

Association of nonionic polymers with micelles, bilayers, and microemulsions

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A unified thermodynamic theory is developed here to explore the nature of association of nonionic polymer molecules with surfactant aggregates such as globular micelles, rod-like micelles, bilayers, oil in water microemulsions, and water in oil microemulsions. The association complex is visualized as consisting of the polymer molecule wrapped around the aggregate at its interface with water. The association with polymer provides enhanced shielding of the hydrophobic aggregate surface from water, increases the steric repulsions at the aggregate surface and gives rise to hydrophobic interactions between the polymer and the aggregate surface. Simple free energy models are formulated to account for these polymer-induced effects. Illustrative calculations have been carried out to examine the behavior of monoalkyl and dialkyl surfactants with nonionic, anionic, and zwitterionic polar head groups. The results show that polymer-aggregate association is almost always preferred in the case of anionic or zwitterionic surfactants. As a result of the association with the polymer, globular micelles transform into smaller globular micelles; large, polydisperse rod-like micelles change into small, monodispersed globular micelles; spherical vesicles and planar bilayers transform into smaller discoids. In all the cases, the polymer-bound aggregates are formed at a critical micelle concentration (CMC) that is significantly lower than the CMC of the polymer-free systems. In marked contrast, aggregates of nonionic surfactants may or may not associate with the polymer molecule. If association occurs, the polymer-induced changes in the aggregate morphologies are similar to those for the anionic surfactants. However, the CMC for the formation of bound aggregates is usually very close to that for the formation of the free aggregates. In many situations, association is not favored and polymer-free aggregates coexist with free polymer molecules in solution. It is found that subtle variations in the hydrophobic characteristics of the polymer molecule can tilt the equilibrium between polymer-bound and polymer-free aggregates. In the case of microemulsions, calculations show that the volume ratio of the dispersed phase to the surfactant is significantly altered by the presence of the polymer. Also, the condition for phase inversion from oil in water to water in oil type of microemulsion is modified by the presence of the polymer. The theoretical results suggest ways by which one may control the morphologies of surfactant aggregates using polymer additives.

I. INTRODUCTION

Surfactant molecules are composed of a part that is soluble in water and a part that is soluble in oil. This dual nature is responsible for the ability of the surfactant molecules to organize themselves into various structures in aqueous and nonpolar solvents, as well as for their ability to orient themselves at various types of interfaces. The self-assembly of surfactants in aqueous media to form small globular micelles, large rod-like micelles, planar and spherical bilayers has received considerable attention in the literature.^{1,2} Also, the formation of microemulsions of oil in water and of water in oil facilitated by the surfactants has been extensively explored.³

In a number of applications of importance to chemical, pharmaceutical, petroleum, and mineral processing industries, the surfactant molecules are present in solution not alone but along with synthetic or biological macromolecules. The presence of the polymer molecules gives rise to changes in the solution and the interfacial properties of the surfactant compared to the corresponding polymer-free systems.⁴⁻⁶ A number of experimental studies have been carried

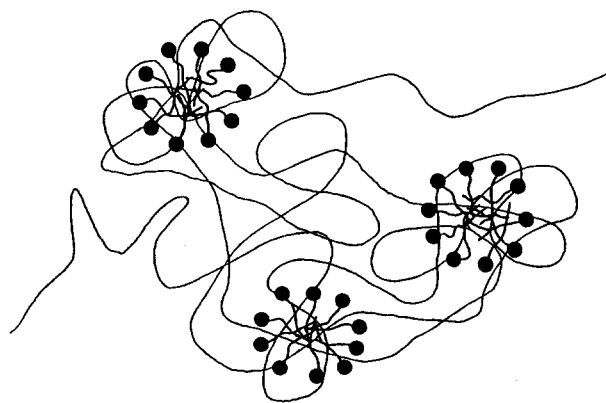
out in recent years to determine these changes induced by the polymer molecule in the solution behavior of surfactants. Most of these studies are focused on surfactant systems that give rise only to small globular micelles in polymer-free solutions. These studies show that nonionic polymer molecules associate with anionic surfactant micelles. Because of this association, the critical micelle concentration (CMC) at which micelles begin to appear is lowered and the micelle sizes are smaller compared to the polymer-free systems. The nonionic polymer molecules appear either not to associate or only weakly associate with nonionic or cationic surfactant micelles.⁵⁻¹³ In addition to these investigations involving surfactant micelles in polymer containing solutions, some studies of the phase behavior of microemulsion systems have also been reported in literature involving surfactant and polymer molecules of interest to the enhanced oil recovery application.^{14,15} These studies show that a microemulsion is destabilized by the addition of polymer molecules leading to a liquid-liquid phase separation.

An understanding of how uncharged polymer molecules affect the aggregation behavior of surfactants is useful for various existing applications. Such an understanding can

also lead to a novel approach of controlling aggregation patterns in surfactant solutions through the addition of polymer molecules. Currently, a treatment of the interactions of nonionic polymers with various kinds of surfactant assemblies is not available. It would be useful to develop such a comprehensive treatment utilizing a common theoretical basis. The present study is an attempt to address this need. The main goal of this work is to examine how surfactant systems that give rise to aggregates such as small globular micelles, large rod-like micelles, planar bilayers, spherical bilayer vesicles, oil in water microemulsions, and water in oil microemulsions are affected by the presence of nonionic polymer molecules.

One may anticipate that, in surfactant solutions containing nonionic polymers, aggregation of the surfactant molecules would occur as in polymer-free solutions with the added feature that these aggregates may be free in solution or be bound by physical interactions to the polymer. The morphologies of the polymer-free and the polymer-bound aggregates may be similar or different. Further, the concentrations of the surfactant at which the polymer-free and the polymer-bound aggregates come into existence can differ from one another. Each polymer molecule can have one or more aggregates associated with it. Alternatively, more than one polymer molecule could be associated with a single aggregate as well. The relative concentrations of the polymer-free and the polymer-bound aggregates would be determined by the nature of interactions between the polymer and the aggregate.

In our earlier work, a theory of association of nonionic polymer with globular micelles was developed.^{16,17} For this purpose, we postulated a structural description of the polymer-micelle association complex (Fig. 1). The complex is visualized as consisting of fully formed surfactant micelles interacting with the polymer segments. Specifically, the polymer segments wrap around the aggregate interface shielding a part of the hydrocarbon core of the micelle from being in contact with water. The structural and physicochemical properties of the polymer molecule are assumed to determine the area of mutual contact between the polymer molecule and the hydrophobic surface of the micelle. A characteristic parameter a_{pol} was defined to represent this area of mutual contact per surfactant molecule in the mi-



MICELLE - NONIONIC POLYMER COMPLEX

FIG. 1. Schematic representation of the polymer-micelle association structure.

celle. Of course, it is not very realistic to anticipate that the polymer molecule can provide a uniform shielding of the micellar surface from water by the amount a_{pol} per surfactant molecule. Nevertheless, this area parameter is defined in the mean field spirit and it serves as a quantitative measure of the nature of polymer-micelle interactions. At the present time no *a priori* method for the estimation of this area is available. However, the magnitude of a_{pol} for a given polymer molecule can be effectively determined from critical micelle concentration measurements in any one surfactant system. One can then use this value of a_{pol} to predict the aggregation behavior of other surfactant molecules.¹⁷

In this work, we visualize the association structures of the nonionic polymer molecule with various types of aggregates to essentially resemble the topology of polymer-micelle complex described earlier. Namely, for all types of aggregates, the nonionic polymer interacts with them by being present in the surface region of the aggregates. Therefore, the parameter a_{pol} can serve as a means of describing the polymer association behavior with surfactants displaying a variety of self-assembling patterns.

In the framework of our earlier theory, the presence of polymer segments at the micellar surface gave rise to two competing effects. One was the reduction in the micellar core-water interfacial energy due to the partial shielding provided by the polymer. This effect favored the formation of the bound micelles compared to the free micelles. The second effect was the increased steric interactions in the micelle surface covered with the polar head groups of the surfactants and the polymer segments. This effect disfavored the polymer-micelle association. In the present paper, we also account for the fact that a part of the polymer molecule (the area that is in contact with the micelle, also equal to a_{pol}) has a changed environment, namely it is removed from contact with water and brought into close proximity of a hydrophobic aggregate surface. The magnitude of this effect depends on the hydrophobicity of the polymer molecule. This factor is favorable to the formation of bound micelles. As will be discussed below, this factor can potentially modify the subtle balance between the bound and free aggregates especially in the case of nonionic surfactant systems. A feature not explicitly considered in the present theory relates to specific interactions between the polar head groups of ionic surfactants and the polymer segments. This factor is expected to account for the relatively weak interactions between nonionic polymer molecules and cationic surfactants. A more complete theory taking into account these specific interactions will be presented later.

In the following section, the general thermodynamic principles of surfactant aggregation are summarized. The association of nonionic polymer with globular micelles, rod-like micelles, bilayers, and microemulsions are discussed in Secs. III-VI, respectively. The last section presents the conclusions from this study.

II. THERMODYNAMICS OF AGGREGATION

A. Multicomponent solution approach

The system consisting of singly dispersed surfactant molecules, aggregates of various sizes and shapes, polymer

molecules and the solvent water can be viewed as a multi-component solution. The aggregates of different sizes and shapes are treated as distinct chemical components characterized by their own standard chemical potentials. The standard states for the aggregates, the singly dispersed surfactant molecules and the polymer molecules are taken to correspond to infinitely dilute solution conditions. The standard state of water is that of a pure solvent. One may note that the interactions of the various species with the solvent water are taken into account by incorporating them within the standard chemical potentials of the various components. For polymer-bound aggregates, the interactions between the polymer and the aggregate are incorporated into the reference state chemical potential of the aggregate. Other interaggregate interactions are considered to be negligible. The total Gibbs energy of the solution can thus be written as

$$G = N_w \mu_w^0 + N_1 \mu_1^0 + \sum N_g \mu_g^0 + N_p \mu_p^0 + kT(X_w \ln X_w + X_1 \ln X_1 + \sum X_g \ln X_g + X_p \ln X_p). \quad (1)$$

In the above equation, N refers to the number of chemical species of a given type, μ^0 are the standard chemical potentials of the various species, k is the Boltzmann constant, and T is the system temperature. The subscripts w , 1 , g , p , refer to water, singly dispersed surfactant molecules, aggregates of aggregation number g , and polymer molecules, respectively. In the expression for G , the entropy of the multicomponent solution is written as for an ideal mixture. The consequences of using other models for the system entropy in the theory of aggregation have been discussed in detail elsewhere.¹⁸ Although this is an important problem, for the purposes of this paper in which various aggregation patterns are compared, the use of the ideal entropy model is quite satisfactory.

