Dynamic Properties of Micellar Solutions

I. Effects of Short-Chain Alcohols and Polymers on Micellar Stability

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The effect of n-alkanols from C_1 to C_5 on both equilibrium and dynamic properties of sodium dodecyl sulfate (SDS) micellar solutions has been investigated using electrical conductivity and pressure-jump methods. Methanol and ethanol were found to decrease the conductance of micellar solutions due to the lowering of dielectric constant of solvent. Higher alkanols from C_3 to C_5 may decrease or increase the conductance of micellar solutions depending on the concentration of SDS. At low surfactant concentration, a minimum of conductance was observed. This has been attributed to both effects of decrease in surfactant monomer concentration (CMC) and the increase in counterion dissociation of micelles upon the penetration of alcohols into micelles. At higher surfactant concentration, the conductance was found to increase directly due to the dominance of the latter effect. Unlike the complex change of conductance, the slow relaxation rate constant, $1/\tau_2$, has been found to increase monotonically upon the addition of all alkanols except pentanol. The labilizing effect (i.e., decreasing τ_2) of alkanols increases with increasing alkanol chain length from C_1 to C_3 and levels off at C_4. The labilizing effect has also been found to vary with SDS concentration depending upon the mechanism of slow relaxation process. Based on the Aniansson and Wall theory, the labilizing effect of alkanols has been attributed to two factors: (1) the stabilization of micelle nuclei either due to a decrease of micelle nucleus size, or due to an increase of micelle nucleus population; (2) the decrease of activation energy for the formation of micelle nuclei. In view of the changes in both slow relaxation time and CMC upon the addition of alkanols, the concept of micelle stability has been discussed in terms of the "thermodynamic stability" and the "kinetic stability" of micelles. Finally, the effect of polymers on the slow relaxation process was also investigated. The slow relaxation rate constant $1/\tau_2$ was found to increase by three orders of magnitude as the concentration of polyvinylpyrrolidone increased up to 8% (w/w). Based on the molecular model of polymer–micelle complex proposed by B. Cabane (*J. Phys. Chem.* **81**, 1639, 1977), the effect of polymer has been interpreted in terms of the polymer being the nucleating agent for micelle nuclei. The result verifies the concept that the rate-limiting step in micelle formation and dissolution process is the formation of micelle nuclei. © 1986 Academic Press, Inc.

I. INTRODUCTION

The studies on kinetics and the dynamic properties of micellar solutions have received considerable attention in recent years. A number of reports (1–25) employing various chemical relaxation techniques, such as stopped-flow, temperature-jump, pressure-jump, and ultrasonic absorption, have provided a new insight into the dynamic aspects and micellization kinetics of surfactant solutions. For pure ionic surfactant systems, it has been shown that micelles form through a step-wise association process at low surfactant concentrations (4), while at high surfactant concentrations they can also form via a reversible coagulation process of submicellar aggregates (15). These two mechanisms occur simultaneously in the nonionic surfactant system above CMC (15). The theoretical frame work, first developed by Aniansson and Wall (2, 4) and supplemented by Kahlweit (15) and Hall (25), successfully correlates the dynamic parameters of a micellar solution with its ther-

modynamic or equilibrium parameters and makes the dynamic study in micellar solutions informative and valuable.

The theory predicts two well-separated relaxation processes in a pure micellar solution. The fast relaxation process with relaxation time τ_1 in microseconds is associated with the fast exchange of monomers between micelles and bulk aqueous phase. Such an exchange reflects a dynamic equilibrium between the monomer and micellar state in the solution. The slow relaxation process with relaxation time τ_2 in milliseconds or longer is attributed to the micelle formation and dissolution process.

Interestingly, the two relaxation times can be used to calculate two important statistical parameters of a micellar system, namely the "residence time" of a surfactant in micelles and the average "lifetime" of micelles. The residence time of a surfactant monomer in micelles is equal to n/k^-, where n is the mean aggregation number and k^- is the dissociation rate constant of a surfactant from a micelle (27). The average lifetime of a micelle T_M can be obtained from the following equation (27):

$$T_M = \tau_2 \frac{na}{1 + (\sigma^2/n)a} \quad [1]$$

and

$$a = \frac{A - A_1}{A_1} \quad [2]$$

where A is the total surfactant concentration, A_1 is the monomer concentration which is often approximated as the CMC, and σ is the half-width of the Gaussian distribution curve of micellar population. When the concentration of surfactant is much greater than CMC, T_M is approximately equal to $n\tau_2$. Thus, the slow relaxation time can be directly related to the lifetime (or stability) of micelles. The above-mentioned analysis and expressions are valid for pure micellar systems. An extension of the framework to mixed micellar systems has also been proposed by Aniansson (5). It predicts two fast and one slow relaxation processes in a two-component mixed micellar

system. The development in the field of dynamics of surfactant solutions has been reviewed (15, 26, 27), and very few studies (28–33) concerning the effect of solubilizates on the dynamics of micellar solutions have been reported. This is the main objective of our studies presented in this paper.

Alcohols and oil are the most commonly used additives in micellar solutions to form various solubilized systems or microemulsions for a wide range of industrial and technological applications. Many studies (34–50) concerning the effects of alcohols on the equilibrium and thermodynamic properties of micellar solutions such as CMC, aggregation number, counterion binding, etc. have been reported. Singh and Swarup (34) have found that the CMC goes through a minimum upon addition of alcohols from C_3 to C_6 in sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTMAB) solutions. Methanol and ethanol also show a similar result (51, 52). It has been shown (45) that the quantity $RT \ln(X_0)$, where X_0 is the CMC in mole fraction unit, is proportional to the Gibbs free energy change for the addition of one more monomer to a micelle, which in turn is related to the hydrophobic driving force for micelle formation. Thus, the lower the CMC, the more negative will be the Gibbs free energy change and hence the more stable the micelle. We can consequently assert from the change in the CMC (34) that the addition of alcohols thermodynamically stabilizes the micelle at lower alcohol concentrations, and destabilizes the micelle at higher alcohol concentrations.

However, this is opposite to the results of dynamic studies in micellar solutions (29). Zana et al. (28–30) have comprehensively investigated the effect of normal alcohols (C_2 to C_6) on both equilibrium and dynamic properties of alkyltrimethylammonium bromide solution. The slow relaxation time τ_2 has been found to decrease upon the addition of alcohols (29), reflecting a shorter lifetime or poorer stability of micelles. Such a paradox between the equilibrium and dynamic studies of mixed micellar solutions stimulated us to reexamine

the effect of alcohols and some other additives on the dynamic properties of micellar solutions, and reevaluate the concept of micelle stability.

II. EXPERIMENTAL

Sodium dodecyl sulfate was used as supplied by BDH (purity ~99%). All normal alkanols with purity above 99% were used directly without further purification. Absolute ethanol was of USP 200 proof (Reagent Grade) from Florida Distillers Corporation. The nonionic polymer polyvinylpyrrolidone (PVP) NP-K90 (average molecular weight 360,000) was supplied by GAF Corporation. 1-Ethyl-2-pyrrolidinone was from Aldrich Chemical Company. In preparing a surfactant–polymer solution, a stock polymer solution at desired polymer concentration (weight of polymer/100 g water) was prepared first. Then the stock was used as solvent to prepare a surfactant solution at desired surfactant concentration. The relaxation time τ_2 was measured using pressure-jump apparatus with conductivity detection from Dia-Log Corporation, West Germany. All measurements were carried at 20°C with pressure jump of 140 bar. The CMC of SDS at 20°C was measured to be 8.5 mM by conductivity method, which is in agreement with the literature (81).

