

Effect of Long Chain Alcohols on Micellar Relaxation Time and Foaming Properties of Sodium Dodecyl Sulfate Solutions

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The effect of long chain alcohols (5 mol% C_nOH for $n = 8, 10, 12, 14,$ and 16) on the micellar stability of sodium dodecyl sulfate (SDS) solutions (SDS concentration ranging from 25 to 200 mM) was investigated and related to foaming properties, such as foamability, dynamic and equilibrium surface tension, and surface viscosity. The slow micellar relaxation time τ_2 , which is directly related to micellar stability, was determined by the pressure-jump technique. It was found that below 150 mM all the long chain alcohols investigated in this study cause an increase in τ_2 and, hence, micellar stability, due to the strong ion–dipole interaction between the SDS and the alkyl alcohol. However, above approximately 150 mM SDS, all alcohols except $C_{12}OH$ decrease the micellar stability due to mismatching of the alkyl chains. When the chain length of the alcohol and SDS are not equal, the excess hydrocarbon chain exhibits thermal motion, thereby increasing the area per molecule in micelles as well as at the air/water interface. Foamability was determined by two methods: air blowing through a single capillary submerged in the surfactant solution or vigorous hand shaking. When enough time is allowed for the interface to form (in case of single bubble foam generation), the dynamic surface tension approaches the equilibrium surface tension. Since the equilibrium surface tension for the SDS/ $C_{12}OH$ mixture is significantly lower (approximately 7 mN/m) than that for the pure SDS solution, more foam is generated with the mixed surfactant system. However, in very high shear rate processes (e.g., vigorous hand shaking), the break up time of micelles determines the flux of surfactant molecules to the interface and hence the foamability. Since the mixed SDS/ $C_{12}OH$ micelles are more stable (longer relaxation time, τ_2) than pure SDS micelles, higher dynamic surface tensions are attained and thus less foam is generated with the surfactant/alcohol mixture by the shaking method. In conclusion, we show that the foamability can exhibit opposite behavior depending upon the rate of foam generation (i.e., specific method used for foaming). © 1998 Academic Press

Key Words: chain length compatibility; sodium dodecyl sulfate; long chain alcohols; micellar stability; mixed micelles; foaming; micelle relaxation time; dynamic and equilibrium surface tension; surface viscosity; flux of surfactant monomers.

INTRODUCTION

Chain length compatibility is an important factor in systems involving interfacial films. As surface active molecules as well as other hydrocarbon molecules are aligned at interfaces, the properties of the interface are impacted to a large extent by the matching or mismatching of the alkyl chain lengths. In general, the chain length of surfactants used in a given system must be the same to maximize lateral molecular interactions that stabilize the surfactant film at the interface. If chain length mismatching is present in a surfactant film, the excess segment of the hydrocarbon tail has more freedom to disrupt the molecular packing through increased tail motion. The disruption in the molecular packing leads to lower interaction energies and, hence, lower film stability relative to systems in which the chain lengths are equal. The effect of chain length compatibility is particularly important to interfacial properties and technologies, such as surface tension, surface viscosity, foamability, lubrication, contact angle, bubble size, environmental remediation, enhanced oil recovery, water solubilization in microemulsions, and microemulsion stability (1–3).

It was shown earlier that chain length compatibility plays a role not only at air/water or oil/water interfaces but also in micelles (4). Sodium dodecyl sulfate (SDS) micelles are stabilized by the addition of alkyltrimethylammonium bromides, showing a maximum for dodecyltrimethylammonium bromide. Earlier investigations by Leung and Shah (5) and Yiv *et al.* (6) showed that short chain alcohols (C_1 to C_5) labilize SDS micelles, which was explained on the basis of the Aniansson and Wall theory (7). In the present paper the influence of long chain alcohols (C_nOH for $n = 8, 10, 12, 14$ and 16) on the SDS micellar stability is discussed. Furthermore, the effect of n -dodecanol ($C_{12}OH$) on the micellar stability is related to foaming properties, such as foamability (by two different methods), dynamic and equilibrium surface tension, and surface viscosity.