B. Aggregate size distribution

At equilibrium, the total Gibbs energy of the system is a minimum for any given concentrations of the surfactant and the polymer molecules. This minimum condition provides the equilibrium population distribution of the aggregates in solution. Corresponding to the minimum Gibbs energy, one obtains the relation

$$\mu_g^0 + kT \ln X_g = g [\mu_1^0 + kT \ln X_1]. \quad (2)$$

The above equation states that the chemical potential of the surfactant molecule in the singly dispersed state is equal to the chemical potential per molecule of an aggregate of size g . Thus, Eq. (2) is the well-known statement of association-dissociation equilibria in surfactant solutions. The above equation can be alternately written in the form of the size distribution of aggregates.

$$X_g = X_1^g \exp - \left(\frac{\mu_g^0 - g \mu_1^0}{kT} \right). \quad (3)$$

In this expression X_g is the mole fraction of aggregates having aggregation number g while X_1 is the mole fraction of the singly dispersed molecules. The quantity $[(\mu_g^0/g) - \mu_1^0]/(kT)$ refers to the difference in the standard state

chemical potentials between a surfactant molecule present in an aggregate of size g and a surfactant molecule present in the singly dispersed state. If an explicit equation for this standard chemical potential difference can be developed, then one can compute the size distribution of the aggregates and all other size dependent solution properties of interest. One may note that the standard chemical potential difference term for the polymer-free aggregate will be different from that of the polymer-bound aggregate, the difference between the two arising due to the interactions between the polymer and the aggregate.

C. Pseudophase approximation of CMC and aggregate size

A convenient approximation useful for describing surfactant solutions can be obtained from Eq. (2) if the aggregation number g is recognized to be appreciably large. Near the critical micelle concentration, the concentration X_g of the aggregates is only of the order of the monomer concentration X_1 . Therefore, one may rewrite Eq. (2) without any significant error as

$$\frac{\mu_g^0}{g} = \mu_1^0 + kT \ln X_1. \quad (4)$$

The above equation represents the description of the aggregates as a pseudophase in equilibrium with the singly dispersed surfactant molecules. The standard chemical potential of this pseudophase depends on the size of the phase. This is a unique feature of small systems such as surfactant aggregates. Since the aggregates are viewed as pseudophases, the equilibrium aggregates must correspond to the minimum of the Gibbs energy per molecule of the aggregate. This condition is met by the relation

$$\frac{\partial}{\partial g} \left[\frac{(\mu_g^0/g) - \mu_1^0}{kT} \right] = 0, \quad \text{at } g = g_e, \quad (5)$$

where g_e is the number of surfactant molecules in the equilibrium aggregate. Equation (4) representing the pseudophase approximation permits the estimation of the critical micelle concentration from the relation

$$\ln X_{\text{CMC}} = \left[\frac{(\mu_{g_e}^0/g_e) - \mu_1^0}{kT} \right], \quad \text{at } g = g_e. \quad (6)$$

The equilibrium size distribution of aggregates defined by Eq. (3) consists of two factors. The first X_1^g arises from the entropy of dispersion of the various species in the entire solution. The second factor $\exp - g \{ [(\mu_g^0/g) - \mu_1^0]/(kT) \}$, originates from the difference in the standard Gibbs energy of a surfactant molecule in its aggregated state compared to that in its singly dispersed state. If the standard free energy difference per surfactant molecule is lower for a given type of aggregate, then Eq. (3) shows that the concentration of that type of aggregate will be the largest at equilibrium compared to other types of aggregates. This is equivalent to saying, in view of Eq. (6), that the aggregate which appears at a lower CMC will be preferred over that which may appear at higher CMC. On the other hand, if the standard Gibbs energy per surfactant molecule is identical for two kinds of aggregates, the first factor related to the system entropy in Eq. (3) de-

cides the preferred aggregate type. The entropic factor favors aggregates of small g since the system entropy is larger and the total free energy is lower for smaller aggregates present in larger numbers. One can explicitly see from Eq. (3) that the concentration of aggregates of lower aggregation number g will be higher compared to aggregates of larger aggregation number. To obtain further quantitative information on the patterns of aggregation in the presence and the absence of nonionic polymers, one needs explicit equations for the standard free energy difference factor as a function of the aggregation number g . Also, the interconnection between the type of the aggregate and the aggregation number should be established.

III. INTERACTIONS OF NONIONIC POLYMERS WITH GLOBULAR MICELLES

A. Geometrical properties of globular micelles

Micelles that are relatively small in size and having spherical or ellipsoidal shapes are designated as globular micelles. It is well recognized¹⁹ that surfactant aggregates of any shape should satisfy the following geometrical conditions: (1) No point within an aggregate can be farther than l_0 from the aggregate core-water interface, where l_0 refers to the extended length of the surfactant molecule. This implies that at least one dimension of the aggregate should be smaller than $2l_0$. (2) The total volume V of the hydrophobic core of the aggregate should satisfy $V = gv_0$, where v_0 is the volume of the hydrophobic tail of the surfactant molecule. (3) The total surface area A of the hydrophobic core of the aggregate should satisfy $A = ga_c$. This implies that the average area per molecule of the hydrophobic core is equal to the equilibrium value a_e .

For spherical micelles with a hydrophobic core of radius r_0 and containing g surfactant molecules, one can write

$$V = gv_0 = \frac{4\pi r_0^3}{3}, A = ga = 4\pi r_0^2, \quad r_0 < l_0. \quad (7)$$

From the above equation, it is evident that spherical micelles should result if at equilibrium

$$\frac{v_0}{a_e l_0} \leq \frac{1}{3}. \quad (8)$$

From Eq. (7) one can relate the aggregation number g_e to the equilibrium area per molecule a_e ,

$$g_e = \left(\frac{4\pi l_0^3}{3v_0} \right) \left(3 \frac{v_0}{a_e l_0} \right)^3. \quad (9)$$

The largest spherical micelle will have a hydrophobic core of radius l_0 . For aggregation numbers larger than that allowed by spherical geometry, but within the realm of small aggregates, we consider the micelles to be prolate ellipsoids. This shape is viewed as a transition shape preceding the formation of large rod-like micelles having a cylindrical middle portion and hemispherical ends (Fig. 2). One may note that in spherocylindrical micelles, the hemispherical ends and the cylindrical middle are characterized by different areas per molecule a_{sp} and a_{cy} , respectively. These, in turn, may be different from the equilibrium area per molecule of the micelle a_e . In contrast, we visualize the transitional ellipsoidal

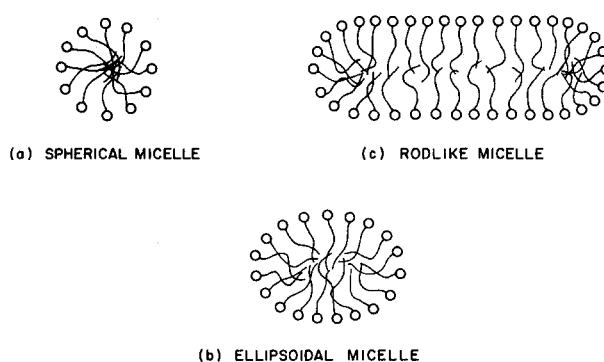


FIG. 2. Spherical, ellipsoidal, and rod-like micelles.

shape as one in which the area per molecule is relatively uniform everywhere on the micelle surface and equal to a_e . The aggregation number of the micelle having the ellipsoidal shape is approximately equal to that of a spherocylinder having the same average area per molecule. For a spherocylinder of radius l_0 and length L in the middle cylindrical part,

$$V = gv_0 = \pi l_0^2 L + \frac{4\pi l_0^3}{3}, A = ga = 2\pi l_0 L + 4\pi l_0^2. \quad (10)$$

Given the equilibrium area a_e , the corresponding aggregation number of the ellipsoidal aggregate g_e is calculated from Eq. (10) to be

$$g_e = \left(\frac{4\pi l_0^3}{3v_0} \right) \left(\frac{a_e l_0}{v_0} - 2 \right)^{-1}, \quad \frac{1}{3} < \frac{v_0}{a_e l_0} < \frac{1}{2}. \quad (11)$$

To proceed further and examine the aggregation behavior in the presence of and in the absence of polymer, we need the value of the equilibrium area per molecule of the aggregate a_e . As mentioned earlier, the equilibrium area per molecule is obtained by the minimization of the standard free energy of the aggregates as indicated in Eq. (5). For this purpose, an expression for the standard free energy of the aggregates needs to be formulated.

B. Free energy of polymer-free globular micelles

An expression for the standard free energy of globular micelles can be developed by considering all the changes experienced by a surfactant molecule when transferred from water into a micelle.^{17,20} First, the formation of the micelle involves the transfer of the hydrophobic tail of the surfactant from water to a hydrocarbon liquid-like core of the micelle. This region differs somewhat from a liquid hydrocarbon because of the chain conformational constraints imposed within the micelle. The net contribution of this transfer free energy is negative and it constitutes the driving force for micellization. Second, the formation of the micelle is accompanied by the generation of an interface between the hydrophobic core of the micelle and water. The corresponding free energy of formation provides a positive contribution to the standard free energy of micellization. Since the area of the micelle-water interface per surfactant molecule decreases with increasing aggregation number, the positive free energy of formation of the micelle (per molecule) decreases with increas-

ing aggregation number. This contribution is thus responsible for the positive cooperativity favoring the growth of the micelle. Finally, the formation of the micelle results in the polar head groups of surfactants being brought into close proximity of one another at the micelle-water interface. This gives rise to steric interactions among the head groups. If the head groups are ionic or zwitterionic, then electrostatic interactions among the head groups are also present. These head group interactions provide a positive contribution to the free energy of micellization. The head group repulsions per surfactant molecule increase with an increase in the micellar size because of the corresponding decrease in the area per molecule of the micelle. As a result, the head group repulsions are responsible for the negative cooperativity limiting the growth of aggregates to finite sizes. Taking into account all the above contributions, one may write

$$\left[\frac{(\mu_g^0/g) - \mu_1^0}{kT} \right] = \frac{\Delta \mu_{hc/w}^0}{kT} + \frac{\Delta \mu_{ex}^0}{kT} + \frac{\sigma(a - a_0)}{kT} - \ln \left(1 - \frac{a_p}{a} \right) + \frac{\phi}{a^2}. \quad (12)$$