III. RESULTS AND DISCUSSIONS

The fast relaxation time τ_1 was too fast to measure by our pressure-jump apparatus, hence only the slow relaxation time τ_2 has been investigated. Figure 1 shows the slow relaxation rate constant $1/\tau_2$ of a 10 mM SDS solution upon the addition of normal alkanols from methanol to pentanol. The concentrations of all alkanols are limited to the CMC-decreasing region as reported by Singh and Swarup (34). The slow relaxation rate constants are found to increase for all alkanols except pentanol at which a reverse trend is observed. This indicates that short chain alcohols from C_1 to C_4 labilize micelles as reflected from dynamic measurements. In con-
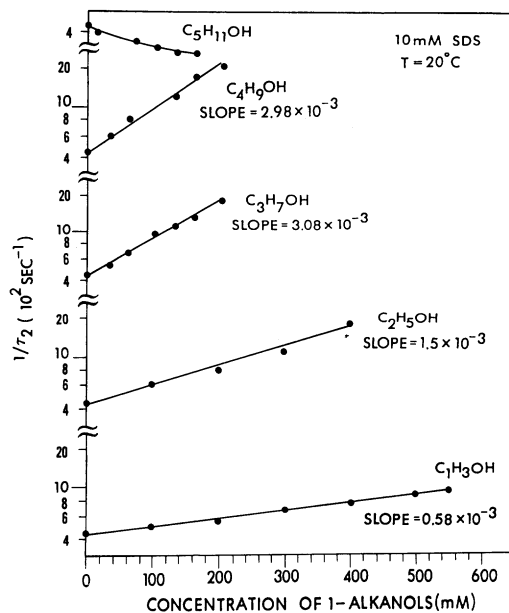

FIG. 1. Variation of the slow relaxation rate constant $1/\tau_2$ of 10 mM SDS as a function of alkanol concentration.

trary to this interpretation, the equilibrium data on the shift in CMC suggests that these alcohols stabilize the micelles. When we extend the alcohol concentrations to much higher values where CMC increases, the rate constant $1/\tau_2$ of 100 mM SDS still increases monotonically as shown in Fig. 2 for all alkanols except pentanol. Based on the dynamic property of micellar solutions reported in Figs. 1 and 2, we can categorize the alcohols from C_1 to C_4 as short-chain alcohols which labilize micelles; and alcohols from C_5 onward as medium- and long-chain alcohols. In the present paper, we shall report the effect of short-chain alcohols on the dynamic properties of micellar solutions.

Effects of Mixed Solvents on Equilibrium Properties of Micellar Solutions

It is informative to first briefly recall the effect of mixed solvents on the equilibrium properties of micellar solutions. Short-chain alcohols are usually known as cosolvents
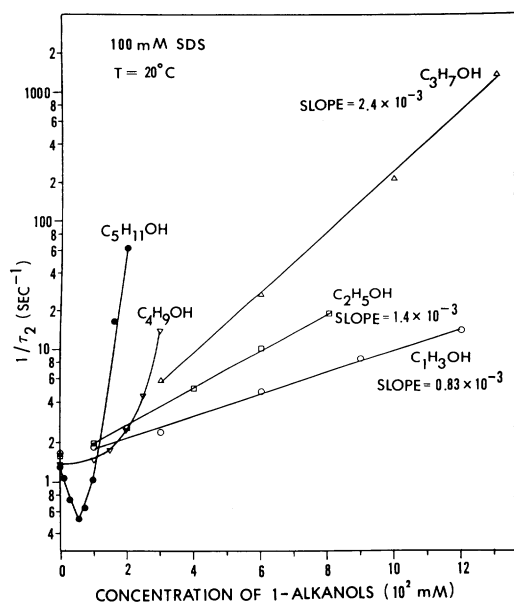
FIG. 2. Variation of the slow relaxation rate constant $1/\tau_2$ of 100 mM SDS as a function of alkanol concentration.

which are highly miscible with water. An extensive review of the solvent effect on amphiphilic aggregation by Magid (53) has indicated that the continuous addition of cosolvents into aqueous micellar solutions usually leads to higher CMC values (but may be preceded by an initial CMC-depression for many "pene-

trating" cosolvents at low concentrations), smaller aggregation number and eventually a break-down of micelles. These complex cosolvent effects cannot be explained or predicted satisfactorily at present. Nonetheless, three factors are generally considered to account for the influence of cosolvents on the equilibrium properties of aqueous micellar solutions. The first one deals with the change of bulk dielectric constant of a solvent. Cosolvents which lower the dielectric constant of water should increase the counterion binding, and hence decrease the conductance of the solution. However, this prediction seems only valid for few cases in Figs. 3 and 4, where the change of conductance as a function of alcohol concentration is shown. Methanol and ethanol decrease the conductance as predicted, while a minimum or a direct increase of conductance is observed for longer chain alcohols. Zana et al. (28) have also found a direct increase in the degree of ionization of tetradecyltrimethylammonium bromide upon the addition of ethanol to hexanol. This contradiction between the expected and observed results thus requires a consideration of second factor.

The second factor concerns the "comicellization" of cosolvents with surfactants. Despite of the high miscibility of cosolvents with
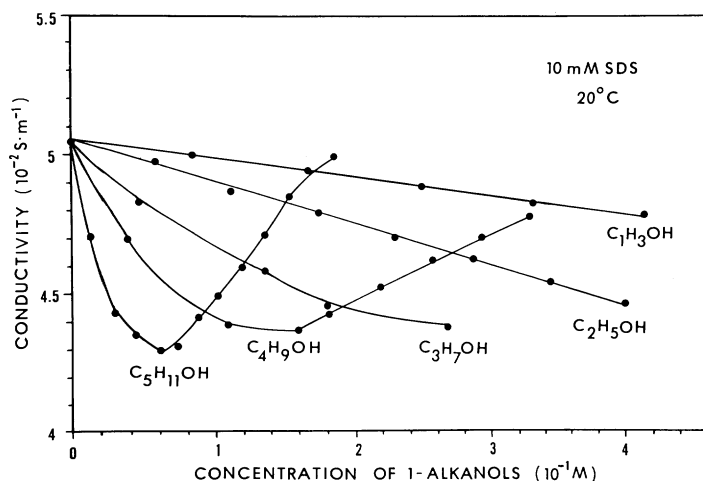

FIG. 3. Variation of the conductivity of 10 mM SDS solution as a function of alkanol concentration.
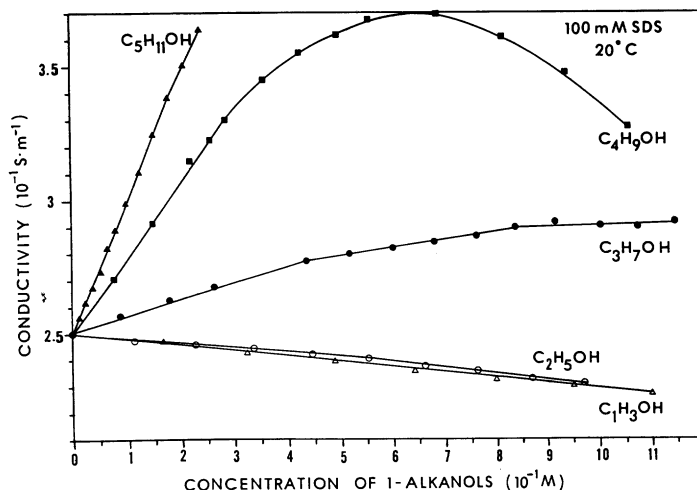
FIG. 4. Variation of the conductivity of 100 mM SDS solution as a function of alkanol concentration.

water, many cosolvents are known to penetrate into micelles (53). The effect of such "penetrating" cosolvents has been analyzed by Zana et al. (28) mainly in two aspects: an increase in distance between surfactant head groups (steric effect) and a decrease in the dielectric constant of micellar palisade layer. Both effects can explain the increase of conductance and the decrease of CMC as a result of dilution of micellar surface charges (28). A quantitative analysis (42) has shown that the factor governing the CMC-depression is the mole fraction of alcohol in the micellar phase, independent of the kind of alcohols. The chemical potential of micelles decreases because the electrical potential of micelles decreases upon alcohol penetration (42). However, a recent paper by Manabe et al. (54) argued that the solubilized alkanols in micelles cause an increase in degree of ionization of surfactants but have little influence on electrical potential at micellar surface due to a compensation from the dissociated counterions. Hence, the depression of CMC has been attributed to the increase in entropy of mixing of mixed micelles due to comicellization (46, 55).