MATERIALS

Sodium dodecyl sulfate (purity 99%) was supplied by Sigma Chemical Company (St. Louis, MO). C_8OH was supplied by Fisher Scientific (Fair Lawn, NJ). $C_{10}OH$ and $C_{12}OH$ were

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supplied by Aldrich Chemical Company, Inc. (Milwaukee, WI). $C_{14}OH$ was supplied by Eastman-Kodak Company (Rochester, NY) and $C_{16}OH$ was supplied by Sigma Chemical Company. All solutions were prepared using water that was both deionized and distilled. All experiments were carried out at 25°C. In all studies the SDS concentration was well beyond the critical micelle concentration (CMC of pure SDS, 8.2 mM) to minimize the effect of possible trace impurities, e.g., $C_{12}OH$.

METHODS

Pressure-jump. The slow relaxation time τ_2 was measured using a pressure-jump apparatus from Dia-Log Corporation (Düsseldorf, Germany) by means of a change in conductivity that results from micelle formation or disintegration. The surfactant solution was pressurized to 100–120 atm and the solution was allowed to reach its new equilibrium state (at high CMC). Subsequently, the pressure was suddenly released to ambient pressure (initial CMC) by rupture of a thin metal diaphragm.

To reduce the monomer concentration after the pressure drop, some monomers will enter micelles already present, which can be seen as the fast relaxation process, commonly referred to as τ_1 . A much slower relaxation process is the formation of new micelles (referred to as τ_2) and can be observed as an exponential drop in electrical conductivity. The relaxation time τ_2 can then be calculated from the exponential decay in electrical conductivity (8).

Surface viscosity. A deep-channel surface viscometer (9, 10) was used to measure the surface viscosity of each solution. Two concentric cylinders form the deep-channel of a viscometer. The walls of this channel are stationary, while the floor moves at a constant angular velocity. To measure the center-line velocity of the air/water interface, a small Teflon particle was placed on the surface, and the time for that particle to make one revolution was recorded from visual observation. Using this value, the surface viscosity can be determined using

$$\epsilon = \frac{\eta y_0}{\pi} \left[\frac{8V_b}{\pi V e^{\pi D}} - 1 \right], \quad [1]$$

where ϵ is the surface viscosity, η the bulk viscosity of the solution, y_0 the channel width, V_b the plate rotational speed, V the center-line velocity of the air/water interface, and D the ratio of depth to width of the liquid channel.

Surface tension. Surface tensions were obtained from freshly prepared solutions by the Wilhelmy plate method. Before each measurement, the platinum plate was cleaned by heating it to a red/orange color with a Bunsen burner.

Foamability by shaking. Foamability measurements were carried out by vigorous shaking a 100-ml graduated cylinder. The measurements were carried out by shaking 15 ml of the sample solution for 10 s. The foamability was recorded as the

volume of foam produced immediately after shaking. Each solution was tested at least seven times.

Foamability by air bubbling. A quartz column, 3.5 cm in diameter, was used to acquire the foamability by air bubbling measurements. At the base of the cylinder a single capillary, 2.5 mm in diameter, was used to generate the bubbles. Fifty milliliters of the sample solution was poured into the column using a long funnel that reached to the bottom to ensure that the walls of the cylinder remained dry and could not act as an additional supply of surfactant molecules, which would increase the foam stability. The air was then turned on at a constant flow rate of 158.2 cc/min. The foam volume produced after 2 min was recorded. The measurement was repeated at least five times for each sample.