In the above expression, the first term represents the transfer of the surfactant tail from water to a liquid hydrocarbon while the second term accounts for the differences between a liquid hydrocarbon and a somewhat ordered micellar core region. The third term refers to the free energy of formation of an interface between the hydrophobic core of the micelle and water. Here, σ is the macroscopic interfacial tension between hydrocarbon and water, a is the surface area of the interface per surfactant molecule and a_0 is the area per molecule of the surface that is shielded from contact with water because of the presence of the polar head group of the surfactant. The fourth term provides an estimate of the steric interactions among the polar head groups at the aggregate surface. It is written in a form analogous to that suggested by the van der Waals equation of state. Here, a_p is the effective cross-sectional area of the polar head group. The last term accounts for the electrostatic interactions between the ionic or zwitterionic head groups at the micelle surface. Here ϕ is a measure of the strength of electrostatic interactions. The origin of this form of electrostatic interaction energy has been presented in an earlier paper.²¹ More detailed discussions of the above free energy contributions may be found in our earlier papers.^{17,20}

Given the explicit expression for the free energy of aggregation, one may obtain the aggregation behavior of surfactants in analytical terms using the pseudophase approximation. The equilibrium area a_e per molecule is obtained from the solution of

$$a = \left[\frac{a_p/a}{1 - a_p/a} + \frac{2\phi}{a^2} \right] \left(\frac{\sigma}{kT} \right)^{-1}. \quad (13)$$

The corresponding CMC is calculated using Eqs. (6) and (12) in which the area per molecule is replaced by the equilibrium area estimated from Eq. (13).

C. Free energy of polymer-bound globular micelles

The standard free energy of surfactant micelles that are associated with the nonionic polymer molecule can be writ-

ten in a form similar to that used to describe the polymer-free micelles. The free energy expression is, however, modified to account for the presence of polymer segments at the micellar core-water interface. As described earlier, the polymer segments wrap around the micelle in such a way that they cover an area a_{pol} per molecule of the surfactant contained in the micelle. This gives rise to three competing contributions to the free energy of micelles. First, a decrease in the hydrophobic surface area of the micelle exposed to water occurs. This decreases the positive free energy of the micelle and thus favors the formation of polymer-bound micelles. Second, steric repulsions arise between the polymer segments and the surfactant head groups at the micellar surface. This increases the positive free energy of head group repulsions and thus disfavors the formation of the polymer-bound micelles. Finally, the contact area a_{pol} of the polymer molecule is removed from water and transferred to an essentially hydrophobic surface of the micellar core. This decreases the free energy of the micelle and thus favors the formation of the polymer-bound micelles. Taking these factors into account, one may write

$$\left[\frac{(\mu_g^0/g) - \mu_1^0}{kT} \right] = \frac{\Delta \mu_{hc/w}^0}{kT} + \frac{\Delta \mu_{ex}^0}{kT} + \frac{\sigma(a - a_0 - a_{pol})}{kT} - \ln \left(1 - \frac{a_p + a_{pol}}{a} \right) + \frac{\phi}{a^2} - \frac{\Delta \sigma_{pol} a_{pol}}{kT}. \quad (14)$$

The above equation is similar to Eq. (12) for the formation of polymer-free micelles. The first two terms and the fifth term are identical to those appearing in Eq. (12). The modified third term accounts for the enhanced shielding of the micellar core from water provided by the polymer. The modified fourth term accounts for the increase in the steric repulsions due to the presence of the polymer. The sixth term is new compared to Eq. (12) and represents the gain in hydrophobic energy for the polymer molecule. This hydrophobic interaction energy is written as the product of an interfacial tension and the area of the polymer that is removed from water and brought into contact with the hydrophobic surface of the micellar core. Here, $\Delta \sigma_{pol}$ is the difference between the macroscopic interfacial tensions of polymer-water and polymer-hydrocarbon interfaces.

Given the above free energy equation, the equilibrium area per molecule of the bound micelle in the pseudophase approximation can be obtained from the solution of

$$a = \left[\frac{(a_p + a_{pol})/a}{1 - (a_p + a_{pol})/a} + \frac{2\phi}{a^2} \right] \left(\frac{\sigma}{kT} \right)^{-1}. \quad (15)$$

The corresponding value of the CMC is estimated from Eqs. (6) and (14) with the area a_e calculated from Eq. (15).

D. Estimation of model parameters

The values of various molecular constants appearing in Eq. (12) are listed in Table I.^{1,17,20} For an aliphatic hydrocarbon tail of length n_c with $(n_c - 1)$ methylene groups and a terminal methyl group, the free energy of transferring the surfactant tail from water to the aggregate core is determined at 25 °C from

$$\frac{\Delta \mu_{\text{hc/w}}^0}{kT} + \frac{\Delta \mu_{\text{ex}}^0}{kT} = -2.55 + 1.25 n_c. \quad (16)$$

When the surfactant tail consists of two aliphatic chains, the transfer free energy is simply not twice the value given above. This is because of the considerable amount of intramolecular interactions among the two chains even in the singly dispersed state of the molecule. Based on available data, the transfer-free energy of the two chains is taken equal to 1.6 times that of the single chain.¹ The interfacial tension σ between the hydrophobic core of the micelle and water is treated to be the same as the macroscopic interfacial tension between liquid hydrocarbon and water. For surfactant tails with aliphatic nature, σ is taken to be 50 dyn/cm. The hydrophobic tail of the surfactant (which has a cross-sectional area of 21 Å² for a single alkyl chain and 42 Å² for a dialkyl chain) is shielded completely from water if the polar head group has a cross-sectional area a_p greater than the cross-sectional area of the hydrophobic tail. For such a surfactant, a_0 is taken to be the cross-sectional area of the hydrophobic tail. If a_p is less than the cross-sectional area of the tail, then the polar head group shields only a part of the cross-sectional area of the tail. In this case, a_0 is taken equal to a_p . The variable ϕ depends on the type of ionic or zwitterionic head group as well as on the amount of any added electrolyte. Different values for ϕ are chosen while performing the illustrative calculations.

The presence of polymer is accounted for by the two parameters, a_{pol} and $\Delta\sigma_{\text{pol}}$. One may note that the interfacial tensions of the polymer against a low molecular weight species can be estimated approximately²² using the expression

$$\frac{\sigma_{\text{pol}}}{kT} = \left(\frac{\chi}{6}\right)^{1/2} v^{-2/3}. \quad (17)$$

Here, χ is the Flory-Huggins interaction parameter for the system and v is the molecular volume of the low molecular weight component. Taking polyethylene oxide as an example of nonionic polymers, we estimate a_{pol} to be approximately 15 Å² and $\Delta\sigma_{\text{pol}}$ to be about 7.94 dyn/cm. All the calculations in this paper have been carried out for these specified values of parameters representing the polymer.

E. Results and discussion

The equilibrium area per molecule of the micelle and the CMC have been calculated in the pseudophase approximation for an anionic surfactant, sodium dodecyl sulfate (designated as SDS) and for a nonionic surfactant, dodecyl pen-

tadecoxyethylene glycol monoether (designated as C₁₂E₁₅). The calculated results are summarized in Table II. In polymer-free solutions the anionic SDS micelles are small, only marginally larger than the largest spherical micelle possible (whose aggregation number will be 57 based on a sphere of radius equal to l_0). In the presence of the polymer, the CMC is substantially decreased corresponding to a lower standard free energy for the polymer-bound micelles. Therefore, polymer-bound globular micelles will be favored over free micelles in this case. The aggregation number of the polymer-bound micelles are somewhat smaller than those of the free micelles. Also shown in Table II are the results calculated ignoring the hydrophobicity of the polymer, namely, ignoring the sixth term in Eq. (14). One may note that the only result affected by this is the magnitude of the CMC. The CMC is still much smaller than that corresponding to the polymer-free solutions. Therefore, polymer-bound globular SDS micelles would have been predicted even if the polymer hydrophobicity effect had been neglected.

Results for the nonionic surfactant C₁₂E₁₅ are also shown in Table II. In the absence of the polymer, small ellipsoidal micelles (slightly larger than the largest spheres that are geometrically allowed) are formed. In the presence of the polymer, the CMC is somewhat decreased. Therefore, micelles that are bound to the polymer will be favored over free micelles. The aggregation number of the polymer-bound spherical micelles are substantially smaller compared to that of the free micelles. The value of the CMC calculated ignoring the polymer hydrophobicity effect is also listed in Table II. In this case, the CMC is larger than that in the polymer-free solution. Therefore, a preference for free micelles over bound micelles would have been predicted if the polymer hydrophobicity effect had been ignored. Evidently, subtle free energy differences associated with the hydrophobicity of the polymer can tilt the equilibrium between free and bound nonionic micelles.

The contrasting behavior of anionic and nonionic surfactants can be interpreted in the framework of the present thermodynamic model. If the polymer associates with the micelle, the presence of the polymer segments increases the equilibrium area per surfactant molecule. For nonionic surfactants, this incremental increase in the equilibrium area a_e is roughly comparable to the polymer-micelle contact area a_{pol} (see Table II). Correspondingly, the negative increment in the free energy of shielding of the micellar core from water

TABLE I. Molecular constants for amphiphiles.

Surfactant	a_p (Å ²)	a_0 (Å ²)	v_0 (Å ³)	l_0 (Å)	v_p (Å ³)
SDS	17	17	351	16.7	100
C ₁₂ E ₁₅	50	21	351	16.7	945
C ₁₂ E ₆	35	21	351	16.7	378
C ₁₂ E ₇ C ₁₂	36	36	702	16.7	441
C ₁₂ E ₆ C ₁₂	35	35	702	16.7	378
C ₁₂ LC ₁₂	35	35	702	16.7	420
C ₃ OH	8	8	162	7.8	17

TABLE II. Polymer association with globular micelles.

