the above two refinements and in which the Poisson–Boltzmann equation was solved in spherical geometry without linearization of the charge den-

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TABLE 1
Definition of Different Models

Model	Poisson's equation geometry	Charge density term[a]	Linearization of Poisson–Boltzmann	Zero surface tension approach[b]
I	Planar	Boltzmann	Yes	No
II	Spherical	Boltzmann	Yes	No
III	Planar	Boltzmann	No	No
IV	Planar	Modified Boltzmann	No	No
V	Planar	Modified Boltzmann	No	Yes
VI	Spherical	Modified Boltzmann	No	Yes

[a] The modified Boltzmann treatment takes into account the finite sizes of the ions in the electrical double layer.

[b] The zero surface tension approach allows prediction of maximum aggregate size.

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sity term. The dependence of the cmc on solution ionic strength and on surfactant dimensions was satisfactory, but the temperature dependence of the cmc predicted by this best model was rather poor, and the explanation of a fitted nonsurface energy term remains unresolved.

We here discuss the most realistic model developed, which is also the most satisfactory one in terms of agreeing with experimental results; we shall make only passing reference to the other five models, which are discussed in detail elsewhere (30).

ANALYSIS

As noted above, our multispecies mass action approach requires a series of stepwise equilibria as follows.

$$\begin{aligned} \mathrm{M} + \mathrm{M} &\rightarrow \mathrm{M}_2 \\ \mathrm{M}_2 + \mathrm{M} &\rightarrow \mathrm{M}_3 \\ \mathrm{M}_n + \mathrm{M} &\rightarrow \mathrm{M}_{n+1} \end{aligned} \tag{1'}$$

The equilibrium constants are

$$K_{n+1} = \frac{[\mathrm{M}_{n+1}]}{[\mathrm{M}][\mathrm{M}_n]} \tag{2'}$$

These are related to the standard free energy changes by

$$\Delta G^\circ_{n+1} = -RT \log_e K_{n+1} \tag{3'}$$

The standard free energy changes are partitioned as follows.

$$\Delta G^\circ_{n+1} = \Delta G^\circ_{\text{hydrophobic}} + \Delta G^\circ_{\text{nonsurface}} + \Delta G^\circ_{\text{electrical}} \tag{10}$$

Our first four models were unable to account for the variations in the maximum aggregation number of surfactant micelles as a function of ionic strength and temperature; this seriously limited their usefulness. Sorensen (21, 22) developed a theory of micellization which incorporates surface tension at the exterior surface of the micelle. As the micelle grows in size, the surface tension gradually decreases as a result of the adsorption of surfactant and finally reaches zero at some aggregation number. This is the maximum aggregation number, as growth of the micelle stops at this point. The aggregation number for this point of zero surface tension is a function of surfactant monomer size, polar head size, temperature, and the electrical interactions on the surface of the micelle. The electrical interaction, as will be seen shortly, is very dependent on ionic strength as well as on the size of the micelle, the size of the surfactant monomer,

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and even the size of the surfactant counterion. It is also weakly dependent upon temperature.

Sorensen's "zero surface tension" (ZST) theory remains rather weakly developed for ionic surfactants because of the approximations he used for electrical interactions. We felt that it might be fruitful to incorporate his ideas for micellar growth into our mass action multispecies approach in order to achieve variability in micellar aggregation numbers as well as better cmc values.

We begin by examining Sorensen's picture of a micelle, given in Fig. 1. The hydrocarbon chains of the surfactants form an "oil-like" hydrophobic core, which is surrounded by the polar head groups. The placement of the surface of tension can be accommodated to fit experimental data, and it reveals information about the structure of the micelle.

In the absence of electrical interactions, the surface tension (γ) of the micelle changes because of the adsorption of polar heads at the surface of tension. By combining the Langmuir isotherm and the Gibbs equation, the Szyszkowski isotherm is obtained (31). This is

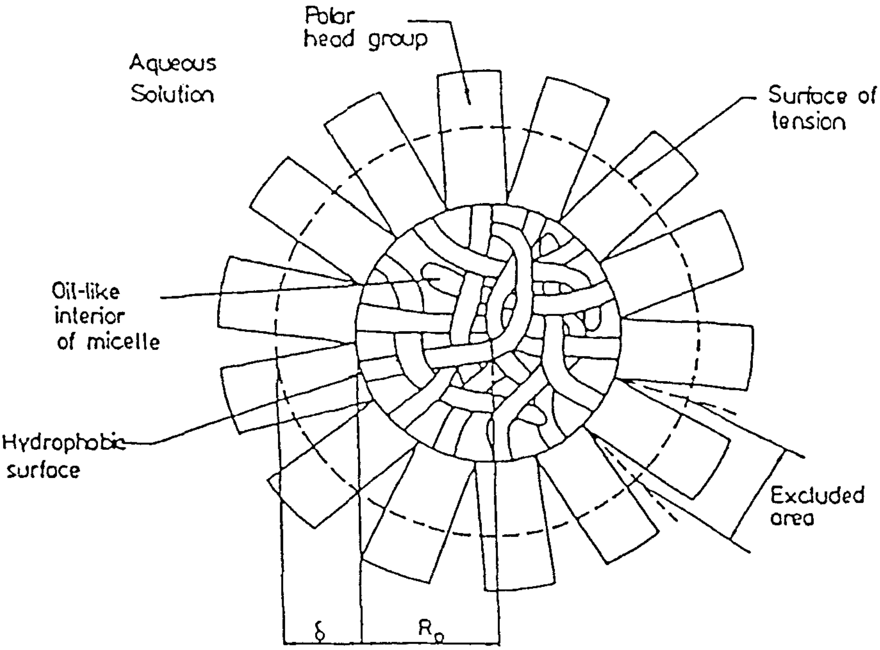

FIG. 1 Model of the micelle as a spherical oil-like droplet surrounded by polar heads. Taken from Sorensen (22).