Dynamic surface tension. The maximum bubble pressure apparatus was constructed using a differential pressure transducer purchased from Omega Engineering, Inc. (Stanford, CT), with a sensitivity of 0 to 10 in. H_2O (0 to 2500 Pa). A No. 23 steel needle was used as a capillary, with a nominal 0.025 in. (0.64 mm) external diameter, 0.013 in. (0.33 mm) internal diameter, and a flush cut tip. The capillary diameter was chosen so that the viscous resistance of water to bubble growth could be ignored. Such internal and viscous effects are a potential source of error that need to be taken into consideration in these measurements (11). All measurements were conducted with the capillary tip 1 cm beneath the liquid surface. Compressed air was used as the bubbling gas and an oscilloscope connected to the pressure transducer was used to determine the bubble frequency and the dynamic surface tension values.

RESULTS AND DISCUSSION

The slow micellar relaxation time τ_2 of the SDS/long chain alcohol mixtures, which is directly related to the micellar stability, was determined using the pressure-jump technique (8). Figure 1 shows the slow relaxation time τ_2 as a function of SDS concentration in the presence of 5 mol% C_nOH for $n = 8, 10, 12, 14,$ and 16 (higher concentrations of C_nOH lead to solubility problems at 25°C). It is clear from Fig. 1 that at lower SDS concentrations ($< \sim 150$ mM) the micellar stability can be maximized by the addition of $C_{12}OH$, where the alcohol chain length is equal to the surfactant chain length. The presence of shorter or longer chain alcohols, however, also results in an increase in micellar stability compared to pure SDS. The values obtained for pure SDS are in perfect agreement with values reported by Oh and Shah (12) and independently by Lessner *et al.* (13). Apparently the introduction of ion-dipole interactions between the hydroxyl group of the alcohol and the sulfate group of the SDS causes a tighter packing of the micelle, resulting in a greater micellar stability. Beyond approximately 150 mM (depending on the alcohol chain length), long chain alcohols other than $C_{12}OH$ start destabilizing micelles, due to mismatching of the chains resulting in a disrup-

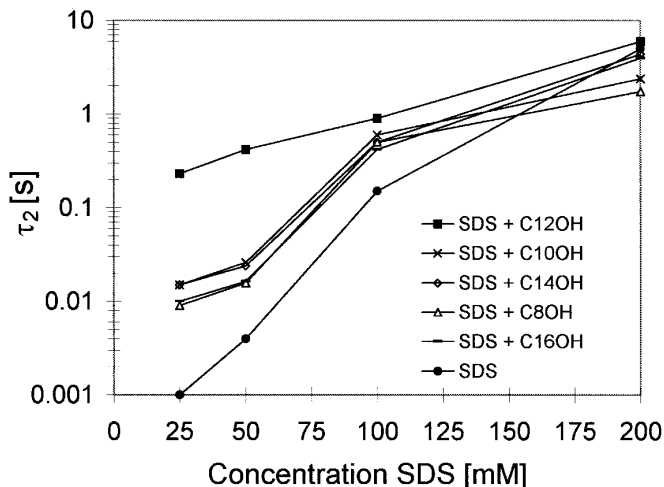


FIG. 1. The effect of 5 mol% C_n OH on the micellar relaxation time (τ_2) in SDS solutions at 25°C.

tion of the molecular packing causing the micelles to destabilize. Hence, lower micellar relaxation times are obtained. The effect of 5 mol% C_n OH on the micelle stability of 25 and 200 mM SDS solutions is presented in Fig. 2. The effect of chain length compatibility on surface properties, fluid displacement efficiency, and effective air mobility was investigated earlier by Shah and co-workers (14). They proposed that when the chain length of surfactant and cosurfactant are not equal the excess hydrocarbon chain will exhibit thermal motion, thereby increasing the molecular area at the air/water interface (Fig. 3). Apparently, a similar effect occurs in micelles (4).