Surfactant	ϕ (Å ⁴)	X_{CMC} (mM)	a_e (Å ²)	g_e	$\frac{v_0}{a_e l_0}$	Shape
C ₁₂ E ₁₅	0	0.782	57.3	78	0.366	Ellipsoid
C ₁₂ E ₁₅ + P ^a	0	0.743	72.5	37	0.29	Sphere
C ₁₂ E ₁₅ + P ^b	0	0.986	72.5	37	0.29	Sphere
SDS	11,700	7.95	59.3	69	0.354	Ellipsoid
SDS + P	11,700	1.54	61.3	62	0.343	Ellipsoid
SDS + P*	11,700	2.04	61.3	62	0.343	Ellipsoid

^a P refers to the polymer-bound aggregate.

^b *denotes the calculations of the CMC for the polymer-bound micelles ignoring the hydrophobicity effect of the polymer.

by the polymer segments is close in magnitude to the positive increment in the free energy of steric repulsions at the aggregate surface. If only these two effects are considered, then the CMC values for the formation of bound and free micelles are always very near one another with the free micelles generally favored over the bound micelles. The effect of the polymer hydrophobicity provides another negative contribution to the formation of the polymer-bound aggregates. This decreases further the CMC and tilts the balance more in favor of bound micelles. One may note, as will be shown in later sections, that the polymer hydrophobicity effect may fail to favor the formation of bound aggregates if the hydrophobicity is not adequately large. Therefore, one may conclude that in the case of nonionic micelles, subtle variations in the properties of the polymer may favor either free or bound aggregates.

The calculated results for the anionic surfactants are markedly different from the above behavior of nonionic surfactants. In the case of anionic surfactants, the incremental increase in the equilibrium area per molecule of the aggregate due to the presence of the polymer is generally much smaller than the polymer-aggregate contact area a_{pol} . This is because of the importance of the electrostatic head group interaction term in determining the equilibrium area of the aggregate. Therefore, the negative increment in the free energy of shielding of the aggregate core from water by the polymer segments more than offsets the positive increment in the free energy of steric repulsions at the micellar surface. In addition, there is a negative increment in the free energy of electrostatic interactions at the aggregate surface because the equilibrium area in the presence of the polymer is somewhat larger. Therefore, irrespective of the magnitude of the polymer hydrophobicity, the polymer-bound anionic micelles are always favored over free micelles.

IV. INTERACTIONS OF NONIONIC POLYMERS WITH ROD-LIKE MICELLES

A. Geometrical properties of rods

Rod-like micelles of large aggregation numbers are formed by surfactants under selected solution conditions. The rod-like micelles are assumed to be spherocylinders with a cylindrical middle portion and hemispherical ends. The area per molecule of the aggregate at the hemispherical ends is a constant a_{sp} independent of the micelle size and corresponds to the largest spherical aggregate that is allowed by the geometry. From Eq. (7) $a_{\text{sp}} = 3v_0/l_0$. The area per molecule of the aggregate in the cylindrical middle part is a constant a_{cy} and corresponds to an infinitely long rod. From Eq. (10), $a_{\text{cy}} = 2v_0/l_0$.

B. Thermodynamics of formation of rod-like micelles

The reference state Gibbs energy of the rod-like micelle of aggregation number g can be written as a sum of two parts, one denoting the hemispherical ends and the other representing the cylindrical middle portion of the aggregate. For an aggregate of size g , the number of molecules at the two ends is g_{sp} while the remaining $(g - g_{\text{sp}})$ molecules are in the cylindrical part. Therefore,

$$\mu_g^0 = (g - g_{\text{sp}}) \mu_{\text{cy}}^0 + g_{\text{sp}} \mu_{\text{sp}}^0. \quad (18)$$

In the above expression, μ_{sp}^0 and μ_{cy}^0 refer to the standard chemical potentials of surfactant molecules in the hemispherical and cylindrical portions of the aggregate, respectively. Consequently, the standard free energy of micellization can be written as

$$\begin{aligned} \frac{\mu_g^0 - g \mu_1^0}{kT} &= g \left(\frac{\mu_{\text{cy}}^0 - \mu_1^0}{kT} \right) + g_{\text{sp}} \left(\frac{\mu_{\text{sp}}^0 - \mu_{\text{cy}}^0}{kT} \right) \\ &= g \left(\frac{\mu_{\text{cy}}^0 - \mu_1^0}{kT} \right) + \ln K. \end{aligned} \quad (19)$$

The parameter K is a measure of the preference for the formation of rod-like micelles compared to that of spherical micelles. Introducing the free energy of micellization given in Eq. (19) in the expression for the aggregate size distribution Eq. (3), one obtains,

$$X_g = \frac{1}{K} \left[X_1 \exp - \left(\frac{\mu_{\text{cy}}^0 - \mu_1^0}{kT} \right) \right]^g. \quad (20)$$

The quantity within the parentheses and K are independent of g and therefore, the summations of aggregate concentrations can be done analytically. It can be shown that the weight and the number average aggregation numbers g_w and g_n are related to the total surfactant concentration as

$$g_w = g_{\text{sp}} + 2 \left[K \sum g X_g \right]^{1/2}, \quad g_n = g_{\text{sp}} + \left[K \sum g X_g \right]^{1/2}. \quad (21)$$

The critical micelle concentration in this case is provided by the relation

$$X_{\text{CMC}} = \exp \left(\frac{\mu_{\text{cy}}^0 - \mu_1^0}{kT} \right). \quad (22)$$

One may observe from Eq. (21) that, when rod-like micelles form they are predicted to be highly polydisperse and the aggregation number varies with the square root of the total surfactant concentration. These general results have been discussed in detail in the literature.^{17,19,23-25}

C. Free energy of sphere-to-rod transition

The parameter K can be expressed in terms of various interactions by introducing Eq. (12) in the definition of K . One obtains,

$$\begin{aligned} \frac{\ln K}{g_{\text{sp}}} &= \left(\frac{\mu_{\text{sp}}^0 - \mu_{\text{cy}}^0}{kT} \right) = \frac{\sigma}{kT} (a_{\text{sp}} - a_{\text{cy}}) - \ln \left(1 - \frac{a_p}{a_{\text{sp}}} \right) \\ &\quad + \ln \left(1 - \frac{a_p}{a_{\text{cy}}} \right) + \frac{\phi}{a_{\text{sp}}^2} - \frac{\phi}{a_{\text{cy}}^2}. \end{aligned} \quad (23)$$

The magnitude of K thus depends upon both the surfactant tail (through g_{sp}) and the nature of the polar head groups. Since the size of the largest spherical micelle g_{sp} depends on the chain length l_0 of the surfactant tail, the propensity to form rod-like micelles is enhanced by increasing the length of the surfactant tail. Further, Eq. (23) shows that the magnitude of K increases if the size of the polar head group a_p decreases because it reduces the steric repulsions at the micelle surface. Also, K increases if the magnitude of the electrostatic interaction parameter ϕ decreases since this reduces

the electrostatic repulsions between the head groups at the micelle surface. The CMC is calculated using Eq. (22) and the following relation:

$$\left(\frac{\mu_{cy}^0 - \mu_1^0}{kT}\right) = \frac{\Delta \mu_{hc/w}^0}{kT} + \frac{\Delta \mu_{ex}^0}{kT} + \frac{\sigma}{kT} (a_{cy} - a_0) - \ln \left(1 - \frac{a_p}{a_{cy}}\right) + \frac{\phi}{a_{cy}^2}. \quad (24)$$

D. Free energy of polymer-bound rod-like micelles

The presence of polymer at the aggregate surface modifies the parameter K and thus alters the propensity for the formation of rod-like micelles. Also, the standard Gibbs energy of the surfactant in the cylindrical part is altered thus causing a variation in the CMC. The influence of polymer can be taken into account in a manner identical to that for globular micelles. Therefore, one obtains for polymer-bound rod-like micelles

$$\begin{aligned} \frac{\ln K}{g_{sp}} &= \left(\frac{\mu_{sp}^0 - \mu_{cy}^0}{kT}\right) \\ &= \frac{\sigma}{kT} (a_{sp} - a_{cy}) - \ln \left(1 - \frac{a_p + a_{pol}}{a_{sp}}\right) \\ &\quad + \ln \left(1 - \frac{a_p + a_{pol}}{a_{cy}}\right) + \frac{\phi}{a_{sp}^2} - \frac{\phi}{a_{cy}^2}, \end{aligned} \quad (25)$$

$$\begin{aligned} \left(\frac{\mu_{cy}^0 - \mu_1^0}{kT}\right) &= \frac{\Delta \mu_{hc/w}^0}{kT} + \frac{\Delta \mu_{ex}^0}{kT} \\ &\quad + \frac{\sigma}{kT} (a_{cy} - a_{pol} - a_0) \\ &\quad - \ln \left(1 - \frac{a_p + a_{pol}}{a_{cy}}\right) + \frac{\phi}{a_{cy}^2}. \end{aligned} \quad (26)$$

The CMC is now calculated by introducing Eq. (26) in Eq. (22).

E. Results and discussion

The association behavior of the polymer molecule with anionic and nonionic rod-like micellar systems has been examined here. The calculated results are summarized in Table III. One may observe that the surfactant solution containing the anionic SDS is considered to include some added electrolyte and this is represented through a decrease in the value of ϕ to about half of the value assumed in Table II. In the absence of the polymer, large rod-like micelles are formed in

solution as shown by the large value for K . The polydispersed rod-like micelles have aggregation numbers given by Eq. (21) at various surfactant concentrations. When the polymer molecules are present, the magnitude of K is dramatically reduced. Consequently, in this case, only small ellipsoidal micelles are allowed. The size of these globular micelles are calculated using Eqs. (15) and (11) while the corresponding CMC is calculated using Eqs. (6) and (14). The calculations show that the CMC of the polymer-bound globular micelles is lower than that of the polymer-free rod-like micelles. Therefore, the equilibrium favors the formation of the smaller ellipsoidal micelles in the presence of the polymer. Thus, a rod to globule transition is induced by the addition of the polymer.