The results in Figs. 3 and 4 can be interpreted in terms of this comicellization effect. The conductance of a micellar solution is mainly attributed to the surfactant monomers at surfactant concentration close to the CMC, while at higher surfactant concentration micelles may contribute dominantly to the conductance of the solution (22). Since the penetration of alcohol into micelles can decrease the CMC and hence the surfactant monomer concentration (42) and increase the counterion dissociation of micelles (54), the addition of alcohols into micellar solutions is expected to decrease the conductance contributed by the surfactant monomers, while increase the conductance by the micelles and their counterions. The initial decrease of conductance observed in Fig. 3 can be attributed to the decrease of the CMC upon the addition of alcohols. As alcohol concentration increases, the increase in conductance due to the increasing ion dissociation of micelles may counteract the decrease in conductance due to the CMC depression, and hence result in a minimum of conductance. Further increase in alcohol concentration will lead to a rise in conductance mainly due to the contribution from the ion dissociation of micelles. The direct increase in conductance observed in Fig. 4 indicates that the conductance of a micellar solution at higher surfactant concentration is indeed dominated by the micelles, and hence

the effect of CMC depression can not be detected by the conductance measurement. Lawrence and Pearson (40) have shown that the increase in conductance of micellar solutions upon the addition of alcohols is related to the increase in counterion activity of surfactants using a sodium-responsive electrode.

The alcohol concentration at the conductance minimum is expected to depend on both surfactant concentration and alcohol chain length. The alcohol/surfactant ratio in the micellar phase at the minimum conductance can be estimated as follows. The two minima in Fig. 3 are at $0.16\ M\ C_4OH$ and $0.062\ M\ C_5OH$. The fraction of alcohols partitioned in SDS micelles is reported to be 0.077 and 0.196 for butanol and pentanol, respectively (70). The CMC of SDS was measured by conductivity method to be 0.0053 and 0.0052 M in the presence of $0.16\ M\ C_4OH$ and $0.062\ M\ C_5OH$, respectively. Then the alcohol/surfactant ratio in micelles at the conductance minimum is equal to $(0.16 \times 0.077)/(0.01 - 0.0053)$ = 2.62 for butanol and $(0.062 \times 0.196)/(0.01 - 0.0052)$ = 2.53 for pentanol system. This calculation seems to suggest that in analogy to the CMC-depression (42), the position of the conductance minimum is also governed by the mole fraction of alcohol in the micellar phase. The slopes of initial linear portion of the three conductance curves in Fig. 4 are calculated to be 1.0, 4.9, and 8.92 for propanol, butanol, and pentanol, respectively, in which the slope of propanol curve is taken as 1. The ratio between slopes can provide at first approximation the relative partitioning of different alcohols in 100 mM SDS micelles.
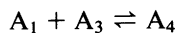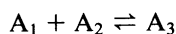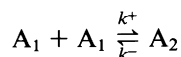
The third factor to account the influence of cosolvents on micellar solutions involves the structural changes in water upon the addition of cosolvents. The hydrophobic association and the micelle formation have been interpreted in terms of the structure of water. When cosolvent is a structure-breaker, the CMC usually increases (hydrophobic interaction decreases), while the CMC decreases when the cosolvent is a structure-maker (53). Frank and Ives (56, 57) have reviewed the structural

properties of alcohol–water mixtures. Various physicochemical properties of short-chain alcohols and water mixtures often show maxima or minima at low alcohol fractions, suggesting the maximum structure promotion of water by alcohols, followed by a structure disruption at higher alcohol fractions. Thus the CMC-depression at low alcohol fractions can also be partly ascribed to the structure promotion of water (49, 53). The increase of CMC and break-down of micelles at higher alcohol fractions is connected with the disruptive effect of alcohols on the structure of water.

In summary, the observed minimum in CMC upon addition of alcohols may be the result of two competing factors: the stabilizing effect on micelles due to the comicellization of alcohols with surfactants versus the destabilizing effect resulting from the disruptive change of the structure of water. The comicellization of alcohols with the surfactant often leads to an increase in the counterion dissociation of micelles, and hence an increase in the conductance of a micellar solution at high surfactant concentration. However, when the surfactant concentration is close to the CMC, this effect together with the depression of CMC results in a minimum of conductance.

*Effects of Mixed Solvents on Dynamic
Properties of Micellar Solutions*

The multiequilibrium, stepwise association process of micelle formation can be described as (4)

$$A_1 + A_1 \underset{k^-}{\overset{k^+}{\rightleftharpoons}} A_2$$

$$A_1 + A_2 \rightleftharpoons A_3$$

$$A_1 + A_3 \rightleftharpoons A_4$$

$$\vdots$$

$$A_1 + A_{n-1} \rightleftharpoons A_n$$

where A_1 denotes the surfactant monomer and A_n represents the micellar aggregate with aggregation number n. It is apparent that each aggregate is in dynamic equilibrium with monomers. The fast relaxation process can

readily be understood as an overall process involving chemical equilibria between monomers and aggregates. However, the origin of slow relaxation process is not as explicit. It actually arises from the fact that the small aggregates (often referred as oligomers or premicellar aggregates), being thermodynamically unstable (58), are in extremely low concentration and thus limit the relaxation flux of micelles (4). The slow relaxation time is thus a measure of the ease of micelle nucleus formation and nucleus population.

The increase of $1/\tau_2$ in Figs. 1 and 2 suggests that the addition of short chain alcohols actually favors the formation of small aggregates and thus eases the micelle nucleus formation. This can be qualitatively explained in parallel with the previous discussion of the cosolvent effect on equilibrium properties of micellar solutions. In the CMC-decreasing region, the addition of alcohol decreases the chemical potential of micelles leading to a decrease of monomer concentration. It also decreases the surfactant aggregation number of mixed micelles (59) resulting in a greater number density of micelles in the solution. This has been confirmed experimentally in a fluorescence study (38) and explained as the result of the replacement of surfactant molecules in micelles by alcohol molecules. In the CMC-increasing region, the diminishing hydrophobic driving force disfavors the formation of large micelles and consequently produces more small aggregates in the solution. The net result of all is a continuous increase in the population of small aggregates and hence a monotonic increase of $1/\tau_2$ upon the addition of short-chain alcohols.