At a concentration of 25 mM of SDS or at approximately three times the CMC, the stabilizing effect of C_{12} OH is much more significant than it is at 200 mM as shown in Figs. 1 and 2. This indicates that the micellar stability of relatively low concentration SDS solutions can be greatly enhanced by the addition of C_{12} OH (at 25 mM almost 230 times). The stabilizing effect of alcohol may be due to shielding of the negative charges of SDS with hydroxyl groups of the alcohol molecules and a stabilizing effect of the hydrocarbon tails, resulting in tightly packed micelles. However, at 200 mM the enhanced micellar stability resulting from the C_{12} OH addition is very small, showing that the contribution of C_{12} OH to already stable micelles is not significant. A simplified schematic representation of the proposed micelles at 25 and 200 mM in the presence and absence of 5 mol% C_{12} OH is given in Fig. 4, which illustrates the proposed effect of SDS and SDS + C_{12} OH concentration on molecular packing in micelles and hence on micellar stability.

It is known that the stability or slow micellar relaxation time of pure SDS micelles is a strong function of concentration. For pure SDS it has been shown that a maximum in micellar relaxation time is observed at 200 mM (12). As the concentration of SDS increases, the intermicellar distance

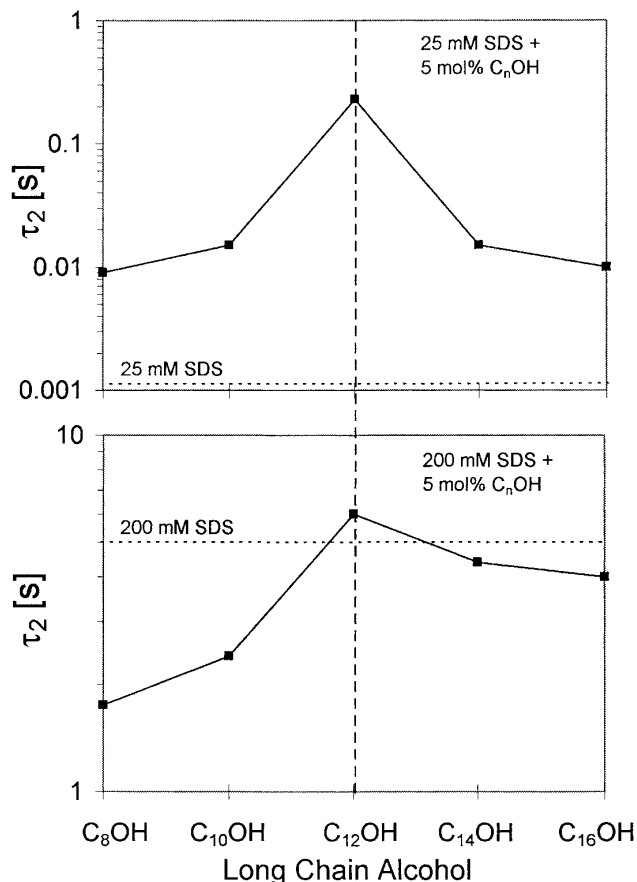


FIG. 2. The effect of 5 mol% C_n OH on the micellar relaxation time (τ_2) of 25 and 200 mM SDS solutions at 25°C.

decreases, resulting in a stronger electric repulsion between the micelles. Therefore, the micelles become more rigid, due to the compressive force of intermicellar repulsion and increased binding of sodium ions. At 200 mM SDS, reduced foamability, longer fabric wetting time, a maximum in gas bubble size and emulsion droplet size, and a maximum in oil and hydrophobic solids (dye) solubilization rates in micellar solutions were observed (15, 16). These phenomena were

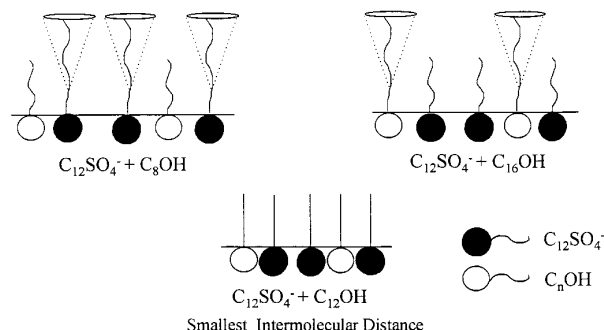


FIG. 3. Schematic diagram showing the effect of chain length compatibility on molecular packing at the interface.