In the case of the nonionic surfactant dodecyl hexoethylene glycol monoether (designated as $C_{12}E_6$), the equilibrium area per molecule is estimated to be 42 \AA^2 using Eq. (13). Therefore, the molecular packing parameter $v_0/(a_e l_0)$ has a value of $1/2$ corresponding to an infinite rod. This implies that very large rod-like micelles are formed in polymer-free solutions as reflected in the large value for K estimated using Eq. (23). In the presence of the nonionic polymer, the formation of the rod-like micelles is disallowed since the area a_{cy} is less than $(a_p + a_{pol})$. This is equivalent to stating that the steric repulsions in the presence of the polymer in the cylindrical part is infinitely large and thus K has a magnitude of 0. The allowed aggregate is thus a small ellipsoid. The aggregation number of this ellipsoid is calculated using Eqs. (11) and (15) while the CMC is calculated using Eqs. (6) and (14). The calculations show that the CMC value in the presence of the polymer is somewhat larger than that in the polymer-free solution. This implies that equilibrium will favor the coexistence of infinitely large rod-like micelles not bound to the polymer and free polymers rather than the smaller polymer-bound ellipsoidal micelles. As discussed earlier, a somewhat more hydrophobic polymer can provide a negative free energy contribution adequate to lower the CMC for polymer-bound micelles thus tilting the equilibrium in favor of the smaller bound micelles.

V. INTERACTIONS OF NONIONIC POLYMERS WITH BILAYERS

A. Geometrical properties of bilayers

In general, surfactant molecules with dialkyl chains in their hydrophobic part aggregate into finite spherical bilayers known as vesicles, infinite planar bilayers or as finite

TABLE III. Polymer association with rod-like micelles.

Surfactant	ϕ (\AA^4)	X_{CMC} (mM)	a_e (\AA^2)	$\frac{v_0}{a_e l_0}$	K	g_e	Shape
$C_{12}E_6$	0	0.097	42.0	0.500	3.8×10^{37}	a	rod
$C_{12}E_6 + P^b$	0	0.099	57.3	0.366	0	78	ellipsoid
SDS	5850	1.20	47.7	0.440	1.55×10^{11}	a	rod
SDS + P	5850	0.244	52.0	0.404	0	120	ellipsoid

^a g_e depends on the total surfactant concentration as given by Eq. (21).

^b P refers to the polymer-bound aggregate.

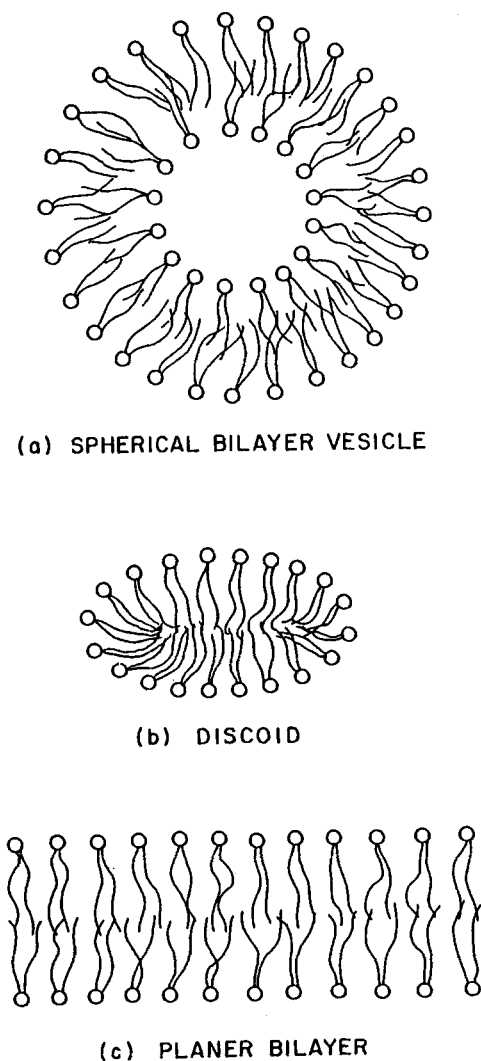


FIG. 3. Structure of spherical vesicles, discoids, and planar bilayers.

disk-like aggregates designated as discoids (Fig. 3). The bilayer vesicles are considered to be spherical with a hydrophobic shell of inner radius r_i and outer radius r_o . The total volume and the total surface area of the spherical hydrophobic shell of the bilayer vesicle are given by

$$V = gv_0 = \frac{4\pi(r_o^3 - r_i^3)}{3}, \quad A = ga = 4\pi(r_o^2 + r_i^2). \quad (27)$$

The surfactant molecules are considered to distribute themselves between the inner and the outer layers in such a way that the surface area per molecule at the two surfaces are equal. This condition need not be met in solutions containing mixtures of surfactants where an asymmetric composition distribution of molecules may be favored by equilibrium. For the present study involving a single surfactant molecule, the distribution of molecules between the inner and the outer layers can be calculated from the condition of equal area per molecule as

$$g_i = g \left(\frac{r_i^2}{r_i^2 + r_o^2} \right), \quad g_o = g - g_i. \quad (28)$$

Here, g_i and g_o are the numbers of molecules in the inner and the outer layers of the vesicle, respectively. The thickness of

the hydrophobic shell should be less than or equal to twice the extended length of the hydrophobic tail of the surfactant molecule. Taking $(r_o - r_i) = 2l_0$, the following geometrical relations are obtained.

$$r_o = \left[\frac{gv_0}{8\pi l_0} - \frac{l_0^2}{3} \right]^{1/2} + l_0, \quad r_i = r_o - 2l_0, \quad (29)$$

$$g = \left(\frac{16\pi l_0^3}{3v_0} \right) \left(\frac{al_0}{v_0} - 1 \right)^{-1}, \quad \frac{1}{2} \leq \frac{v_0}{a_e l_0} < 1. \quad (30)$$

Further, if the volume of the polar head group of the surfactant is v_p then the formation of the vesicle is allowed only when the volume of the interior aqueous cavity of the vesicle is sufficiently larger than the total volume of the polar groups in the inner layer of the vesicle, namely

$$\frac{4\pi r_i^3}{3} \gg g_i v_p. \quad (31)$$

In situations wherein finite spherical vesicles are disallowed, the surfactant molecules may form finite closed aggregates. One can visualize a disk-like aggregate, having a planar middle portion and hemicylindrical rims. In such an aggregate, the area per molecule in the hemicylindrical portion a_{cy} and in the planar lamellar portion a_{lam} will be constants that differ from one another. Both these areas in turn may be different from the equilibrium area a_e of the aggregate. A similar situation was encountered earlier in the discussion about spherocylindrical micelles. Alternately, one can visualize the finite closed aggregates to be roughly discoidal with the area per molecule being more uniform everywhere on the aggregate surface and equal to the equilibrium value. The aggregation number of the discoid will be approximately equal to that of the disk-like aggregate having hemicylindrical rims at the edge, whose average area per molecule is equal to that of the discoid. For a disk-like aggregate having a planar part of radius R and a thickness equal to twice the extended length of the surfactant tail, the total volume and the total surface area are given by the equations

$$V = gv_0 = 2\pi R^2 l_0 + \pi^2 R l_0^2 + \frac{4\pi l_0^3}{3},$$

$$A = ga = 2\pi R^2 + 2\pi^2 R l_0 + 4\pi l_0^2. \quad (32)$$

The radius R of the planar part and the aggregation number g of the discoid can be approximately calculated from Eq. (32) to be

$$R = \left(\frac{gv_0}{2\pi l_0} \right)^{1/2} - \frac{\pi l_0}{4}, \quad g = \left(\frac{16\pi l_0^3}{3v_0} \right) \left(\frac{al_0}{v_0} - 1 \right)^{-2},$$

$$\frac{1}{2} \leq \frac{v_0}{a_e l_0} < 1. \quad (33)$$

Infinitely large lamellar bilayers correspond to the limiting value of unity for the geometrical packing parameter $v_0/(a_e l_0)$. In this case, the area per molecule of the aggregate is constant everywhere and is given by the relation

$$a_{lam} = \frac{v_0}{l_0}. \quad (34)$$

B. Free energy of formation of bilayer aggregates

The free energy of formation of bilayer aggregates is given by an expression identical to Eq. (12) developed for the globular micelles. This would not be the case if the area per molecule of the aggregate at the inner and the outer surfaces of the bilayer are not equal as in some mixed surfactant systems. For a single surfactant in solution that forms bilayers, one can write,

$$\left(\frac{\mu_g^0/g - \mu_1^0}{kT}\right) = \frac{\Delta\mu_{hc/w}^0}{kT} + \frac{\Delta\mu_{ex}^0}{kT} + \frac{\sigma(a - a_0)}{kT} - \ln\left(1 - \frac{a_p}{a}\right) + \frac{\phi}{a^2}. \quad (35)$$

The physical origin of the various terms appearing in the above free energy expression have already been discussed in detail in Sec. III. No new terms are introduced here. The interactions between the two polar head group surfaces across the hydrophobic region of the bilayer are negligibly small and hence they are ignored here. The equilibrium area per molecule of the aggregate is calculated from the equation

$$a = \left[\frac{a_p/a}{1 - a_p/a} + \frac{2\phi}{a^2} \right] \left(\frac{\sigma}{kT} \right)^{-1} \quad (36)$$

as for the globular micelles. Knowing the equilibrium area and the geometrical relations for a spherical vesicle, planar bilayer and discoids, the shape of the aggregate and the aggregation number can be calculated. The CMC value is obtainable from the relation

$$X_{CMC} = \exp\left(\frac{\mu_g^0/g - \mu_1^0}{kT}\right) \text{ at } a = a_e, \quad (37)$$

where the free energy difference term is introduced from Eq. (35) and the equilibrium area is introduced from Eq. (36) or (34).

C. Free energy of polymer-bound bilayers

The association of polymer molecules with the aggregates is represented as before by the characteristic mutual contact area a_{pol} . One may note that the polymer molecules are assumed to be present at both the inner and the outer surfaces of the spherical bilayer vesicle and on both the surfaces of the finite discoidal or infinite lamellar aggregates. The free energy of formation of aggregates in association with the polymers is written as for globular micelles.

$$\left(\frac{\mu_g^0/g - \mu_1^0}{kT}\right) = \frac{\Delta\mu_{hc/w}^0}{kT} + \frac{\Delta\mu_{ex}^0}{kT} + \frac{\sigma(a - a_0 - a_{pol})}{kT} - \ln\left(1 - \frac{a_p + a_{pol}}{a}\right) + \frac{\phi}{a^2} - \frac{\Delta\sigma_{pol}a_{pol}}{kT}. \quad (38)$$

From this free energy expression, the equilibrium area per molecule of the bound aggregates can be calculated as follows:

$$a = \left[\frac{(a_p + a_{pol})/a}{1 - (a_p + a_{pol})/a} + \frac{2\phi}{a^2} \right] \left(\frac{\sigma}{kT} \right)^{-1}. \quad (39)$$

The shape of the aggregate and its aggregation number are determined from Eq. (30) for spherical bilayers, Eq. (33) for discoids, and Eq. (34) for planar bilayers. The CMC is calculated from

$$X_{CMC} = \exp\left(\frac{\mu_g^0/g - \mu_1^0}{kT}\right) \text{ at } a = a_e, \quad (40)$$

where the free energy expression Eq. (38) and the equilibrium area calculated from Eq. (39) or (34) are introduced.