$$\pi = \gamma_o - \gamma = -\frac{kT}{a_{\min}} \log_e\left(1 - \frac{a_{\min}}{a}\right) \tag{11}$$

where π is the surface pressure, γ_o is the surface tension at the oil–water interface, γ is the surface tension after adsorption of surfactant, k is Boltzmann's constant, $a_{\min}$ is the excluded cross-section area of the polar head of the surfactant, and a is the total surface area per monomer in the micelle. The variable a can be calculated from the radius of the micelle r_n and the number of monomers in the micelle n as follows:

$$a = 4\pi r_n^2/n \tag{12}$$

For the case of ionic surfactants, the surface tension decrease also involves a contribution from the electrical interactions at the surface of the micelle. Incorporation of this term in Eq. (11) and rearrangement gives

$$\gamma = \gamma_o + \frac{kT}{a_{\min}} \log_e\left(1 - \frac{a_{\min}}{a}\right) - \int_0^{\Psi_o} \sigma d\Psi \tag{13}$$

with $-\int_0^{\Psi_o} \sigma d\Psi$ representing the electrical work, the chemical potential energy change associated with the formation of the electric double layer. This electrical work term can be obtained for a micelle of given size once its surface potential Ψ_o is known. A Guntelberg charging process is used to find the electrical energy required to charge a micelle composed of n monomers

$$\int_0^{\Psi_o} \sigma d\Psi = \int_0^1 \Psi(r_n, \lambda)(-en d\lambda) \tag{14}$$

The surface potential Ψ_o of the micelle is determined by the solution to the nonideal, modified Poisson–Boltzmann equation in spherical geometry, which will be described later.

In our first four models the surfaces of the micelles were partitioned into hydrophobic and hydrophilic areas. The hydrophobic standard free energy for each species of micelle was computed as the product of the hydrophobic surface of the micelle and a constant surface tension (50 erg/cm^2 for an oil–water interface). To incorporate the zero surface tension approach, we use the computed value of the surface tension for each species of micelle and multiply by the total surface area of that micelle.

Both approaches to the hydrophobic surface standard free energy give a hydrophobic free energy value which decreases with increasing micellar size, but the advantage of the ZST approach is obvious. It allows the prediction of maximum aggregate size as a function of changes in ionic strength, temperature, surfactant monomer size, radius of surfactant polar head, and surfactant counterion size.

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We next turn to the calculation of the electrical contribution to the standard free energy of a micelle. This was done at several levels of approximation in our modeling. The electrical potential in the solution is given by Poisson's equation,

$$\nabla^2\Psi = -4\pi\rho/D \tag{15}$$

where ρ is the charge density and D is the dielectric constant of the medium. The charge density ρ is given by

$$\rho = z^+ec^+ - z^-ec^- \tag{16}$$

where z^+ and z^- are the magnitudes of the charges (in units of e, the electronic charge) of the cation and anion, respectively, in the solution which are available to establish the ionic atmospheres of the micelles, and c^+ and c^- are the concentrations of these species. In the following we shall assume that $z^+ = z^- = 1$.

Two major factors influence the level of approximation of the calculation of the electric potential Ψ in the solution. The first is whether or not the charge density term in the Poisson–Boltzmann equation is simplified by expanding it in ascending powers of Ψ and retaining only the linear term. The second is the choice of planar geometry (an approximation) or spherical geometry (correct) for Poisson's equation itself.

The linearization of the charge density ρ, which involves sinh $e\Psi/kT$, implies that $e\Psi/kT$ must be substantially less than 1 throughout the domain of interest. This is not true unless one is at very high ionic strengths. Figure 2 shows how the linearized Models I and II predict much too high values of the surface potential at low ionic strengths.

It is intuitive, but perhaps less obvious mathematically, that the use of planar geometry for the calculation, as opposed to spherical, is also a poor choice. This is particularly true if the Debye length is comparable in size to, or larger than, the radius of the micelle. This, in turn, typically requires ionic strengths which are 1 M or greater as shown in Fig. 3.

The breakdown of the two approximations (linearization of the charge density and the use of planar geometry) rules out analytical solutions to the Poisson–Boltzmann equation. Since we are therefore going to have to use numerical solutions throughout, rather than analytical solutions, there is no reason not to include the effect of the finite sizes of the ions in our Poisson–Boltzmann equation. Some years ago we followed an approach used by Macdonald and Brachman (32) to develop a Poisson–Boltzmann equation which includes this effect (33). The result, for spherical geometry, is

$$\frac{1}{r^2}\left[\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right)\right] = \frac{A\,\sinh(e\Psi/kT)}{1 + B\,\cosh(e\Psi/kT)} \tag{17}$$

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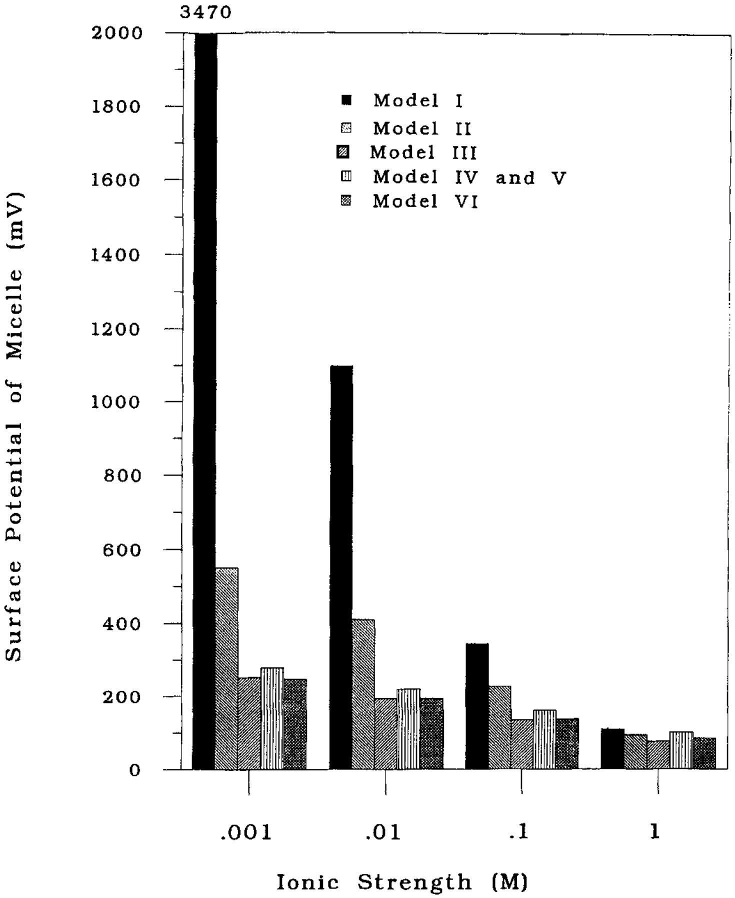

FIG. 2 The surface potential of a micelle as a function of ionic strength for the various models at 298 K. See Table 1 for the definitions of the various models.