Additive	SDS Concentration	
	25 mM SDS	200 mM SDS
0 mol% C ₁₂ OH	 Loosely Packed Micelle ($\tau_2 = 1$ ms)	 Tightly Packed Micelle ($\tau_2 = 5$ s)
5 mol% C ₁₂ OH	 Tightly Packed Micelle ($\tau_2 = 230$ ms)	 Tightly Packed Micelle ($\tau_2 = 6$ s)

FIG. 4. Schematic diagram showing the proposed effect of C₁₂OH on the micellar stability in 25 and 200 mM SDS solutions at 25°C. (●) SDS molecule; (○) C₁₂OH molecule.

explained based upon the monomer flux to newly created interfaces. If the micelles in solution are very stable, they cannot provide monomer quickly to the surface and the interfacial tension remains higher. However, if the micelles are relatively unstable, their disintegration provides monomers to the surface and a lower interfacial tension is obtained.

The effect of C₁₂OH on the SDS micellar stability was related to the following interfacial properties: surface viscosity, equilibrium surface tension, and foamability (by shaking and air bubbling through a single capillary). Figure 5B shows the results of the surface viscosity measurements in the presence and absence of C₁₂OH. From this graph it becomes clear that a phenomenon similar to that which occurs in micelles (Fig. 5A) occurs at the air/water interface. At low SDS concentration (25 mM) the effect of C₁₂OH is much more pronounced than it is at 200 mM. The alcohol causes the molecules to pack tighter, resulting in a high surface viscosity. However, at 200 mM the SDS molecules are already tightly packed, which does not allow the alcohol to increase the surface viscosity significantly. The equilibrium surface tension of 25–200 mM SDS solutions in the presence and absence of 5 mol% C₁₂OH is shown in Fig. 5C. It is clear that in the presence of C₁₂OH the surface tension is lowered by approximately 7 mN/m due to a closer packing of the molecules at the air/water interface. The alcohol decreases the molecular area due to the ion–dipole interactions between the SDS head group and the hydroxyl group of the long chain alcohol and a maximum hydrophobic interaction between the carbon chains.

Two different methods were applied for the foamability experiments: vigorous hand shaking and air bubbling through a single capillary. Both methods show different results. In the first case, larger foam volumes were obtained for pure SDS solutions than for SDS/C₁₂OH mixtures as shown in Fig. 5D. Especially at low SDS concentrations (25

mM) the SDS/C₁₂OH mixtures produced much less foam than the pure SDS samples. This can be explained based on the ability of micelles to break up in order to provide monomers to stabilize the newly created interface. Very stable micelles cannot break up fast enough to augment the flux of monomers necessary to stabilize the new air/water interface, resulting in higher interfacial tensions and, hence, foaming ability is low (Fig. 5D). So, apparently the break up of micelles is a rate-limiting step in the supply of monomers to the new air/water interface created by vigorous hand shaking. At 200 mM the SDS and SDS/C₁₂OH micelles are equally stable (see Figs. 1 and 5A) and, hence, equal foam volumes are produced (Fig. 5D).