D. Results and discussion

Calculations have been carried out for surfactant systems containing two hydrocarbon chains in the tail group and a nonionic or ionic polar head group. The results are summarized in Table IV. The didodecyl lecithin molecule (designated as $C_{12}LC_{12}$), represents a zwitterionic or an ionic molecule in the illustrative calculations because of the presence of the electrostatic interactions free energy term. The magnitude of the electrostatic repulsion parameter ϕ is taken to be much smaller than that used in Table II for the globular SDS micelles. In the absence of the polymer, calculations show that this surfactant forms spherical bilayer vesicles. The inner and the outer radii of the hydrophobic shell are 81.9 and 48.5 Å, respectively. The volume of the aqueous core per surfactant molecule is approximately 707 \AA^3 whereas the volume of the polar head group of lecithin is about 420 \AA^3 . Therefore, the formation of a bilayer vesicle is geometrically allowed. When the nonionic polymer molecule is present, the equilibrium area calculated from Eq. (39) corresponds to an aggregation number of 291 for a spherical bilayer vesicle as estimated from Eq. (30). Based on Eq. (29), such a vesicle will have inner and outer radii of 3.1 and 36.5 Å, respectively. This implies, in view of Eq. (28), that the inner layer will contain only two surfactant molecules

TABLE IV. Polymer association with bilayers.

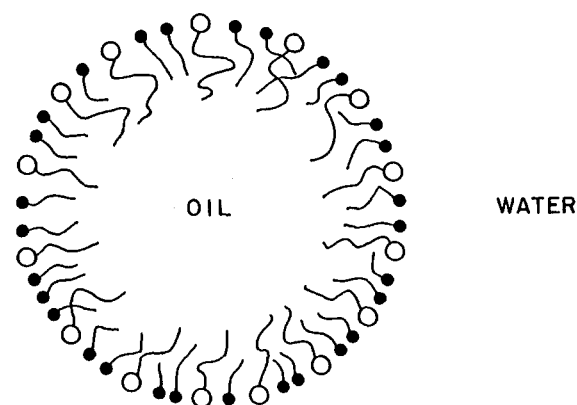
Surfactant	ϕ (\AA^4)	X_{CMC} ($\times 10^{10}$ M)	a_e (\AA^2)	g_e	$\frac{v_0}{a_e l_0}$	Shape
$C_{12}E_7C_{12}$	0	5.03	43.03	4536	0.976	vesicle
$C_{12}E_7C_{12} + P^a$	0	5.10	58.35	734	0.72	discoid
$C_{12}E_6C_{12}$	0	4.91	42.0	...	1.0	planar bilayer
$C_{12}E_6C_{12} + P$	0	5.013	57.3	830	0.732	discoid
$C_{12}LC_{12}$	1170	9.29	43.8	2596	0.959	vesicle
$C_{12}LC_{12} + P$	1170	7.13	58.05	761	0.724	discoid

^a P refers to the polymer-bound aggregates.

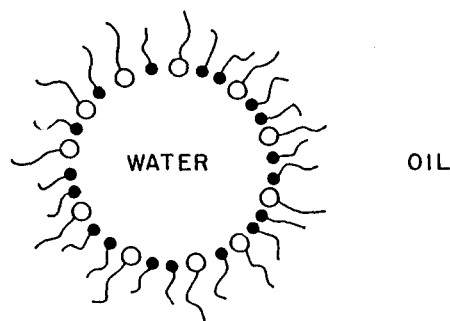
while the outer layer will contain practically all the surfactant molecules. Such an aggregate is geometrically not possible. However, since the geometrical packing ratio $v_0/(a_e l_0)$ is less than unity but greater than $1/2$, the only other allowed aggregate is a discoid. The aggregation number of the discoid is obtained from Eq. (33). Since the CMC value is lower in the presence of the nonionic polymer compared to the polymer-free solution, equilibrium favors the formation of polymer-bound discoidal aggregates rather than the polymer-free spherical vesicles. Thus, the addition of polymer to the surfactant solution causes a disruption of the vesicle structure and generates a closed aggregate having a discoidal shape.

The aggregation behavior of a nonionic surfactant with heptoxyethylene glycol monoether head group and didodecyl tail (denoted by $C_{12}E_7C_{12}$) has been examined. In the absence of the polymer, the surfactant forms large spherical bilayer vesicles having inner and outer hydrophobic shell radii of 69.8 and 103.2 Å, respectively. The volume of the inner aqueous cavity of the vesicle per molecule is about 1001 \AA^3 , whereas the volume of the polar head group is only 441 \AA^3 . Thus a spherical bilayer vesicle is geometrically allowed. In the presence of the nonionic polymer, the equilibrium area predicted for the system corresponds to a bilayer vesicle of aggregation number 286. This corresponds to vesicle hydrophobic shell radii of 36.3 and 2.9 Å at the outer and the inner surfaces, respectively. Such an aggregate is geometrically not allowed. As in the previous case, the geometrical packing parameter $v_0/(a_e l_0)$ lies between unity and $1/2$, implying that the formation of a discoid is geometrically allowed. The calculated CMC and the aggregation number of the discoid are listed in Table IV. One may observe that the CMC for the formation of the polymer-bound discoid is somewhat larger than the CMC for the formation of the polymer-free vesicle. This suggests that at equilibrium, polymer-free spherical vesicles will coexist with free polymer molecules rather than giving rise to polymer-bound discoidal aggregates. It should be noted that the CMC values for the polymer-free and the polymer-bound aggregates are very close to one another, a feature whose origin was discussed in detail in Sec. III. It is obvious that a slightly more hydrophobic polymer would cause the bilayer vesicle to break down into the closed aggregate of discoidal shape.

Illustrative calculations have been carried out for another nonionic surfactant with didodecyl hydrocarbon tail and hexoxyethylene glycol monoether polar head group (designated as $C_{12}E_6C_{12}$). This surfactant has an equilibrium area a_e equal to 42 \AA^2 . This corresponds to a value of unity for the geometrical packing parameter $v_0/(a_e l_0)$. Consistent with this geometrical packing parameter is the occurrence of infinite planar bilayers. The corresponding CMC has also been calculated. In the presence of the nonionic polymer, the calculations show (as in the earlier examples) that the formation of a spherical bilayer vesicle is geometrically disallowed. The equilibrium area calculated using Eq. (39) is consistent with the formation of a finite discoidal aggregate. The CMC value calculated for the formation of the polymer-bound discoid is also shown in Table IV. As in the case of the other nonionic surfactant system $C_{12}E_7C_{12}$, the CMC for the



(a) OIL IN WATER DROPLET



(b) WATER IN OIL DROPLET

FIG. 4. Models of microemulsion droplets of oil in water-type and water in oil-type.

formation of the polymer-bound discoids is larger than that for the formation of the polymer-free planar bilayer. Therefore, equilibrium favors the occurrence of free polymer coexisting with the infinite planar bilayer rather than the polymer-bound discoids. Again, the close proximity of the CMC values for the free and the bound aggregates suggests that a polymer with somewhat larger hydrophobicity can disrupt the planar bilayer structure and give rise to the formation of finite discoidal aggregates.

VI. INTERACTIONS OF NONIONIC POLYMERS WITH MICROEMULSIONS

A. Geometrical characteristics of microemulsions

The microemulsions of oil in water and of water in oil are both considered here. A spherical droplet structure is visualized for the two kinds of microemulsions (Fig. 4). This is the conventional picture for microemulsions designated in literature as either lower or upper phase microemulsions. There is yet another domain of microemulsion that is called the middle phase microemulsion in the literature. Here, the domain structure is not spherical and is less well defined. The present work focuses on the oil-continuous and the wa-

ter-continuous spherical microemulsion droplets and excludes the region of middle phase microemulsions.

The microemulsions, often contain an alcohol as a co-surfactant. Therefore, we formulate a model for a system consisting of a mixture of surfactant and alcohol. The oil is chosen to be an aliphatic hydrocarbon similar in nature to the hydrophobic tails of the surfactant and the alcohol. The various geometrical properties of the microemulsion droplet can be estimated from the composition of the surfactant-alcohol mixture and the molecular properties of the two amphiphiles.^{26,27} The microemulsion droplet can be visualized as consisting of a membrane region separating the oil and the water domains. The membrane region is assumed to include all the surfactant and alcohol molecules. In reality, some alcohol will also be present in the oil phase. This does not modify any of the results presented here since the calculated values will be shown as functions of the membrane composition rather than of the total system composition. The surfaces of the membrane region are assumed to have radii of R_w and R_o , respectively, depending upon whether they are in contact with water or the oil regions. One may note that when $R_o/R_w < 1$, the microemulsion is of the oil in water type. For $R_o/R_w > 1$, one obtains the water in oil microemulsions. The thickness of the membrane region is taken to be the number average length of the extended hydrocarbon chains of the surfactant and the alcohol. Therefore,

$$|R_w - R_o| = \frac{g l_o + g_a l_{oa}}{g + g_a} = l_o \frac{[1 + (g_a l_{oa})/(g l_o)]}{(1 + g_a/g)} \quad (41)$$

Here, g and g_a are the numbers of surfactant and alcohol molecules in a spherical microemulsion droplet and l_o and l_{oa} are the extended lengths of their respective hydrophobic tails. The total volume and the surface area of the membrane region are given by

$$V = g v_o + g_a v_{oa} = \frac{4\pi |R_w^3 - R_o^3|}{3}, \quad A = g a = 4\pi R_w^2 \quad (42)$$

v_o and v_{oa} refer to the volumes of the hydrophobic tails of the surfactant and the alcohol, respectively. From Eqs. (41) and (42), one obtains

$$1 + \left(\frac{R_o}{R_w}\right) + \left(\frac{R_o}{R_w}\right)^2 = \left[\left(\frac{3v_o}{a l_o}\right) \left(1 + \frac{g_a v_{oa}}{g v_o}\right) \left(1 + \frac{g_a}{g}\right) \right] / \left[\left(1 + \frac{g_a l_{oa}}{g l_o}\right) \right] \quad (43)$$