where $A = \dfrac{8\pi e c_\infty}{(1 - 2c_\infty/c_{\max})D}$

$B = 2c_\infty/(c_{\max} - 2c_\infty) \qquad (18)$

c_∞ = concentration of 1-1 electrolyte in bulk solution, cations/cm^3

$c_{\max} = 1/v$

v = volume of a hydrated anion if $\Psi > 0$

v = volume of a hydrated cation if $\Psi < 0$

Equation (17) cannot be solved in closed form, so numerical techniques must be used. First, this second-order nonlinear differential equation is

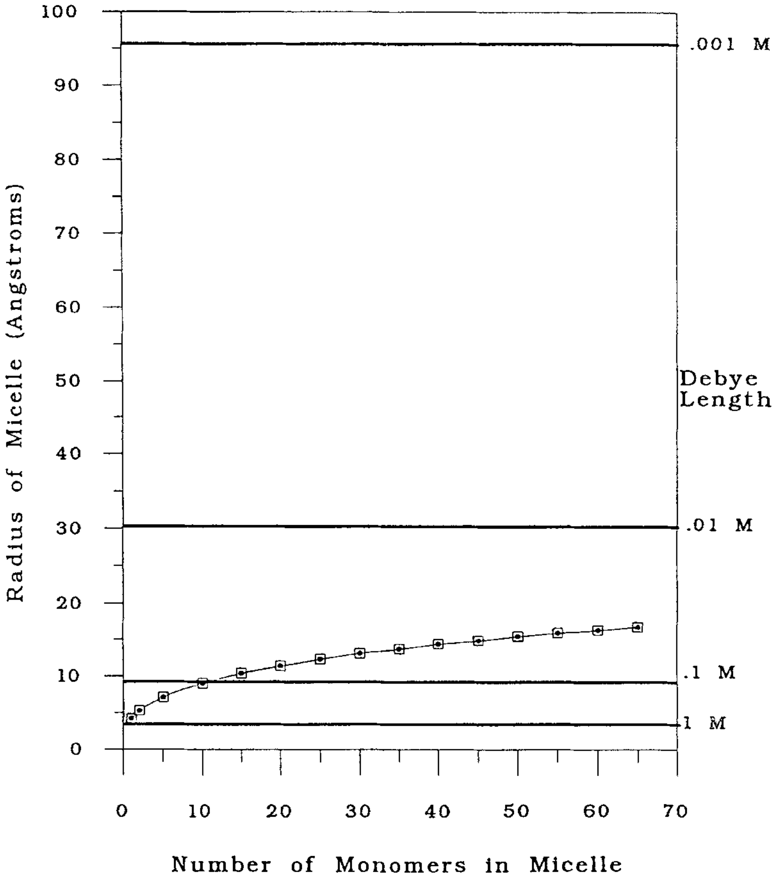

FIG. 3 The radius of an SDS micelle as a function of the number of monomer units. The heavy lines indicate the Debye length for the ionic atmosphere at various ionic strengths.

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replaced by two first-order equations,

$$d\Psi/dr = X \tag{19}$$

and

$$\frac{dX}{dr} = -\frac{2}{r}X + \frac{A\sinh(e\Psi/kT)}{1 + B\cosh(e\Psi/kT)} \tag{20}$$

The known boundary conditions are at $r = \infty$ and $r = r_n$, unfortunately. At $r = \infty$,

$$\Psi(\infty) = 0 \tag{21}$$

At $r = r_n$ we make use of the requirement that the micelle plus its ionic atmosphere must be electrically neutral; for a micelle containing n ions of a singly-charged anionic surfactant this gives

$$-\frac{ne}{4\pi r_n^2} = -\frac{D}{4\pi}\frac{d\Psi(r_n)}{dr} \tag{22}$$

so the boundary condition at the surface of the micelle is

$$\frac{d\Psi(r_n)}{dr} = \frac{ne}{Dr_n^2} \tag{23}$$

The fact that the boundary conditions are at opposite ends of the range of r necessitates that we use a so-called shooting technique to construct the desired solution. This is done as follows. For the integration of Eqs. (19) and (20) a predictor–corrector method of the following type is used.

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Starter Formulas:

Predictor

$$\Psi^* (r + \Delta r) = \Psi(r) + \Delta r \frac{d\Psi(r)}{dr} \tag{24}$$

$$X^* (r + \Delta r) = X(r) + \Delta r \frac{dX(r)}{dr} \tag{25}$$

Corrector

$$\Psi(r + \Delta r) = \Psi(r) + \frac{\Delta r}{2}\left(\frac{d\Psi(r)}{dr} + \frac{d\Psi^* (r + \Delta r)}{dr}\right) \tag{26}$$

$$X(r + \Delta r) = X(r) + \frac{\Delta r}{2}\left(\frac{dX(r)}{dr} + \frac{dX^* (r + \Delta r)}{dr}\right) \tag{27}$$

General Formulas:

Predictor

$$\Psi^* (r + \Delta r) = \Psi(r - \Delta r) + 2\Delta r \frac{d\Psi(r)}{dr} \tag{28}$$

$$X^* (r + \Delta r) = X(r - \Delta r) + 2\Delta r \frac{dX(r)}{dr} \tag{29}$$

Corrector

$$\Psi(r + \Delta r) = \Psi(r) + \frac{\Delta r}{2}\left(\frac{d\Psi(r)}{dr} + \frac{d\Psi^*\,(r + \Delta r)}{dr}\right) \tag{30}$$

$$X(r + \Delta r) = X(r) + \frac{\Delta r}{2}\left(\frac{dX(r)}{dr} + \frac{dX^*\,(r + \Delta r)}{dr}\right) \tag{31}$$

This algorithm is used to integrate the differential equations from some distance r_{max} (several Debye lengths) away from the surface of the micelle (where Ψ is assumed to have the boundary value 0) back to the surface of the micelle. The range of r is divided into subintervals Δr, an initial guess for $d\Psi(r_{\text{max}})/dr$ is chosen, and $d\Psi/dr$ values are predicted and corrected at each step in the numerical integration. At the surface of the micelle the value of $d\Psi/dr$ resulting from the numerical integration is compared to the correct value from Eq. (23). If these are not sufficiently close, the initial guess for $d\Psi(r_{\text{max}})/dr$ is rescaled by multiplication by the ratio $[d\Psi(r_n)/dr]_{\text{true}}/[d\Psi(r_n)/dr]_{\text{numerical}}$, and the process of numerical integration is carried out again with this new value for $d\Psi(r_{\text{max}})/dr$. This process is continued until the calculated value of $d\Psi(r_n)/dr$ converges to the boundary value specified by Eq. (23). Then the value of $\Psi(r_n)$ is the desired value of Ψ_0. The values of Ψ_0 obtained from these calculations allow an examination of the surface potential of the micelle as a function of ionic strength and micelle size.