This can further be illustrated by the theory of Aniansson and Wall (4). The simplest equation for the slow relaxation process takes the form of

$$\frac{1}{\tau_2} = \frac{n^2}{A_1} k_r^- A_r \frac{1}{1 + \frac{\sigma^2}{n} a} \qquad [3]$$

where the subscript r denotes the aggregation number at the minimum of the theoretical

distribution curve of micelle population; A_r is the number density of micelles at the minimum (i.e., the concentration of micelle nuclei); k_r^- is the dissociation rate constant of a surfactant molecule from a micelle nucleus, and the rest of the parameters assume the same definition as that of Eqs. [1] and [2]. According to Eq. [3], the rate of slow relaxation process is a function of aggregation number (n), monomer concentration (A_1), surfactant concentration ($1 + (\sigma^2/n)a$), the dissociation rate constant of a surfactant from a micelle nucleus (k_r^-) and the concentration of micelle nuclei (A_r). One often observes orders of magnitude change in $1/\tau_2$ when small amount of additives is added (4). Such drastic change in the rate of slow relaxation process is not likely to be attributed to any of the above parameters except A_r (4, 29). This is partly due to the simple physical constraint of a system, i.e., many parameters such as aggregation number of micelles can not change by orders of magnitude upon small perturbation. Hence the slow relaxation process is primarily a function of the number density of micelle nuclei (or oligomers) in solution: the more oligomers in the solution, the more rapid is the formation or dissolution of micelles.

For experimental data analysis, the theory of kinetics of mixed micellar solution (5) is too complex to use. However, when the additive concentration is relatively low, the kinetic theory applied to pure micellar solutions can be extended to the case of mixed micelles, provided that all parameters are not changed significantly by additives. For 10 mM SDS solution, we can write the equation of slow relaxation process as (4, 29)

$$\frac{1}{\tau_2} = k^+ \bar{K}^{r-2} A_1^{r-1} n^2 \left(1 + \frac{\sigma^2}{n} a\right)^{-1} \qquad [4]$$

where k^+ is the association rate constant of a surfactant molecule into a micelle; $\bar{K}$ is the average equilibrium constant of the association processes in the oligomer region. As shown by Yiv et al. (29), we can estimate how the r and $\bar{K}$ change upon addition of C_3OH

in terms of two limiting cases. We first calculate the value of $\bar{K}$ for pure dilute SDS micellar solution: using the parameters as follows (4): $\tau_2 = 2.32 \times 10^{-3}$ s, $n = 64$, CMC = 8.5 $\times 10^{-3}$ M, $k^+ = 1.2 \times 10^9$ M^{-1} s^{-1}, $\sigma = 13$, and $r = 7$, $\bar{K}$ is thus obtained as 3.51 M^{-1}. Upon the addition of propanol, k^+ is practically constant due to the fact that the association of a surfactant molecule to a micelle is close to a diffusion-controlled process (7). Moreover, there is no sizable change in CMC (34) and there is only a small change (less than 10%) in aggregation number (36) for propanol concentration up to 0.1 M. Hence, we assume that all parameters do not change upon addition of C$_3$OH except r and $\bar{K}$. Approximate 30 and 130% increase of $1/\tau_2$ were observed in Fig. 1 in the presence of 0.03 and 0.1 M propanol, respectively, as compared to pure 10 mM SDS at 20°C. Assuming $\bar{K}$ does not change as the first limiting case, we obtain r = 6.93 and 6.76 for 0.03 and 0.1 M C$_3$OH, respectively. As the second limiting case, $\bar{K}$ is calculated to be 3.69 and 4.16 for 0.03 M and 0.1 M C$_3$OH, respectively, provided that r does not change. The increase in $\bar{K}$ indicates the stabilization of micelle nuclei by the alcohol.

It is clear from the above calculation that a small variation of r or $\bar{K}$ can result in a large change of $1/\tau_2$ (7). As pointed out by Yiv et al. (29) of the physical significance of these two limiting cases: the first limiting case corresponds to the case where no alcohol partitions into the species at the minimum of the size distribution function, whereas the second limiting case implies that all the species are assumed to contain alcohol and therefore are stabilized by the alcohol. In real case both r and $\bar{K}$ may change simultaneously and hence make the data analysis difficult.

Influence of Alkanol Chain Length and Surfactant Concentration on Labilizing Effect of Alcohols

Since the plot of log $1/\tau_2$ vs concentration of alcohols is linear as shown in Figs. 1 and 2, the comparison of the slopes can provide the

information about the effect of alkanol chain length on the labilization of micelles. Figure 5 shows the plot of slopes in Figs. 1 and 2 as a function of alkyl chain length of alcohols. For 10 mM SDS, the labilizing power of alcohols increases with alkyl chain length up to $L = 3$, then levels off at $L = 4$.

Considerable hydrocarbon/water contact in micelles has been suggested from some theoretical considerations of micelles (60–63). A few experimental evidences (64–69) support the view that water does penetrate into the micellar surface, but differs with respect to the exact depth to which water really penetrates. Accordingly, the existence of a loosely packed palisade layer with considerable water hydration or penetration on the surface of micelles has been suggested. The thickness of the palisade layer may be equivalent to about three carbon–carbon bond lengths as suggested from the CMC measurement (28) and the partial molar volume measurement of the solubilized alcohols in micelles (70). The abrupt change in the slopes of C$_3$OH and C$_4$OH shown in Fig. 5 may be attributed to this water penetration effect. It is likely that short-chain alcohols with three carbons or less mainly partition in the palisade layer, where the microenvironment of alcohols is probably not much different from the bulk water. Hence the exchange of alcohols between bulk phase and micellar phase is extremely fast without much hindrance. The measured relaxation rate is mainly due to the micellization kinetics of surfactant molecules. However, as the al-
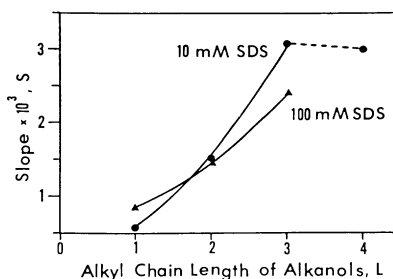

FIG. 5. Plot of the labilizing power of alkanols as a function of alkanol chain length. Slopes in Y axis are from Figs. 1 and 2.

cohol chain length increases to four carbons or more, alcohols start penetrating into the hydrocarbon core of micelles. The exchange of alcohol between the micelles and the bulk solution will then be hindered and slowed down (33), and therefore the relaxation rate of mixed micelles reflects partly the rate of solubilization of alcohols into micelles. This can explain the negative slope observed in the pentanol case of Figs. 1 and 2. More details regarding how the solubilization of alcohols into micelles influences the micellization kinetics are to be discussed in part II of this series.

Both curves in Fig. 5 can be best fit into second order equations by least-square method:

$$S = 0.32 - 0.07L + 0.33L^2 \qquad [5]$$

$$S = 0.69 - 0.075L + 0.215L^2 \qquad [6]$$

where $S \times 10^{-3}$ is the slope of linear lines in Figs. 1 and 2, and L is the number of carbon atoms in alkanols. Equation [5] is for 10 mM SDS and Eq. [6] for 100 mM SDS. Two points emerge from this result. First, the effect of alcohols in labilizing micelles increases with increasing alkyl chain length up to propanol. This can be explained by the increasing partition of alcohols in micelles and the stronger disruptive effect on water structure as the alkyl chain length increases (82). Secondly, the nonlinearity of the curve implies the varying power of each additional methylene group on an alcohol for labilizing the micelles: the deeper the penetration of the methylene group into a micelle, the higher is its labilizing power. Each additional methylene group probably also experiences a progressively changing environment from more of hydrophilic (bulk water) to more of hydrophobic (hydrocarbon core). Equations [5] and [6] can be rewritten as

$$S' = \frac{S - 0.32}{L} = -0.07 + 0.33L \qquad [7]$$

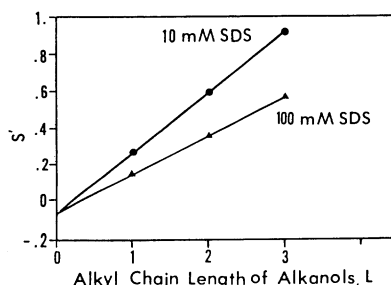$$S' = \frac{S - 0.69}{L} = -0.075 + 0.215L. \qquad [8]$$

FIG. 6. Plot of average labilizing power per methylene group of alkanols as a function of alkanol chain length.