Since the hydrophobic parts of the surfactant and the alcohol are taken to be aliphatic chains, one can write

$$\frac{v_{oa}}{v_o} \approx \frac{l_{oa}}{l_o} \quad (44)$$

The ratio between the radii of the two interfaces of the membrane region is obtained from Eqs. (43) and (44) to be

$$\frac{R_o}{R_w} = \left[\left(\frac{3v_o}{a l_o}\right) \left(1 + \frac{g_a}{g}\right) - \frac{3}{4} \right]^{1/2} - \frac{1}{2} \quad (45)$$

The radii R_w and R_o , can be calculated explicitly using Eqs. (41) and (45). Given these two radii, the volume of the oil solubilized per unit volume of the surfactant molecule in a water continuous microemulsion can be estimated using the relation

$$\frac{V_{oil}}{V_{surf}} = \left(\frac{R_o^3}{R_w^3 - R_o^3}\right) \left(1 + \frac{g_a v_{oa}}{g v_o}\right) \left(\frac{v_o}{v_o + v_p}\right), \quad \frac{R_o}{R_w} < 1. \quad (46)$$

Note that the volume of the surfactant molecule includes that of the hydrophobic part denoted by v_o as well as that of the polar head group denoted by v_p . Similarly, the volume of water solubilized per unit volume of surfactant molecule is given by the expression

$$\frac{V_{water}}{V_{surf}} = \left(\frac{R_w^3}{R_o^3 - R_w^3}\right) \left(1 + \frac{g_a v_{oa}}{g v_o}\right) \left(\frac{v_o}{v_o + v_p}\right) - \left(1 + \frac{g_a v_{pa}}{g v_p}\right) \left(\frac{v_p}{v_o + v_p}\right), \quad \frac{R_o}{R_w} \geq 1. \quad (47)$$

Here, v_{pa} refers to the volume of the polar group of the alcohol molecule. All the necessary geometrical relations are now available to calculate the structural features of the microemulsion droplets. For a given ratio of alcohol to the surfactant, the only unknown is the equilibrium area per molecule of the surfactant a_e appearing in Eq. (45). This equilibrium area is calculated knowing the free energy of formation of the microemulsion droplet.

B. Free energy of a microemulsion droplet

Microemulsions that are saturated with either water or oil present as the solubilize are considered here. Therefore, the amount of solubilization calculated here will correspond to the maximum value possible. The standard free energy of a microemulsion droplet can be estimated by an expression similar to that used above for various surfactant aggregates. However, the expressions for the surfactant aggregates are modified to include additional contributions arising from the presence of alcohol in the membrane region. The polar group of alcohol provides partial shielding of the hydrocarbon-water interface. It also increases the steric repulsions at the aggregate surface. The equilibrium area per surfactant molecule present in the microemulsion droplet is obtainable from the relation

$$a = \left\{ \frac{[a_p + (g_a/g)a_{pa}]/a}{1 - [a_p + (g_a/g)a_{pa}]/a} + \frac{\phi}{a^2} \right\} \left(\frac{\sigma}{kT}\right)^{-1} \quad (48)$$

The equilibrium area per surfactant molecule calculated from the above equation in conjunction with the geometrical relations Eqs. (41) and (45) determines the radius of the microemulsion droplet. The extent of solubilization of oil or water within the droplets is calculated using Eqs. (46) or (47), respectively.

C. Free energy of a polymer-bound microemulsion droplet

In the presence of the nonionic polymer, the polymer segments are considered to be at the aggregate-water interface as before. The resulting modifications in the steric re-

pulsions at the droplet surface and the enhanced shielding of the droplet surface are taken into account in the free energy of microemulsification. Correspondingly, the equilibrium area per molecule is obtained from the expression

$$a = \left\{ \frac{[a_p + (g_a/g)a_{pa} + a_{pol}]/a}{1 - [a_p + (g_a/g)a_{pa} + a_{pol}]/a} + \frac{\phi}{a^2} \right\} \left(\frac{\sigma}{kT} \right)^{-1} \quad (49)$$

As before, the radii R_o and R_w are calculated from Eqs. (41) and (45) and the volume ratios of the solubilize to the surfactant are calculated using Eqs. (46) and (47).

D. Results and discussion

Calculations of the microemulsification behavior have been carried out for a mixture of the nonionic surfactant dodecyl nonoxyethylene glycol monoether (designated as $C_{12}E_9$) and normal pentanol (designated as C_5OH). No electrostatic interactions are involved in this case and correspondingly, the parameter ϕ is equal to zero. At low alcohol-to-surfactant ratios water-continuous microemulsions are formed. With an increasing ratio of alcohol-to-surfactant, a phase inversion to the oil-continuous microemulsion occurs. For intermediate ranges of alcohol-to-surfactant ratios the structure of the microemulsion is not likely to be that consisting of spherical droplets. In this region, the middle phase, so-called bicontinuous microemulsions are likely to be generated.

The calculated results are presented in Figs. 5 and 6. The volume of oil or water solubilized per unit volume of the

surfactant is shown in Fig. 5 for various ratios of alcohol to the surfactant. The calculations show that the presence of the polymer essentially causes a shift in the ratio of the alcohol to the surfactant required to achieve a certain extent of solubilization. Further, the phase inversion from oil in water microemulsion to water in oil microemulsion occurs at a larger ratio of alcohol to surfactant. However, the qualitative trend of increasing oil solubilization with increasing amount of alcohol in the water-continuous microemulsion and that of decreasing water solubilization with increasing amounts of alcohol in the oil-continuous microemulsion are displayed by both the polymer-free system as well as the polymer-containing system. If one adds nonionic polymer molecules to a stable microemulsion, the calculated results imply that a liquid-liquid phase separation will result to expel the excess amount of oil or water that is beyond the equilibrium solubilization capacity of the polymer-bound microemulsion droplets. The droplet radii are shown in Fig. 6 for the polymer-free and the polymer-bound microemulsion droplet systems. The trend parallels that of the solubilization capacity curves shown in the previous figure.

VII. CONCLUSIONS

The consequences of the presence of a nonionic polymer in surfactant solutions has been explored here theoretically. In polymer-free solutions, the surfactants aggregate to form small globular micelles, large rod-like micelles, planar and spherical bilayers. The nonionic polymer is considered to

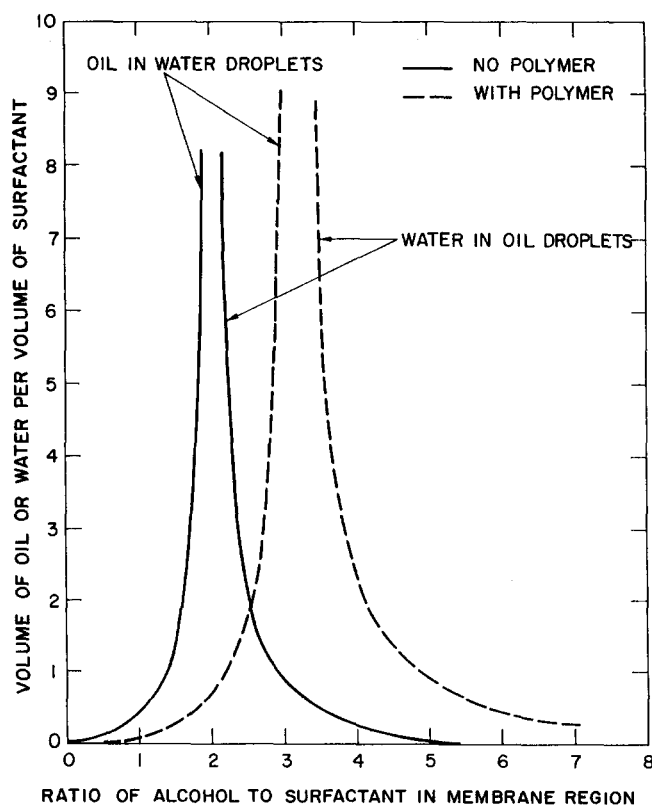


FIG. 5. Volume ratio of the solubilize to the surfactant in the microemulsion droplet. Continuous lines refer to the polymer-free system while the dotted lines refer to the system containing polymer.

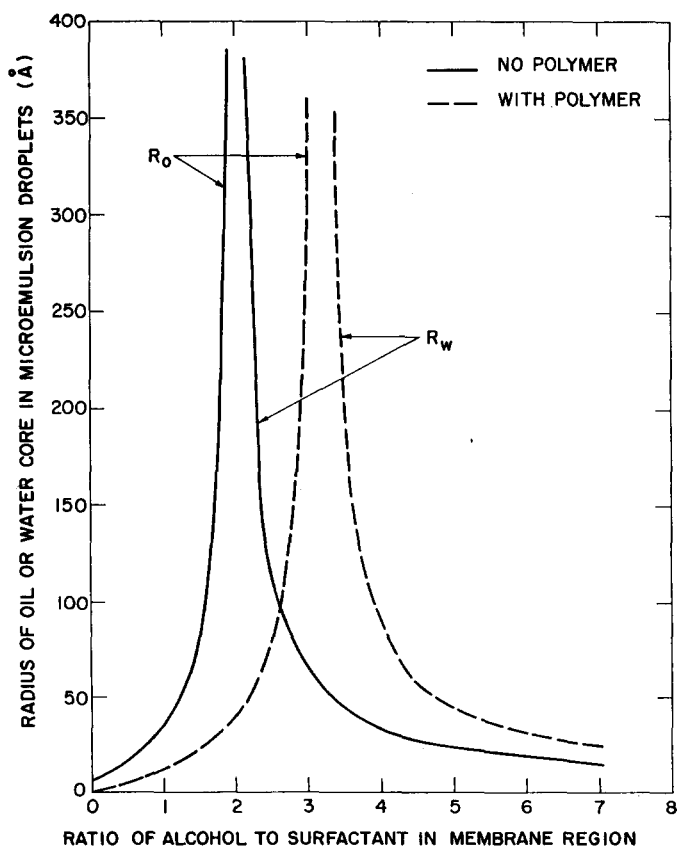


FIG. 6. Radii of the membrane-water and membrane-oil interfaces in microemulsion droplets. Continuous line refers to the polymer-free system while the dotted line refers to the polymer containing system.

associate with the aggregates by wrapping around the aggregate–water interface. This gives rise to enhanced shielding of the hydrophobic surface of the aggregate from water, increased steric repulsions between the polar head groups of the surfactants and the polymer segments at the aggregate surface and increased hydrophobic interactions between the polymer and the aggregate surface. A simple free energy model has been formulated to describe these changes arising from the association of the nonionic polymer with the surfactant aggregates.