The calculation of the electrical interaction energy via the Guntelberg charging process also requires numerical integration. Since the free energy of the charging process of the n ionic heads of the micelle is

$$G^{\circ}_{\text{electric}} = \int_0^1 \Psi_{\text{o}(r_n,\lambda)}(-en\,d\lambda) \tag{32}$$

The charging parameter λ must be incorporated into the differential equations (from which Ψ is calculated) by replacing e by λe in Eqs. (19), (20), and (23). Values of $\Psi_0(\lambda)$ are then calculated as a function of λ for a set of values of λ spanning the range (0, 1). These values of Ψ_0 are used in the numerical integration of Eq. (32) to calculate the electrical free energies of the various micellar species, from which, in turn, the $\Delta G^{\circ}_{n(\text{electric})}$ are calculated.

The zero surface tension (ZST) approach was then used to predict the maximum micellar size as a function of ionic strength and the surface tension for micelles of each size. At this point the attractive hydrophobic energy and the repulsive electrical interaction energy are determined for each species of micelle. The equilibrium constants are then computed and

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the concentration of each species of micelle is determined. The sharp break in a plot of mean association number versus surfactant concentration then gives the cmc. The mean association number $\langle n \rangle$ is calculated from

$$\langle n \rangle = \frac{\sum_{n=1}^{n_{\max}} n^2[\mathrm{M}_n]}{\sum_{n=1}^{n_{\max}} n[\mathrm{M}_n]} \tag{33}$$

A subroutine for calculating electrical free energies from the nonlinearized, nonideal Poisson–Boltzmann equation in spherical coordinates described above and the Guntelberg charging process was written in TurboBASIC (Borland) and incorporated into a program using the ZST approach for calculating the hydrophobic free energies and the maximum micellar size. The validity of the subroutine was tested by varying the number of steps in the integration of the differential equations and computing the values of Ψ_0. Table 2 shows that the calculated surface potential values do converge to a definite limit as the number of steps in the numerical integration is increased.

When 25 steps were used in the predictor–corrector numerical integration for Ψ_0 and 20 steps were used in the Guntelberg charging process integration, a computer run for 20 surfactant concentrations took about 10 hours on an MMG 286 machine running at 12 MHz and equipped with an 80287 math coprocessor. The use of 50 steps in the numerical integration for Ψ_0 required nearly 20 hours of computer time for a similar run. For the studies reported here, it was felt that 25 steps in the integration for Ψ_0 and 20 steps in the integration for the Guntelberg charging process

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TABLE 2

Variation of Surface Potential with Integration Step Size

Number of integration steps	Potential at micelle surface (mV)[a]
25	172
50	187
75	193
100	195
125	195
150	196

[a] Calculated for a 65 monomer SDS micelle with 0.01 M added 1-1 electrolyte, integration starts 150 Å from the micelle surface.

would be sufficient to establish trends. For more quantitative work it would be advisable to increase the number of steps in the integration for Ψ_0 to 75 or 100 and to increase the number of steps in the Guntelberg charging process integration to at least 50.

Model parameters were assigned as follows.

- The surface tension of the hydrocarbon–water interface was assigned a value of 50 erg/cm^2, the value given by Adamson (34) for a heptane–water interface.
- The dielectric constant of water at 298 K was taken as 78.4 (35).
- The value for $a_{\min}$, the cross-sectional area of a sulfate polar head, was assumed to be 17 Å^2 (36).
- The nonsurface standard free energy change was regarded as an adjustable parameter and was assigned to give a correct cmc value for SDS from the theory.
- A value for $c_{\max}$ of 10 M was chosen. Results are not very sensitive to the exact value selected for this parameter, and this value seemed to be well within the range of reasonable values.
- Temperature, surfactant concentration, and bulk added electrolyte concentration ($c\infty$) were allowed to vary.

Data for sodium alkylsulfate surfactants are given in Table 3. A value of 65 was used as the experimental value of aggregation number for SDS at 298 K, 0.0082 M surfactant concentration (the cmc), and zero added ionic strength (26–28). The effective value of r_n, which defines the radius of the spherical surface of tension, was obtained by trial-and-error fitting

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TABLE 3
Data for Sodium Alkylsulfate Surfactants

No. of carbons in chain	Partial molar volume (mL/mol)[a]	Effective radius (Å)	Cmc (mol/L)[b]
8	172.7	4.09	0.13
9	188.4	4.21	0.055
10	204.1	4.33	0.033
11	219.8	4.43	0.015
12	234.4	4.53	0.0081–0.0085
13	251.2	4.64	N/A[c]
14	266.7	4.73	0.002

[a] Partial molar volumes from Corkill et al. (37).
[b] Cmc's from Mukerjee and Mysels (28).
[c] Not available.

to the known aggregation number under these conditions. The value was determined to be 16.9 Å, which is 1.3 Å from the outer surface of the micelle, the radius of which is defined by

$$r_n = r_1 n^{1/3} = 18.2 \text{ Å} \tag{34}$$

where r_1 is calculated from the partial molar volume of SDS; see Table 3. The effective value for r_n, 16.9 Å, is then used to calculate an effective value for r_1 by use of Eq. (34); this yields a value of 4.20 Å, which was used in the calculations for SDS.

The location of a surface of tension inside the surface of the micelle has been explained by Sorensen in two ways: (1) water penetration past the ionic heads, and (2) head group burial into the hydrophobic core. Sorensen gives the following relationship for the hydrophobic core that is based on the volume V_0 in Å^3 of a single alkane chain composed of n_c carbons:

$$V_0 = 27.4 + 26.9n_c \tag{35}$$

For a 12-carbon chain this corresponds to a volume of 350 Å^3. If this volume is spherical, its radius would be 4.37 Å, so our model thus gives a surface of tension which lies slightly within the hydrophobic core.

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RESULTS AND DISCUSSION

Figure 4 shows the break in the plot of mean association number versus nominal SDS concentration. To get a cmc of 0.008 M requires a value of 7.3×10^{-13} ergs for the nonsurface free energy change associated with micelle formation. This is substantially greater than one would expect from the entropy contribution due to loss of translational and rotational degrees of freedom, and implies the existence of other, as yet unknown, nonsurface repulsive energy terms.