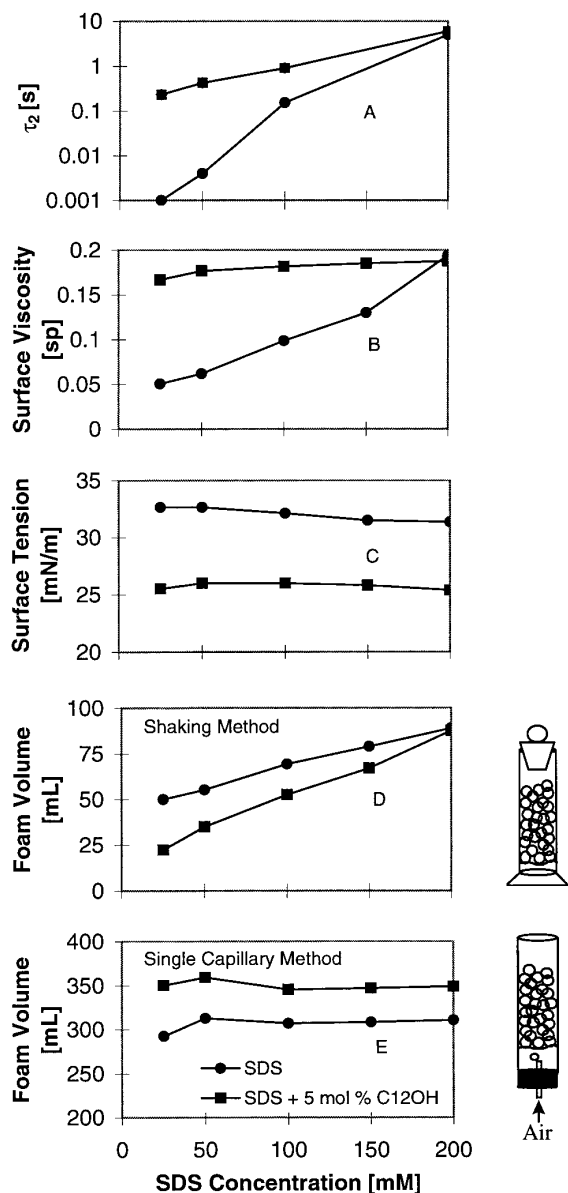


FIG. 5. The effect of 5 mol% C₁₂OH on foaming properties of SDS solutions.

Foamability measurements performed by blowing air through a single capillary yielded different results. Figure 5E shows that the foam volume of the SDS/C₁₂OH mixtures is consistently higher than that of pure SDS solutions, irrespective of the SDS concentration. Apparently, by using a single capillary the surfactant molecules have enough time to diffuse and stabilize the newly created air/water interface. Therefore, a lower dynamic surface tension is obtained. The relation between the dynamic surface tension and the amount of foam created is given by (17)

$$W = \gamma \cdot \Delta A, \quad [2]$$

where W is the work done, γ the interfacial tension at the air/water interface, and ΔA the change in interfacial area. The same relation holds for emulsification processes (18). Obviously, when the same amount of work is applied, a lower surface tension results in more interfacial area (either by decreasing the bubble size or by increasing foam volume), provided the presence of a surface active specie. Since the surface tension of the SDS/C₁₂OH mixtures is significantly lower than that of pure SDS (Fig. 5C), the former one will produce more foam using the single capillary foam column.

The results of the foamability measurements were evaluated by a more quantitative experiment, namely, dynamic surface tension by the maximum bubble pressure method. The understanding of dynamic surface tension is important in any technological application where a new gas/liquid interface is rapidly being created in a surfactant solution. In most cases the equilibrium surface tension is never reached and the actual surface tension experienced at the air/water interface is much higher. The dynamic surface tension depends on several factors: monomer concentration (CMC), micellar stability, diffusion rate of the surfactant molecule to the interface, and surfactant concentration. The measurement of dynamic properties is relevant to technological processes where an air/water interface is being formed, such as foaming or film formation, as well as situations where surfactants diffuse to a new liquid/liquid interface, such as emulsification, or to a solid/liquid interface, such as fabric wetting. In this study two solutions of 15 mM SDS and one containing SDS + 5 mol% C₁₂OH were investigated. A concentration of 15 mM was chosen, since at too high surfactant concentrations, deviations from equilibrium surface tension are negligible at the bubble frequencies accessible with the current setup. The dynamic surface tension as a function of bubble lifetime (reciprocal value of bubble frequency) is given in Fig. 6.