The plot of S' vs L gives a straight line as shown in Fig. 6. The term S' can be interpreted as average labilizing power per methylene group of an alcohol assuming all methylene groups exert the same effect on micelles. Figure 6 suggests that the average labilizing power per methylene group is lower in 100 mM SDS than in 10 mM SDS for all alcohols. One could attribute this to the lower alcohol/surfactant ratio of 100 mM SDS than that of 10 mM SDS. However, this reasoning should be discarded in view of the result shown in Fig. 7, in which the effect of propanol on slow relaxation process at various SDS concentrations are reported. The slope decreases as the concentration of SDS increases from 10 to 50 mM, then keeps constant when the concentration of SDS doubles from 50 to 100 mM, and increases thereafter as the concentration further increases.

It may not be easy to interpret such abnormal change completely without ambiguity. However, it has been shown that two extrema exist in the plot of $1/\tau_2$ vs SDS concentration: a maximum around 20 mM SDS (4) and a minimum at about 200 mM SDS (15). This trend is very similar to that in the change of labilizing power of propanol vs SDS concentration shown in Fig. 7. It seems that higher labilizing power of alcohols always occurs in the region where $1/\tau_2$ increases. The increase in $1/\tau_2$ indicates a decreasing resistance for micelle formation. The first $1/\tau_2$-increasing region at SDS concentrations lower than 20 mM has been interpreted in terms of the de-
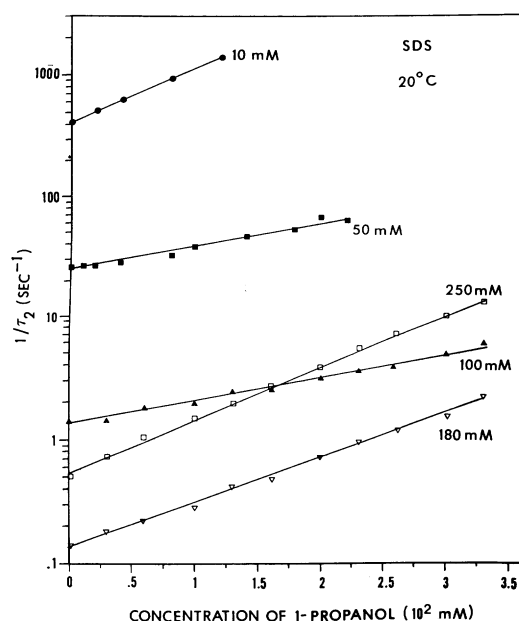
FIG. 7. Variation of the slow relaxation rate constant $1/\tau_2$ of various SDS concentrations as a function of propanol concentration.

creasing r, or the increasing $\bar{A_r}$ with increasing surfactant concentrations (8). The high labilizing power of alcohols in this region is probably due to the partition of alcohols into the micelle nuclei. However, as the surfactant concentration further increases, the population of micelles is expected to outgrow that of micelle nuclei, and hence a diminishing concentration ratio of nuclei to micelles results. We then expect a smaller labilizing effect on 50 mM SDS due to less partition of alcohols into micelle nuclei. The fact that no change in the slopes of 50 and 100 mM SDS, even under the condition of twice less alcohol concentration in micelles may be expected for 100 mM SDS solution as compared to 50 mM SDS solution, strongly support our previous assertion that the slow relaxation process is more dominated by the parameters related to micelle nuclei rather than the parameters related to micelles. The second $1/\tau_2$-increasing region at SDS concentrations higher than 200 mM has been explained by the reversible coagulation of micelles (15). We suspect that the

addition of alcohols leads to a fluidization of micellar interior (44) and a higher degree of ionization of micellar surface, which consequently accelerate the mutual coagulation of micelles.

The Concept of Micelle Stability

In analogy to a nucleation process, the rate-determining step in the process of micelle formation and dissolution has been found to be the micelle nucleus formation (7, 8, 20). The study of thermodynamics of micelle formation regards the picture of micelles as a thermodynamically stable, statistical entity existing at the most probable size with a statistically distributed population, while the study of kinetics of micellar solutions emphasizes the concept that such statistical entity is actually in dynamic equilibrium with monomers. Each micellar aggregate may fluctuate in size around the vicinity of its mean value by picking up or releasing some monomers at a time as reflected from the fast relaxation process, but a complete formation or dissolution of a micelle by passing through the micelle nucleus formation steps is a much slower process than the former as reflected from the slow relaxation process. The latter is the governing factor in controlling the lifetime of micelles. The difference, by orders of magnitude, in the rate of both processes can be understood partly from the energetics of both reactions. As calculated by Aniansson et al. (4) from the temperature dependence of relaxation rate, the activation energy for the exchange of monomers has been found to be −4.3 kcal/mole, while the activation energy for the nucleus formation is around 33 kcal/mole for SDS micelles.

The conventional thermodynamic analysis via CMC measurement only leads to a conclusion about the "*thermodynamic stability*" of micelles in terms of how the surfactant distributes between the monomer and micellar state; while the dynamic study leads to the concept of "*kinetic stability*" of micelles depicting the average lifetime of a micellar aggregate. It is possible that on one hand the

addition of short chain alcohols increases the thermodynamic stability of micelles driving more surfactant into micellar state, while on the other hand it can decrease the kinetic stability of micelles leading to faster formation and dissolution of micellar aggregates in solution. In addition to the possible change of r and $\bar{K}$ in Eq. [4] due to the addition of alcohols as analyzed previously, the labilizing effect of alcohols may also be attributed to the decreasing activation energy of micelle nucleus formation. We have found a decrease of activation energy from 37.5 to 36.4 kcal/mole and 34 kcal/mole for 10 mM SDS upon the addition of 20 and 140 mM propanol, respectively.

Micelle Nucleus Formation as the Rate-Limiting Step: Evidence from the Polymeric Additives

One could argue that since the rate-limiting step of micelle formation depends on the rate of nucleus formation, one may observe only a single relaxation process in micellar solutions if there was no constraint on the formation of micelle nuclei. As a matter of fact, $1/\tau_2$ of 100 mM SDS is too fast to measure on pressure-jump apparatus at propanol concentrations higher than 1.5 M (Fig. 2). We propose that the slow relaxation time τ_2 may progressively merge with the fast relaxation time τ_1 at higher propanol concentrations. The surfactant aggregates at this stage may resemble the oligomers which are formed through a continuous association process (9), in contrast to a true micellization process. The major difference between these two processes is that no minimum exists between monomers and aggregates in the distribution curve of micelle population for continuous association process.