The effect of an added 1:1 electrolyte on the maximum aggregation number for SDS is given in Fig. 5 and is compared with results from our Model V, which assumed planar geometry for calculating the electrical free energies. Both geometries are in satisfactory agreement with the literature, but the growth in micellar size with ionic strength is less pronounced in the model which assumes spherical geometry (our Model VI). Literature values are highly variable, but the general trend is a rapid rise in aggregation number as the ionic strength increases up to 0.1 M, followed by a leveling off in aggregation number in the 100–200 range.

Increasing the ionic strength also causes a decrease in the cmc within the framework of Model VI, although the decrease is not as large as is

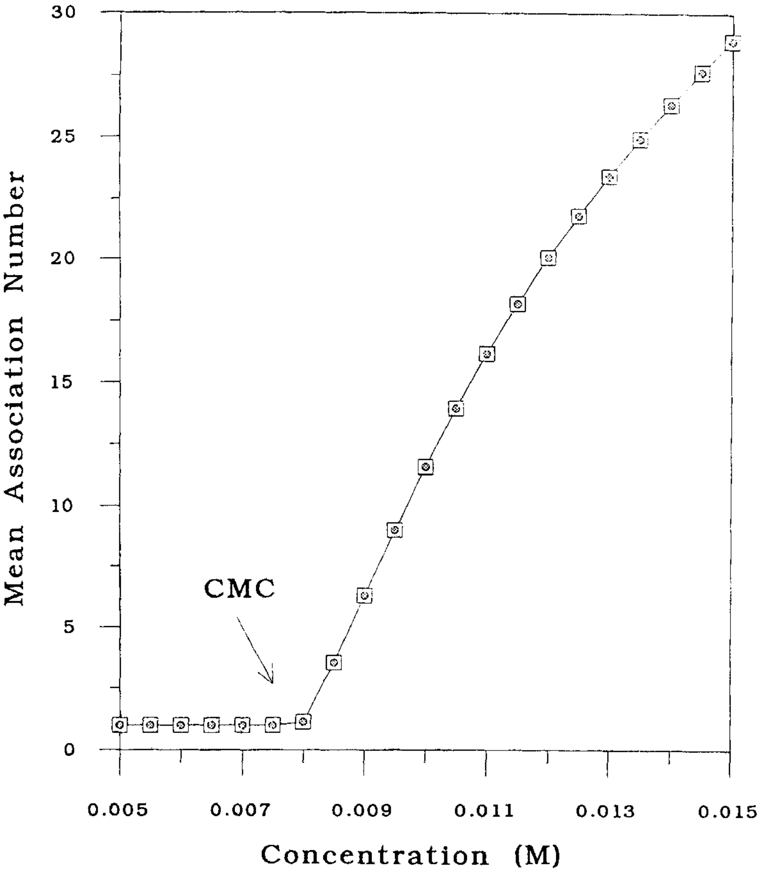

FIG. 4 Mean association number (average aggregation number) as a function of SDS concentration for Model VI. Salt concentration = 0, T = 298 K.

observed experimentally. Figure 6 shows plots of experimental and theoretical cmc values versus ionic strength.

Figures 7 and 8 show the SDS monomer concentration and overall speciation of SDS as functions of total SDS concentration at room temperature in the absence of any added salt. In Fig. 7 we see that, as expected, the SDS monomer concentration increases negligibly above the cmc. A logarithmic concentration scale covering an enormous range is used in Fig. 8. At a total SDS concentration of 0.005 M, the concentrations of the larger micelles are all vanishingly small. At total SDS concentrations

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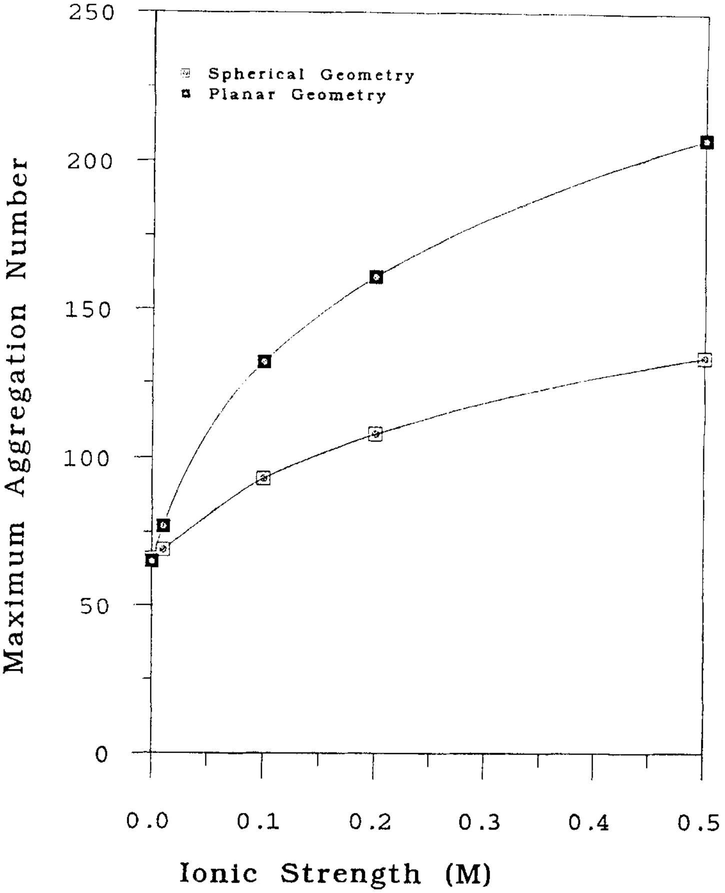

FIG. 5 The effect of a 1-1 electrolyte on the maximum aggregation number of SDS as predicted by Model VI (spherical geometry) and Model V (planar geometry).

of 0.0085 (just above the cmc) and 0.0145 (well above the cmc), quite substantial concentrations of the larger micelles are present. Micelles in the intermediate size range, say from 10 to 50 monomer units, are never present to any great extent because of the relatively high free energies associated with the rather hydrophobic character of their surfaces (or, equivalently, their relatively high surface tensions).