The effect of 5 mol% C₁₂OH is clearly visible: at higher bubble lifetimes the SDS/C₁₂OH mixture shows a surface tension significantly lower than that of pure SDS, indicating that the equilibrium surface tension of the SDS/C₁₂OH

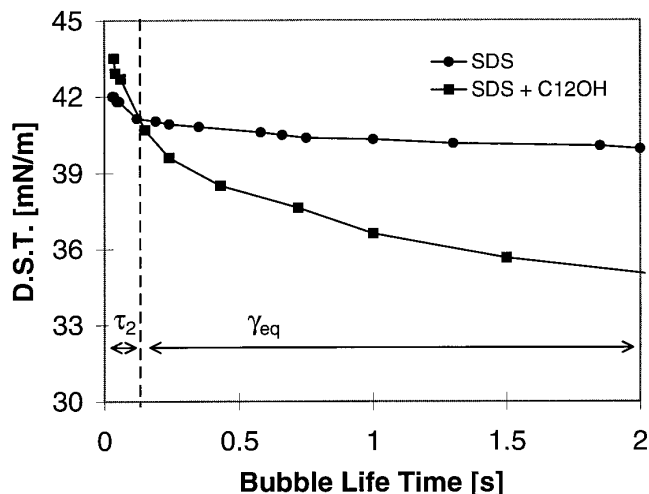


FIG. 6. Dynamic surface tension (γ_D) of SDS and SDS/C₁₂OH mixtures at 25°C (15 mM SDS, 5 mol% C₁₂OH).

solution is much lower, which was observed earlier (Fig. 5C). However, when the bubble lifetime decreases and thus the bubble frequency increases, the curves are getting closer to each other up to a bubble life time of approximately 0.15 s where they actually cross (Fig. 6). This means that at bubble life times smaller than 0.15 s (frequencies higher than $\sim 7 \text{ s}^{-1}$), the SDS/C₁₂OH mixed micelles are not able to augment the flux of monomers necessary to stabilize the newly formed bubbles as compared to pure SDS. In this region the micellar stability, and thus the ability of micelles to break up fast enough, determines surface tension lowering. During the formation of bubbles, surfactant monomers adsorb onto the freshly created interface from the bulk solution. If the monomer is depleted by the adsorption process, micelles must break up to provide additional monomers. If the micelles in solution are very stable, they cannot provide monomer quickly enough and the dynamic surface tension remains higher. However, if the micelles are relatively unstable, their disintegration resupplies the depleted monomer and lower dynamic surface tensions are obtained. In conclusion, for long bubble lifetimes the equilibrium surface tension determines the interfacial tension at the air/water interface. However, when the bubble lifetime decreases, more and more monomer is depleted from the bulk solution and thus micelles have to break up in order to provide additional monomers. In that case the break up of micelles, and thus the micellar stability, determines the surface tension lowering.

To show the importance of micellar break up in the dynamic surface tension measurement, a dimensionless parameter θ was introduced,