In addition to many cosolvents, the presence of polymers in micellar solutions also expedites the slow relaxation process (71). We can actually utilize this polymer effect to further delineate the mechanism of slow relaxation process in a micellar solution. Figure 8 shows the change of $1/\tau_2$ for 100 mM SDS
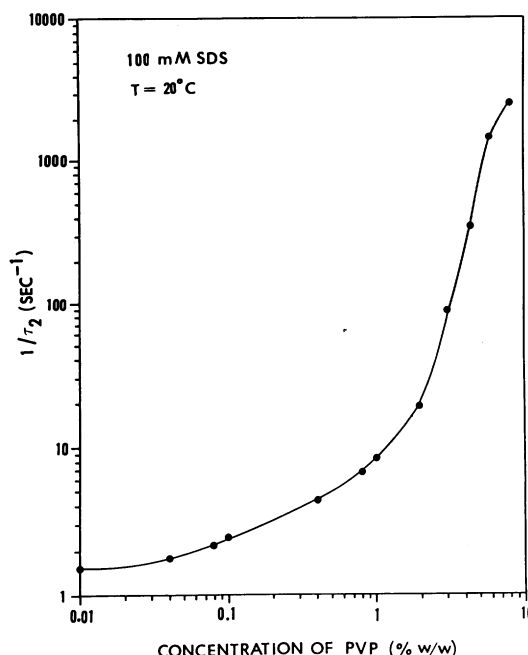

FIG. 8. Variation of the slow relaxation rate constant $1/\tau_2$ of 100 mM SDS as a function of PVP concentration.

upon the addition of a nonionic polymer polyvinylpyrrolidone (PVP). It is surprising to observe a three orders of magnitude increase in $1/\tau_2$ as PVP concentration increases from 1 to 8% (w/w). Contrary to this experimental observation, we may theoretically expect a decrease in $1/\tau_2$ by two orders of magnitude as far as the diffusion of surfactant is concerned. This is because that the viscosity of the solution increases by two orders of magnitude as concentration of PVP increases from 1 to 8% (72), a decrease by the same orders on k^+ in Eq. [4] is thus anticipated assuming a simple Stokes-Einstein diffusion relation (73). This contradiction poses an interesting problem for the mixed surfactant–polymer systems.

It is well known that surfactant interacts with polymer in many systems (74–79). The specific association between surfactants and polymers leads to a decrease of free surfactant monomer concentration in solution, and induces a surfactant–polymer complex formation. Despite a lack of complete understanding

about the exact nature and structure of this surfactant–polymer complex, there has been strong indication from various experimental evidence (74–79) that the complex resembles the characteristics of mixed micelles between the surfactant and polymer, and may even mimic the true micelles of pure surfactant solutions at high surfactant concentrations. Three regions with distinct surfactant–polymer binding are often identified experimentally upon increasing surfactant concentration in a polymer solution (74–79): very little surfactant–polymer binding in region I, specific stoichiometric binding of surfactants onto polymer in the form of clusters of premicellar aggregates in region II, and true micellization in region III.

The boundary between regions I and II denotes the effective CMC of the surfactant with the addition of polymer. The effective CMC is always found smaller than that of pure surfactant, suggesting the formation of mixed micelles in region II. Cabane (77, 78) has characterized the structure of mixed micelles in region II (referred as stoichiometric aggregates) based on NMR and neutron scattering studies of SDS–poly(ethylene oxide) systems. The essential features are the follows: (i) each stoichiometric aggregate contains a single macromolecule with associated SDS molecules; (ii) the SDS molecules in the stoichiometric aggregate are clustered in subunits which are small sphere similar to the micelles formed by pure SDS solution at low ionic strength; (iii) these subunits are adsorbed on the polymer strands. No penetration of polymer through the hydrocarbon core is observed, hence the adsorption occurs on water–micelle interface and involves weak binding. The overall picture of the complex is that the polymer is wrapped around micelles in a random coil block. The formation of such stoichiometric aggregate continues through region II up to region III where the stoichiometric binding saturates. In region III, the excess surfactant forms regular micelles in equilibrium with the stoichiometric aggregates of region II. This picture of surfactant–polymer complex

is expected applicable to SDS–PVP system due to the existence of similar transitions of three regions (74, 75).

It is clear from the above description that the presence of polymer does not alter the micellization characteristics of SDS significantly, hence the steep increase of $1/\tau_2$ in Fig. 8 should be interpreted in terms of the effect of polymer on micellization kinetics of SDS. In analogy to a heterogeneous nucleation process, PVP is likely to act as a nucleating agent for surfactants and stabilize the micelle nuclei in the solution, thus accounting for the increase of $1/\tau_2$. Moreover, the formation of stoichiometric aggregates in region II may lead to a smaller aggregation number (83) as well as a greater mutual coagulation of micelles, and consequently to a faster relaxation rate, simulating the case of pure micellar solution with SDS concentration higher than 200 mM (15). This is suggested in light of Cabane's picture regarding the structure of surfactant–polymer complex (78). The greater mutual coagulation between micelles partly results from the large configuration entropy associated with the polymer chain. We have measured the activation energy of 100 mM SDS in presence of 2% PVP to be 24 kcal/mole, close to 23 kcal/mole of activation energy for pure 250 mM SDS. We have also observed that the activation energy for micelles below 200 mM SDS, where the slow relaxation process is mainly controlled by stepwise association, is always around 33–37 kcal/mole. This value is obviously higher than the activation energy of slow relaxation process controlled by mutual coagulation of micelles. This substantiates the conjecture that the slow relaxation process in the presence of high PVP concentration is dominated by mutual coagulation of micelles.

We have further examined this by comparing the labilizing power of propanol on SDS micelles in the presence of 1% PVP with that of pure SDS micelles. The results are tabulated in Table I. It is interesting to see that unlike the complex change in pure SDS micelles, the labilizing effect of propanol is monotonically decreasing with increasing surfactant concen-

TABLE I

Comparison of Labilizing Effect of Propanol on SDS Micelles with/without 1% PVP

	Concentration of SDS (mM)				
Slope × 10³	10	50	100	180	250
Pure SDS[a]	3.0	1.9	1.9	3.65	4.3
1% PVP[b]	—	6.4	2.7	—	2.4

[a] Slopes were obtained directly from Fig. 7.

[b] Slopes were obtained by plotting $\log(1/\tau_2)$ of SDS micellar solution in the presence of 1% PVP vs concentration of propanol.

tration in the presence of 1% PVP. This confirms our observation that the effect of alcohol is strongly dependent on the mechanism and the rate of slow relaxation process. Here the presence of 1% PVP has turned the slow relaxation process to more of coagulation-controlled process, hence much greater effect of alcohol on 50 mM SDS is observed than that of pure 50 mM SDS. As surfactant concentration increases, more regular micelles will form from excess surfactants, then the slow relaxation process is progressively turning back to partly stepwise association controlled. This explains the monotonic decrease of slopes with increasing surfactant concentrations.

At very high polymer concentrations, the complication of cross-over of the polymer coil may occur (78). However, as far as micellization kinetics is concerned, the model described above should still be valid except two additional factors must be taken into account. Upon increasing PVP concentration, the amount of stoichiometric binding increases, thus decreasing the population of regular micelles formed in region III. It is possible that at very high PVP concentration, most SDS molecules are present in the form of stoichiometric aggregates which is of highly labile structure. Second, Fishman and Eirich (74) have shown that increasing the polymer concentration at constant surfactant concentration increases the degree of counterion dissociation of SDS, and thus the ionic strength of the solution. Since the configurational en-

tropy of polymer dominates the system at high ionic strength (78), the interaction between adsorbed micelles may then turn from repulsion into attraction. Both factors can actually labilize micelles significantly, thus accounting for the steep increase of $1/\tau_2$ at high PVP concentrations as shown in Fig. 8.