The temperature dependence of the cmc was not modeled satisfactorily by any of our models. In the results calculated with Model VI the temperature dependence of the dielectric constant was included by fitting a quad-

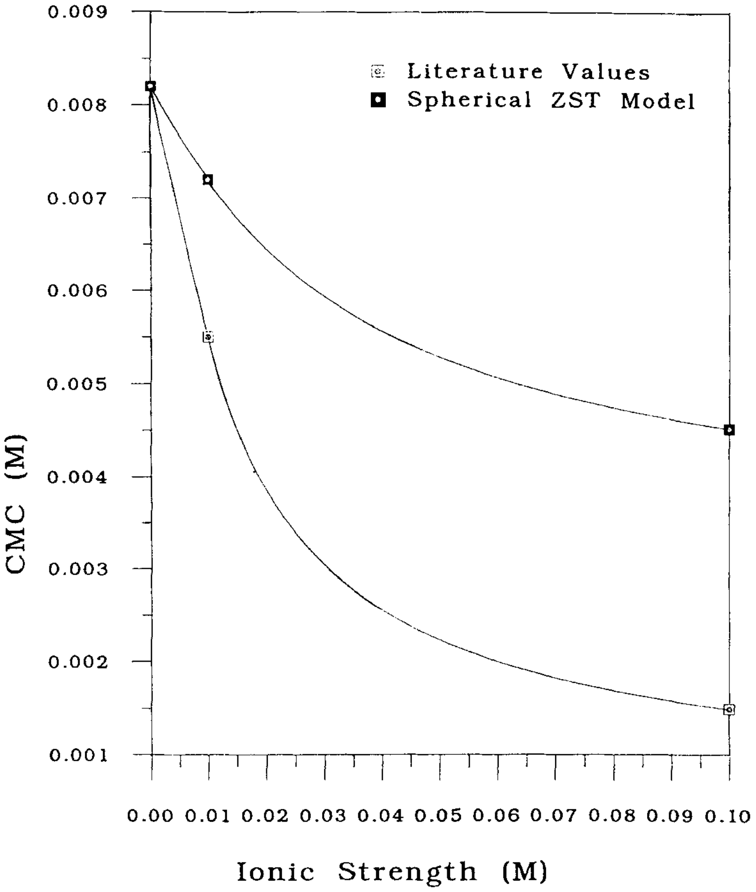

FIG. 6 The effect of a 1-1 electrolyte on the cmc of SDS at 298 K as predicted by Model VI. Literature values from Mukerjee and Mysels (28).

ratic to data published in Bockris and Reddy (38); these data are given in Table 4. Experimentally, the effect is complex; Rosen (26) states that the cmc appears to decrease with increasing temperature to some minimum value and then to increase with further increase in temperature. He ascribes this to competition between two factors. A temperature increase causes a decrease in hydration of the hydrophilic ionic head, which would favor micelle formation. On the other hand, increasing temperatures also cause disruption of the structured water surrounding the nonpolar hydro-

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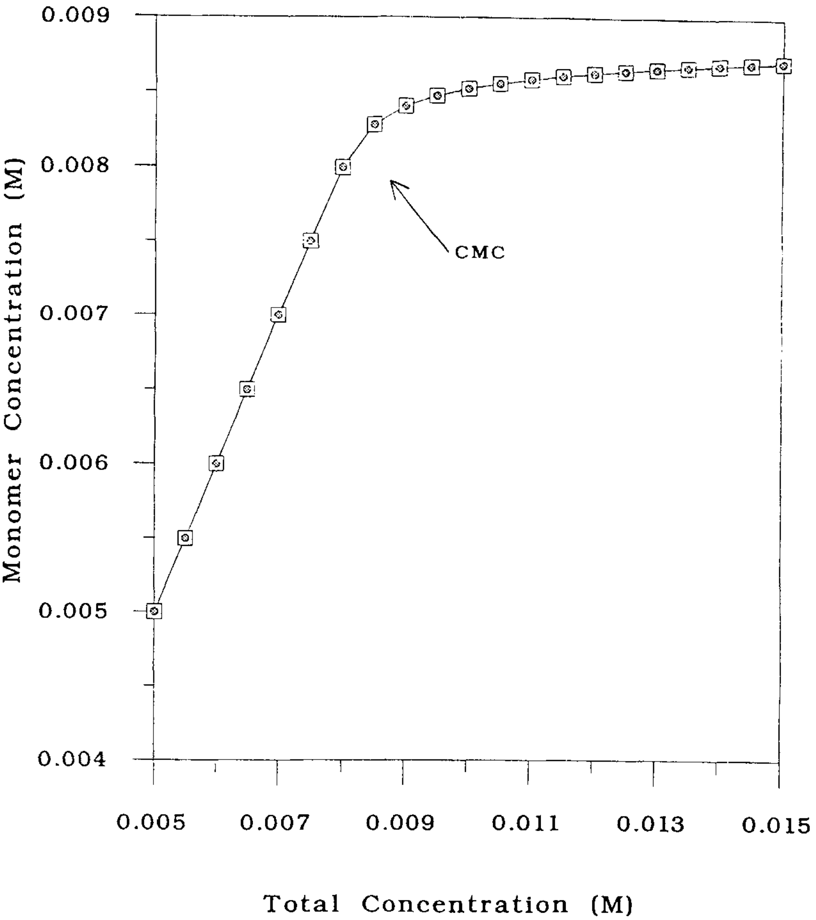

FIG. 7 The monomer concentration as predicted by Model VI as a function of total SDS concentration. Salt concentration = 0, T = 298 K.

carbon part of the surfactant, which would oppose micelle formation. These factors are not directly taken into account in any of our models.

Figure 9 shows plots of theoretical values for the cmc from Model VI versus temperature, along with experimental values for the cmc, both for SDS. A least-squares plot of $\log_e$ cmc versus $1/T$ yielded a value of the enthalpy of micellization of about -11.2 kcal/mol, far different from the reported value (6) of 0.6 kcal/mol.