$$\theta = \frac{\gamma_D - \gamma_{eq}}{\gamma_w - \gamma_{eq}}, \quad [3]$$

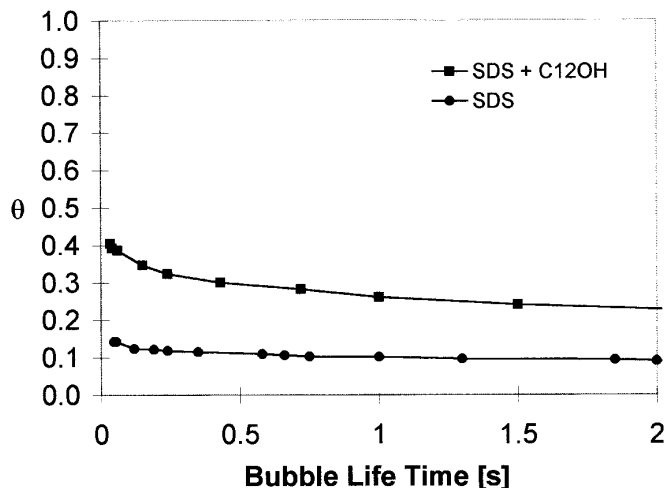


FIG. 7. Dimensionless dynamic surface tension (θ) of SDS and SDS/ $C_{12}OH$ mixtures at 25°C (15 mM SDS, 5 mol% $C_{12}OH$).

where γ_D is the dynamic surface tension, γ_{eq} the equilibrium surface tension as measured by the Wilhelmy plate method, and γ_w the surface tension of pure water at 25°C (72.96 mN/m). This equation normalizes with respect to the surface activity of the solution. The denominator ($\gamma_w - \gamma_{eq}$) can be considered as the effectiveness of the surfactant mixture (19). At $\theta = 0$, $\gamma_D = \gamma_{eq}$, which indicates that the surfactant concentration at the surface of the bubble is the same as that under equilibrium conditions. However, at $\theta = 1$, $\gamma_D = \gamma_w$, indicating that no surfactant is present at the interface of bubbles. Values between 0 and 1 are a measure for the surfactant concentration at the surface, and hence, the stability of micelles, assuming the diffusion time of monomers to be negligible (20). The more stable the micelles, the less monomer flux and hence θ values closer to 1 will be obtained. Figure 7 shows the dimensionless parameter θ versus the bubble lifetime for SDS and SDS/ $C_{12}OH$ solutions of 15 mM SDS and 5 mol% $C_{12}OH$. In this graph the θ values are consistently higher for SDS/ $C_{12}OH$ than for pure SDS over all bubble lifetimes. Apparently, when accounted for the surface activity of SDS and SDS/ $C_{12}OH$, the break up of SDS/ $C_{12}OH$ mixed micelles is a rate-limiting step in high-speed dynamic processes. Therefore, it is very important to consider the time scale of generating newly created interfaces in industrial processes, since that determines whether the break up of micelles and the dynamic surface tension are the dominant factors in producing foams, emulsions, and wetting and solubilization processes.

CONCLUSIONS

1. Long chain alcohols (C_nOH for $n = 8, 10, 12, 14$, and 16) stabilize SDS micelles, up to approximately 150 mM SDS (depending on the carbon chain length of the alcohol) due to the strong ion-dipole interaction between the nega-

tively charged SDS head group and the hydroxyl group of the alcohol. Beyond this critical concentration the chain length compatibility starts playing an important role. Therefore, only $C_{12}OH$ will cause a further increase in micellar stability, whereas the mismatch in chain length between the other alcohols and the SDS results in a disruption of the molecular packing in the micelle, thereby decreasing the stability.

2. The effect of adding $C_{12}OH$ is most pronounced when the stability of pure SDS micelles is very low, i.e., at low SDS concentrations (25 mM). At higher SDS concentrations, the micellar stability increases, which makes the effect of $C_{12}OH$ less pronounced.

3. The effect of micellar stability plays an important role in processes involving a rapid increase in surface area. If enough time is allowed for the interface to form, the dynamic surface tension approaches the equilibrium surface tension and thus more foam is generated (more in case of SDS/ $C_{12}OH$ mixtures). However, in very high speed processes, the micellar stability, and thus the time it takes for micelles to break up, determines the rate of adsorption of surfactant molecules and therefore higher surface tensions will be attained for SDS/ $C_{12}OH$ solutions. In that case less foam is generated, even though the equilibrium surface tension of the SDS/ $C_{12}OH$ system is lower. In conclusion, different methods of foaming can produce opposite results as illustrated by the foam-ability measurements in this study.

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