In regard to how the degree of polymerization influences our conclusion, Bloor et al. (71) has reported that at fixed PVP concentration, an increasing effect of PVP on labilizing micelles was observed with decreasing molecular weight of polymer. This may be correlated with the decreasing number of SDS subunits in a single stoichiometric PVP coil because of the increasing number of polymer coil in solution with decreasing molecular weight. We have performed an experiment at the extreme case of degree of polymerization equal to 1 by adding 1% 1-ethyl-2-pyrrolidinone, a water soluble monomer of PVP, into 100 mM SDS solution. Interestingly we observed a drastic increase in $1/\tau_2$ from 1.59 s^{-1} of pure 100 mM SDS to 22.2 s^{-1}, while a less increase to 8.9 s^{-1} is observed upon addition of 1% PVP (mol wt = 360,000) into 100 mM SDS. This can be viewed as the cosolvent effect of PVP monomer on micelles, similar to the case of short-chain alcohols. Unlike the PVP polymer which wraps around the micelles without penetrating into the micellar core (78), the PVP monomer is expected to penetrate into micelles.

In summary, it has been shown that both polymer and cosolvent can decrease the kinetic stability of micelles. Unlike the cosolvent which may greatly alter the structure of micelles and the hydrophobic driving force of the system, the addition of low concentration polymer may exert minimum perturbation on micelles. Thus the change of $1/\tau_2$ upon addition of polymer strongly support the concept about the rate-limiting of micelle nucleus formation. Consequently, the surfactant–polymer system can also serve as a model system to study how the kinetic stability of micelles influence the properties of micellar systems. Interestingly there has been some indication (80) that the kinetic stability of micelles influ-

ences the solubilization rate of a micellar solution. Thus a further study along this line can lead to a better understanding of both fundamental and applicational aspects of micellar systems.

IV. CONCLUSIONS

The effect of short-chain alcohols on both equilibrium and dynamic properties of SDS micellar solutions has been investigated. The conclusions from this study are as follows:

1. Methanol and ethanol decrease the conductance of micellar solutions due to the lowering of dielectric constant of the solvent.

2. Propanol, butanol, and pentanol may decrease or increase the conductance of micellar solutions depending upon the concentration of SDS. The penetration of alcohols into micelles can decrease the surfactant monomer concentration (CMC) and increase the counterion dissociation of micelles. When the surfactant concentration is close to the CMC, both effects influence the conductance of the solution resulting in a minimum of conductance. At higher surfactant concentrations, only the latter effect dominates and hence a direct increase of conductance is observed.

3. Short-chain alcohols C_1 to C_4 labilize micelles as reflected from the increase in slow relaxation rate constant $1/\tau_2$.

4. The labilizing power of alcohol increases with increasing alcohol chain length from C_1 to C_3, and levels off at C_4. This result is in agreement with the experimental observation that a palisade layer of about three carbon–carbon bond lengths may exist on the micellar surface, which is penetrated by water.

5. The labilizing power of alcohol also varies with SDS concentration: more pronounced effect of alcohol on micelles was observed at higher SDS concentrations. The labilizing effect of alcohol is related to the mechanism of slow relaxation process and micelle nucleus formation, irrespective of the ratio of alcohol molecules per micelles.

6. The concept of micelle stability should be subdivided into two terms: the "thermodynamic stability" and the "kinetic stability" of micelles. The "thermodynamic stability" of micelles concerns the distribution of surfactants between monomer and micellar state; while the "kinetic stability" of micelles is related to the lifetime of micellar aggregates, which is dependent on the rate of formation of micelle nuclei.

7. The addition of PVP up-to 8% (w/w) in micellar solution can increase $1/\tau_2$ by three orders of magnitude. The role of PVP in micellar solutions has been interpreted as a nucleating agent for micelle nucleus formation, thus supporting the concept that the rate-limiting step in micelle formation and dissolution process is the formation of micelle nuclei.

REFERENCES

1. Folger, R., Hoffmann, H., and Ulbricht, W., *Ber. Bunsenges. Phys. Chem.* **78,** 986 (1974).
2. Aniansson, E. A. G., and Wall, S. N., *J. Phys. Chem.* **78,** 1024 (1974).
3. Lang, J., Tondre, C., Zana, R., Bauer, R., Hoffmann, H., and Ulbricht, W., *J. Phys. Chem.* **79,** 276 (1975).
4. Aniansson, E. A. G., Wall, S. N., Almgren, M., Hoffmann, H., Kielmann, I., Ulbricht, W., Zana, R., Lang, J., and Tordre, C., *J. Phys. Chem.* **80,** 905 (1976).
5. Aniansson, E. A. G., *in* "The Techniques and Application of Fast Reaction in Solutions" (W. J. Gettins and E. Wyn-Jones, Eds.), p. 249. Reidel, Dordrecht, 1979.
6. Inoue, T., Shibuya, Y., and Shimozawa, R., *J. Colloid Interface Sci.* **65,** 370 (1978).
7. Baumuller, W., Hoffmann, H., Ulbricht, W., Tondre,

C., and Zana, R., *J. Colloid Interface Sci.* **64,** 418 (1978).

8. Hoffmann, H., *Ber. Bunsenges. Phys. Chem.* **82,** 988 (1978).

9. Zana, R., Lang, J., Yiv, S. H., Djavanbakt, A., and Abad, C., *in* "Micellization, Solubilization, and Microemulsions" (K. L. Mittal, Ed.), Vol. 1, p. 291, Plenum, New York, 1977.

10. Aniansson, E. A. G., *Ber. Bunsenges. Phys. Chem.* **82,** 981 (1978).

11. Almgren, M., and Aniansson, E. A. G., *Chem. Phys.* **19,** 1 (1977).

12. Aniansson, E. A. G., *J. Phys. Chem.* **82,** 2805 (1978).

13. Wall, S. N., and Aniansson, E. A. G., *J. Phys. Chem.* **84,** 727 (1980).

14. Tondre, C., and Zana, R., *J. Colloid Interface Sci.* **66,** 544 (1978).

15. Kahlweit, M., *Pure Appl. Chem.* **53,** 2069 (1981).

16. Kahlweit, M., and Teubner, M., *Adv. Colloid Interface Sci.* **13,** 1 (1980).

17. Kahlweit, M., *J. Colloid Interface Sci.* **90,** 92 (1982).

18. Lessner, E., Teubner, M., and Kahlweit, M., *J. Phys. Chem.* **85,** 1529 (1981).

19. Lessner, E., Teubner, M., and Kahlweit, M., *J. Phys. Chem.* **85,** 3167 (1981).

20. Chan, S. K., Herrmann, U., Ostner, W., and Kahlweit, M., *Ber. Bensenges. Phys. Chem.* **81,** 60 (1977).

21. Chan, S. K., Herrmann, U., Ostner, W., and Kahlweit, M., *Ber. Bunsenges. Phys. Chem.* **81,** 396 (1977).

22. Teubner, M., Diekmann, S., and Kahlweit, M., *Ber. Bunsenges. Phys. Chem.* **82,** 1278 (1978).

23. Aniansson, E. A. G., and Wall, S. N., *J. Colloid Interface Sci.* **78,** 567 (1980).

24. Kegeles, G., *in* "Solution Behavior of Surfactants" (K. L. Mittal and E. J. Fendler, Eds.), Vol. 1, p. 299. Plenum, New York, 1982.

25. Hall, D. G., *J. Chem. Soc., Faraday Trans. 2* **77,** 1973 (1981).

26. Zana, R., and Lang, J., *in* "Solution Behavior of Surfactants" (K. L. Mittal and E. J. Fendler, Eds.), Vol. 2, p. 1195. Plenum, New York, 1982.