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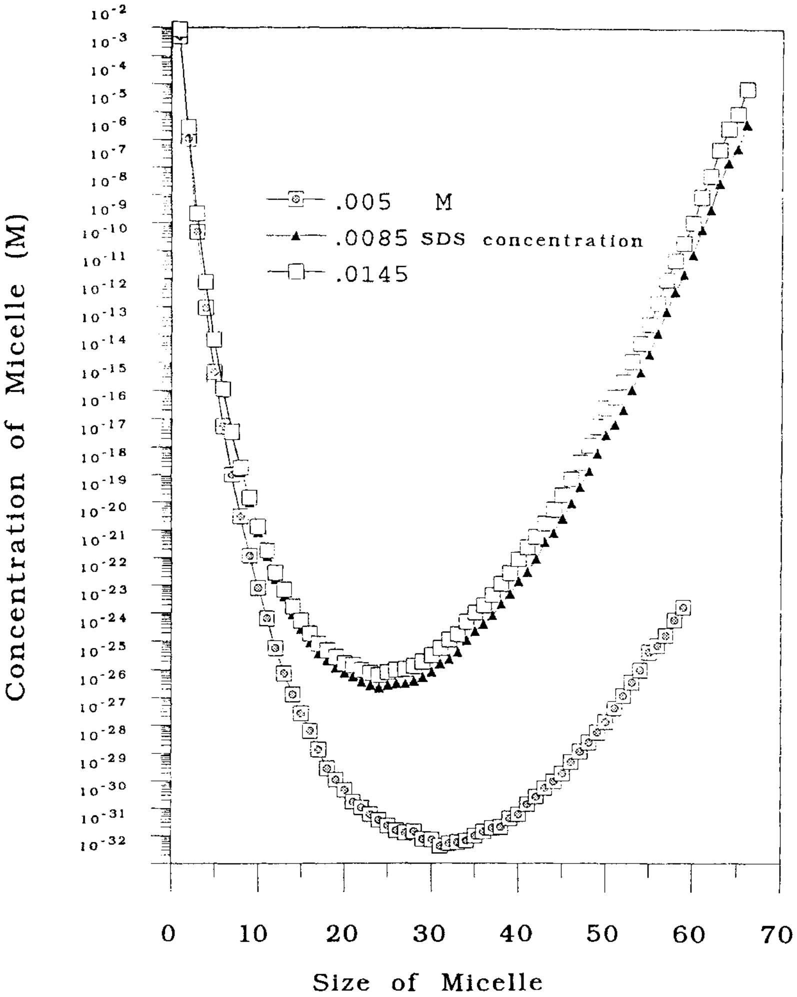

FIG. 8 Speciation diagram for micellar aggregates at different SDS concentrations as predicted by Model VI. cmc = 8.03×10^{-3}, salt concentration = 0, T = 298 K.

If one assumes that the electrical and hydrophobic interactions have been handled approximately correctly, then the most obvious source of error for the temperature dependence becomes the nonsurface contribution to the free energy change, a fitted parameter of rather unclear origin. It would appear that this must involve both entropy and enthalpy terms,

TABLE 4
Temperature Dependence of the Dielectric Constant of Water

Temperature (°C)	Dielectric constant
10	84.2
25	78.4
62	66.2

of which the latter would contribute to the overall enthalpy change for the process.

Another possibility is that the electrical interactions may still not be correct because of our use of a model in which the micelle is imbedded

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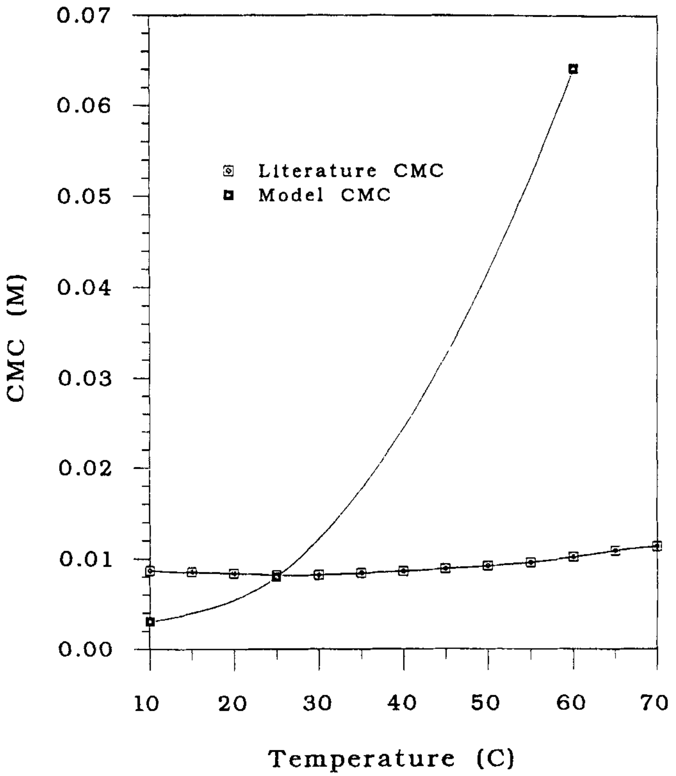

FIG. 9 The effect of temperature on the cmc of SDS as predicted by Model VI. Literature values from Ref. 28. Salt concentration = 0.

in a medium of constant dielectric constant. In Hill's (39) discussion of Debye–Huckel theory he states, "If one is interested in temperature and pressure effects on an electrolyte solution, the solvent must be treated explicitly as a molecular species." The difficulties involved in developing a treatment for micelle formation at that level of complexity are mind-boggling, and we must therefore resign ourselves for the present to models which do not describe the effects of temperature variations adequately.

The ability to predict the behavior of other ionic surfactants provides another test of our model. A series of sodium alkylsulfates was examined. The ZST approach allows the investigation of the dependence of maximum aggregation number, as well as cmc, on chain length of the surfactant.

Model VI involves the location of a surface of tension at a distance r_n from the center of the micelle. In the model r_n is a function of aggregation number n and the effective radius of the surfactant monomer r_1, given by $r_n = r_1 n^{1/3}$. Since reliable aggregation numbers were not available except for SDS, the surface of tension could not be fitted for the other surfactants. Estimates of the effective r_1 for the other sodium alkylsulfates were obtained by assuming similar values for water penetration into the micelle as had been calculated for SDS. Earlier in this paper, water penetration into an SDS micelle (as predicted by Model VI) was estimated to be 1.3 Å in from the outer surface of the micelle, which gave a decrease of 0.33 Å for r_1 below the value calculated from the partial molar volume; the effective r_1 for SDS was taken as 4.20 Å. This same quantity (0.33 Å) was subtracted from the r_1 values calculated from partial molar volume data for the other alkylsulfate surfactants. These r_1's were then used in the determination of the maximum aggregation number for each surfactant concentration. At the computed cmc's the estimated r_1 was found to give a total micellar size that has the same approximate water penetration as SDS (1.3 Å), so this approach is at least self-consistent.

The effect of chain length on the cmc for the series of sodium alkylsulfates is shown in Fig. 10 for zero and 0.1 M added inert 1-1 electrolyte. Agreement with the experimental results is respectable but not outstanding, and gets worse as we move farther away from SDS (12 carbons). This may be due to the manner in which the effective r_1 values were obtained, and suggests that the water penetration may not be constant within a homologous series of surfactants.