Model calculations show that anionic or zwitterionic surfactants and nonionic surfactants behave in contrasting ways in the presence of the polymer. Anionic surfactants that generally form small globular micelles in the absence of the polymer molecules give rise to yet smaller polymer-bound micelles at a substantially lower value of the critical micelle concentration. Anionic surfactants that generate large, polydisperse rod-like micelles associate with the polymer to produce smaller globular micelles that are monodispersed at a significantly lower CMC. Zwitterionic or anionic surfactants that usually aggregate as spherical bilayer vesicles are disrupted by the polymer to give rise to smaller discoidal aggregates at a lower CMC. In general, for anionic and zwitterionic surfactants, the CMC associated with the polymer-bound aggregates is substantially lower than the CMC associated with the polymer-free aggregates.

In contrast, nonionic surfactant aggregates may or may not form association structures with nonionic polymer molecules. When the association structures are favored, the polymer-free globular micelles transform into much smaller polymer-bound spherical micelles. Large, polydispersed rod-like free micelles transform into smaller globular-bound micelles. Planar or spherical bilayers transform into polymer-bound discoidal aggregates. In all the cases, the CMC for the formation of the polymer-bound aggregates is usually very close to that for the formation of the polymer-free aggregates. For the illustrative examples considered in this study, in most situations, the formation of the polymer-bound aggregates was not favored. Thus, the polymer-free aggregates are predicted to coexist with free polymer molecules. It is very interesting to observe that subtle free energy contributions associated with the polymer hydrophobicity can tilt the balance between the free aggregates and bound aggregates in the case of nonionic surfactants.

The model has also been applied to the multicomponent system of microemulsions. The model predicts that qualitatively, the microemulsification behavior as a function of the increasing ratio of alcohol to the surfactant is the same for the polymer-free and polymer-containing systems. However, at a given ratio of the alcohol to the surfactant, the extent of solubilization of the oil or water, and the radius of the microemulsion droplet are substantially altered by the presence of the polymer molecule. Consequently, a stable microemulsion will undergo liquid–liquid phase separation to expel excess water or excess oil due to the addition of the polymer. The substantive changes in the aggregate morphologies caused by the presence of the polymer molecule suggests that polymer molecules may be used to induce desired changes in the patterns of surfactant self-assembly.

APPENDIX

a	surface area of the aggregate–water interface per molecule of the surfactant
a_e	surface area per molecule of the aggregate at equilibrium
a_0	area per molecule of the aggregate–water interface that is shielded from contact with water because of the presence of the polar head group of the surfactant
a_p	cross-sectional area of the polar head group of the surfactant
a_{pa}	cross-sectional area of the polar head group of the alcohol
a_{sp}	area per molecule of the largest spherical micelle
a_{cy}	area per molecule of the infinitely long rod-like micelle
a_{lam}	area per molecule of the infinite planar bilayer
a_{pol}	contact area between the polymer and the hydrophobic surface of the aggregate per molecule of the surfactant
E_x	nonionic polar head group consisting of x units of ethylene oxide
g	number of surfactant molecules in an aggregate
g_e	number of surfactant molecules in the equilibrium aggregate
g_{sp}	number of surfactant molecules in the largest spherical micelle
g_a	number of alcohol molecules in an aggregate
g_i	number of surfactant molecules in the inner layer of the bilayer vesicle
g_o	number of surfactant molecules in the outer layer of the bilayer vesicle
k	Boltzmann constant
l_0	extended length of the hydrophobic tail of the surfactant
l_{0a}	extended length of the hydrophobic tail of the alcohol
L	length of the cylindrical middle portion of the spherocylindrical micelle
n_c	number of methylene and methyl groups in the hydrophobic tail of the surfactant molecule
r_0	radius of the hydrophobic core of the spherical micelle
r_i	inner radius of the spherical bilayer vesicle
r_o	outer radius of the spherical bilayer vesicle
R_0	radius of the membrane–oil interface in a microemulsion droplet
R_w	radius of the membrane–water interface in a microemulsion droplet
R	radius of the planar part of the discoidal aggregate
T	absolute temperature of the solution
v_0	molecular volume of the hydrophobic tail of the surfactant
v_{0a}	molecular volume of the hydrophobic tail of the alcohol
v_p	molecular volume of the polar head group of the surfactant
v_{pa}	molecular volume of the polar head group of the alcohol
X_1	mole fraction of singly dispersed surfactant molecules
X_g	mole fraction of aggregates containing g surfactant molecules

X_w	mole fraction of water in the solution
X_p	mole fraction of polymer in the solution
μ_1^0	standard chemical potential of singly dispersed surfactant molecule
μ_g^0	standard chemical potential of an aggregate containing g surfactant molecules
μ_{sp}^0	standard chemical potential per molecule of the largest spherical micelle
μ_{cy}^0	standard chemical potential per molecule of the infinite rod-like micelle
σ	macroscopic hydrocarbon-water interfacial tension
$\Delta\sigma_{pol}$	difference between the macroscopic polymer-water interfacial tension and polymer-hydrocarbon interfacial tension
ϕ	electrostatic interaction parameter describing repulsions between surfactant polar head groups at the aggregate surface
χ	Flory-Huggins polymer-solvent interaction parameter

¹C. Tanford, *The Hydrophobic Effect* (Wiley, New York, 1973).

²J. H. Fendler, *Membrane Mimetic Chemistry* (Wiley, New York, 1982).

³*Microemulsion Systems*, edited by H. L. Rosano and M. Clause (Dekker, New York, 1987).

⁴I. D. Robb, in *Anionic Surfactants*, edited by E. H. Lucassen-Reynders (Plenum, New York, 1981), p. 109.

⁵E. D. Goddard, *Colloid Surf.* **19**, 255 (1986).

⁶S. Saito, in *Nonionic Surfactants*, edited by M. J. Schick (Dekker, New York, 1987), p. 881.

⁷(a) M. N. Jones, *J. Colloid Interface Sci.* **23**, 36 (1967); (b) M. J. Schwuger, *ibid.* **43**, 491 (1973); (c) H. Lange, *Kolloid. Z. Z. Polym.* **243**, 101 (1971); (d) H. Arai, M. Murata, and K. Shinoda, *J. Colloid Interface*

Sci. **37**, 223 (1971); (e) Y. Moroi, H. Akisada, M. Saito, and R. Matuura, *ibid.* **61**, 233 (1977).

⁸(a) B. Cabane, *J. Phys. Chem.* **81**, 1639 (1977); (b) B. Cabane and R. Duplessix, *J. Phys.* **43**, 1529 (1982); (c) *Colloids Surf.* **13**, 19 (1985); (d) *J. Phys.* **48**, 651 (1987).

⁹(a) F. M. Witte, P. L. Buwalda, and J. B. F. N. Engberts, *Colloid Polym. Sci.* **265**, 42 (1987); (b) F. W. Witte, Doctoral dissertation, University of Groningen, 1988.

¹⁰K. Shirahama, A. Himuro, and N. Takisawa, *Colloid Polym. Sci.* **265**, 96 (1987).

¹¹(a) F. M. Winnik, M. A. Winnik, and S. Tazuke, *Macromolecules* **91**, 594 (1987); (b) R. Zana, P. Lianos, and J. Lang, *J. Phys. Chem.* **89**, 41 (1985); (c) N. J. Turro, B. H. Baretz, and P. L. Kuo, *Macromolecules* **17**, 1321 (1984).

¹²(a) R. Nagarajan and B. Kalpakci, in *Microdomains in Polymer Solutions*, edited by P. L. Dubin (Plenum, New York, 1985), p. 368; (b) J. Francoise, J. Dayantis, and J. Sabbadin, *Eur. Polym. J.* **21**, 165 (1985); (c) K. E. Lewis and C. P. Robinson, *J. Colloid Interface Sci.* **32**, 539 (1970).

¹³(a) M. L. Fishman and F. R. Eirich, *J. Phys. Chem.* **75**, 3135 (1971); (b) M. L. Smith and N. Muller, *J. Colloid Interface Sci.* **52**, 507 (1975); (c) T. Gilanyi and E. Wolfram, *Colloids Surf.* **3**, 181 (1981).

¹⁴S. P. Trushenski, in *Improved Oil Recovery by Surfactant and Polymer Flooding*, edited by D. O. Shah and R. S. Schechter (Academic, New York, 1977).

¹⁵M. T. Szabo, *Soc. Pet. Eng. J.* **19**, 4 (1979).

¹⁶R. Nagarajan, *Colloids Surf.* **13**, 1 (1985).

¹⁷R. Nagarajan, *Adv. Colloid Interface Sci.* **26**, 205 (1986).

¹⁸R. Nagarajan, *Colloids Surf.* (in press).

¹⁹J. N. Israelachvili, D. J. Mitchell, and B. W. Ninham, *J. Chem. Soc. Faraday Trans. 2* **72**, 1525 (1976).

²⁰R. Nagarajan and E. Ruckenstein, *J. Colloid Interface Sci.* **71**, 580 (1979).

²¹R. Nagarajan, *Chem. Eng. Commun.* **55**, 261 (1987).

²²E. Helfand and Y. Tagami, *J. Polym. Sci. Part B* **9**, 741 (1971).

²³P. Mukerjee, *J. Phys. Chem.* **76**, 565 (1972).

²⁴(a) R. J. M. Tausk, C. Oudshoorn, and T. Th. G. Overbeek, *Biophys. Chem.* **2**, 53 (1974); (b) R. J. M. Tausk and T. Th. G. Overbeek, *ibid.* **2**, 175 (1974).

²⁵P. J. Missel, N. A. Mazer, G. B. Benedek, C. Y. Young, and M. C. Carey, *J. Phys. Chem.* **84**, 1044 (1980).

²⁶D. J. Mitchell and B. W. Ninham, *J. Chem. Soc. Faraday Trans. 2* **77**, 601 (1981).

²⁷D. Oakenfull, *J. Chem. Soc. Faraday Trans. 1* **76**, 1875 (1980).