27. Zana, R., *in* "Surfactants in Solution" (K. L. Mittal Ed.). Plenum, New York, in press.

28. Zana, R., Yiv, S., Strazielle, C., and Lianos, P., *J. Colloid Interface Sci.* **80,** 208 (1981).

29. Yiv, S., Zana, R., Ulbricht, W., and Hoffmann, H., *J. Colloid Interface Sci.* **80,** 224 (1981).

30. Candau, S., and Zana, R., *J. Colloid Interface Sci.* **84,** 206 (1981).

31. Candau, S., Hirsch, E., and Zana, R., *J. Colloid Interface Sci.* **88,** 428 (1982).

32. Zana, R., Picot, C., and Duplessix, R., *J. Colloid Interface Sci.* **93,** 43 (1983).

33. Hall, D., Jobling, P. L., Wyn-Jones, E., and Rassing, J. E., *J. Chem. Soc. Faraday Trans. 2* **73,** 1582 (1977).

34. Singh, H. N., and Swarup, S., *Bull. Chem. Soc. Japan* **51,** 1534 (1978).

35. Nishikido, M., Moroi, Y., Uehara, H., and Matuura, R., *Bull. Chem. Soc. Japan* **47,** 2634 (1974).

36. Birdi, K. S., Backlund, S., Sorensen, K., Krag, T., and Palsager, S., *J. Colloid Interface Sci.* **66,** 118 (1978).

37. Oakenfull, D., *J. Colloid Interface Sci.* **88,** 562 (1982).

38. Almgren, M., and Swarup, S., *J. Colloid Interface Sci.* **91,** 256 (1983).

39. Guveli, D. E., Kayes, J. B., and Davis, S. S., *J. Colloid Interface Sci.* **82,** 307 (1981).

40. Lawrence, A. S. C., and Pearson, J. T., *Trans. Faraday Soc.* **63,** 495 (1967).

41. Tominaga, T., Stem, T. B., Jr., and Evans, D. F., *Bull. Chem. Soc. Japan* **53,** 795 (1980).

42. Hayase, K., and Hayano, S., *J. Colloid Interface Sci.* **63,** 446 (1978).

43. Hayase, K., Hayano, S., and Tsubota, H., *J. Colloid Interface Sci.* **101,** 336 (1984).

44. Lianos, P., Lang, J., Strazielle, C., and Zana, R., *J. Phys. Chem.* **86,** 1019 (1982).

45. Larsen, J. W., and Tepley, L. B., *J. Colloid Interface Sci.* **49,** 113 (1974).

46. Shirahama, K., and Kashiwabara, T., *J. Colloid Interface Sci.* **36,** 65 (1971).

47. Miyagishi, S., *Bull. Chem. Soc. Japan* **47,** 2972 (1974).

48. Suzuki, H., *Bull. Chem. Soc. Japan* **49,** 1470 (1976).

49. Nishikawa, S., Mashima, M., Mackawa, M., and Yasunaga, T., *Bull. Chem. Soc. Japan* **48,** 2353 (1975).

50. Emerson, M. F., and Holtzer, A., *J. Phys. Chem.* **71,** 3320 (1967).

51. Ward, A. F. H., *Proc. R. Soc. London Ser. A* **176,** 412 (1940).

52. Parfitt, G. D., and Wood, J. A., *Kolloid Z. Z. Polym.* **229,** 55 (1969).

53. Magid, L., *in* "Solution Chemistry of Surfactants" (K. L. Mittal, Ed.), Vol. 1, p. 427. Plenum, New York, 1979.

54. Manabe, M., Koda, M., and Shirahama, K., *J. Colloid Interface Sci.* **77,** 189 (1980).

55. Malliaris, A., and Binana, W., *J. Colloid Interface Sci.* **102,** 305 (1984).

56. Franks, F., and Ives, D. J. G., *Quart. Rev. Chem. Soc.* **20,** 1 (1966).

57. Franks, F., "Physico-chemical Processes in Mixed Aqueous Solvents." Elsevier, New York, 1967.

58. Ruckenstein, E., and Nagarajan, R., *J. Phys. Chem.* **79,** 2622 (1975).

59. It is important to note that although the surfactant aggregation number decreases, the total aggregation number (surfactant + alcohol) of a mixed micelle may increase.

60. Dill, K. A., and Flory, P. J., *Proc. Natl. Acad. Sci., USA* **77,** 3115 (1980).

61. Dill, K. A., and Flory, P. A., *Proc. Natl. Acad. Sci., USA* **78,** 676 (1981).

62. Dill, K. A., Koppel, D. E., Cantor, R. S., Dill, J. D., Bendedouch, D., and Chen, S. H., *Nature* **309**, 5963, 42 (1984).

63. Gruen, D. W. R., *J. Colloid Interface Sci.* **84**, 281 (1981).

64. Menger, F. M., Jerkunica, J. M., and Johnston, J. C., *J. Amer. Chem. Soc.* **100**, 4676 (1978).

65. Cabane, B., *J. Phys. (Paris)* **6**, 848 (1981).

66. Ulmius, J., and Lindman, B., *J. Phys. Chem.* **85**, 4131 (1981).

67. Muller, N., and Simsohn, H., *J. Phys. Chem.* **75**, 942 (1971).

68. Corkill, J. M., Goodman, J. F., and Walker, T., *Faraday. Soc. Trans.* **63**, 768 (1967).

69. Kurz, J. L., *J. Phys. Chem.* **66**, 2239 (1962).

70. Manabe, M., Shirahama, K., and Koda, M., *Bull. Chem. Soc. Japan* **49**, 2904 (1976).

71. Bloor, D. M., Knoche, W., and Wyn-Jones, E., *in* "Techniques and Applications of Fast Reactions in Solution" (W. J. Gettins and E. Wyn-Jones, Eds.), pp. 265–270. Reidel, Dordrecht, 1979.

72. Davidson, R. L., "Handbook of Water-Soluble Guns and Resins," Chap. 21. McGraw–Hill, New York, 1980.

73. Graciaa, A., Lachaise, J., Chabrat, P., Letamendia, L., Rouch, J., Vaucamps, C., Bourrel, M., and Chambu, C., *J. Phys. Lett.* **38**, L-253 (1977).

74. Fishman, M. L., and Eirich, F. R., *J. Phys. Chem.* **75**, 3135 (1971); *J. Phys. Chem.* **79**, 2740 (1975).

75. Rudd, P. J., and Jennings, B. R., *J. Colloid Interface Sci.* **48**, 302 (1974).

76. Kale, K., Kresheck, G. C., and Erman, J., *in* "Solution Behavior of Surfactants" (K. L. Mittal and E. Fendler, Eds.), Vol. 1, p. 665. Plenum, New York, 1982.

77. Cabane, B., *J. Phys. Chem.* **81**, 1639 (1977).

78. Cabane, B., and Duplessix, R., *J. Phys. (Paris)* **43**, 1529 (1982).

79. Cabane, B., *in* "Solution Behavior of Surfactants" (K. L. Mittal and E. Fendler, Eds.), Vol. 1, p. 661. Plenum, New York, 1982.

80. Lianos, P., Viriot, M. L., and Zana, R., *J. Phys. Chem.* **88**, 1098 (1984).

81. Goddard, E. D., and Benson, G. C., *Canad. J. Chem.* **35**, 986 (1957).

82. Manabe, M., and Koda, M., *Bull. Chem. Soc. Japan* **48**, 2367 (1975).

83. Zana, R., Lianos, P., and Lang, J., *J. Phys. Chem.* **89**, 41 (1985).