Figure 11 shows plots of maximum aggregation number as a function of hydrocarbon chain length for Model VI. The figure indicates that with no added electrolyte the aggregation numbers decrease as the chain length increases, but at high added ionic strengths (i.e., 0.1 M) the aggregation number increases with chain length. It is generally accepted that, experimentally, aggregation numbers are found to increase with the hydrophobic

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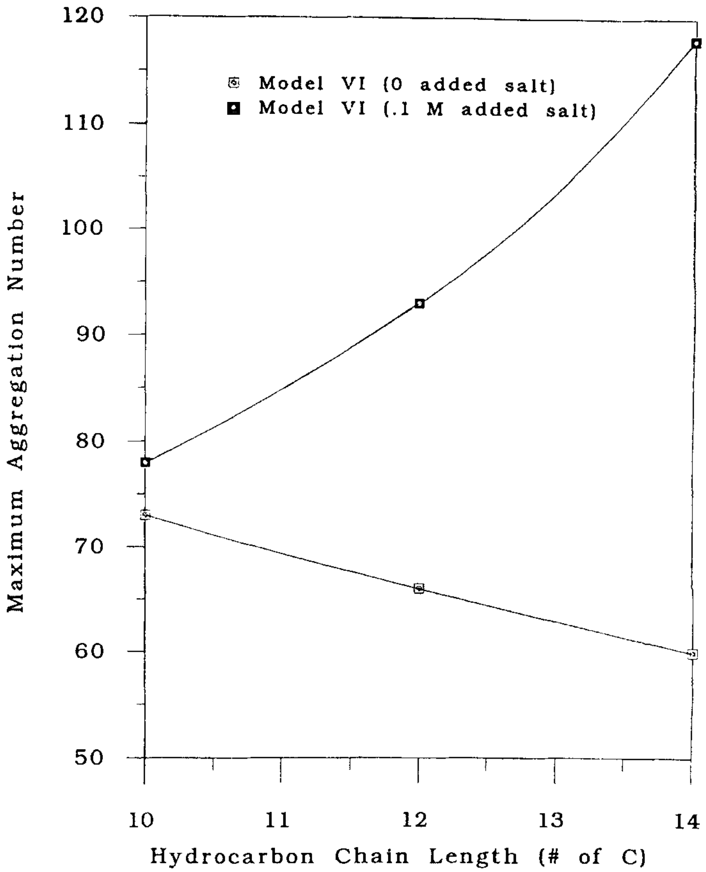

FIG. 10 The effect of hydrocarbon chain length on the maximum aggregation number as predicted by Model VI for a series of sodium alkyl sulfate surfactants.

character of the surfactant (6, 17, 26). The problem at zero ionic strength lies in the fact that in our model the surfactant itself contributes to the total ionic strength of the solution. The micelles "see" a salt concentration due to the surfactant cations even if there is no added electrolyte. Since the cmc decreases with increasing chain length, the decreased surfactant concentrations for surfactants having longer hydrocarbon chain lengths mean that the ionic strengths of these solutions at the cmc are quite a lot less than the ionic strengths of solutions of surfactants having shorter chains at their cmc's. This in turn results in lower aggregation numbers

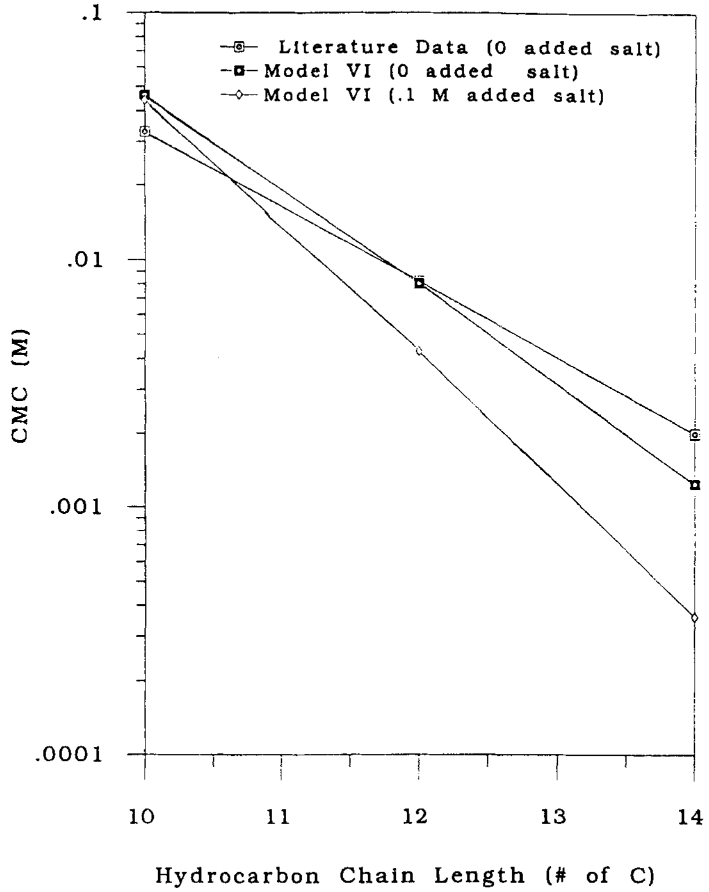

FIG. 11 The effect of hydrocarbon chain length on cmc for a series of sodium alkyl sulfate surfactants as predicted by Model VI. Literature data from Ref. 28.

for the longer chain surfactants in the absence of any added inert salt. When one models solutions to which inert salt has been added, the importance of the contribution of the surfactant's cations to the ionic strength decreases, the ionic strengths of the solutions of the various surfactants at their cmc's become very similar, and we find the expected increase in aggregation number with increasing chain length.

Model VI is a hybrid theory based on the zero surface tension concept of Sorensen, a mass action multispecies approach, and a nonlinearized Poisson–Boltzmann equation in spherical geometry which includes the

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finite sizes of the ions in the micellar ionic atmospheres. Computationally, it is extremely difficult to work with. It predicts semiquantitatively correct dependences of the cmc and aggregation number on ionic strength and surfactant chain length, but fails badly on temperature dependence of the cmc. It predicts a virtually constant surfactant monomer concentration above the cmc (as expected), a sharp onset of the cmc (as is observed), and intuitively reasonable distributions of micellar species below, at, and above the cmc. One unsatisfying aspect of the theory is its inclusion of a nonsurface contribution to the free energy change of micelle formation which is vaguely defined and poorly understood; an improved understanding of this will probably require a model in which the molecular structure of the aqueous solvent is explicitly taken into account.

One rather disquieting feature of our results is that they indicate it would be quite unwise to use any of the available theories, including the one discussed here, for extrapolating cmc's from room temperature down to ambient soil and aquifer temperatures, presumably of the order of 12–15°C.

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