

Importance of Micellar Relaxation Time on Detergent Properties¹

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ABSTRACT: As we enter the new millennium, manufacturers of laundry detergents would like to provide new products for the twenty-first century. With the goal of achieving new and better performance characteristics, design strategies for research and development should be defined. This paper highlights the importance of micellar relaxation kinetics in processes involved in detergency. Earlier Shah and coworkers showed that the stability of sodium dodecyl sulfate (SDS) micelles plays an important role in various technological processes. The slow relaxation time (τ_2) of SDS micelles, as measured by the pressure-jump technique, was in the range of 10^{-4} to 10^1 s, depending on the surfactant concentration. A maximal relaxation time and thus a maximal micellar stability were found at 200 mM SDS (5 s), corresponding to the least-foaming, largest bubble size, longest wetting time of textile, largest emulsion droplet size, and the most rapid solubilization of oil. These results are explained in terms of the flux of surfactant monomers from the bulk to the interface, which determines the dynamic surface tension. More stable micelles lead to less monomer flux and hence to a higher dynamic surface tension. The relaxation time for nonionic surfactants (as measured by the stopped-flow technique) was much longer than for ionic surfactants because of the absence of ionic repulsion between the head groups. The τ_2 was related to dynamic surface-tension experiments. Stability of SDS micelles can be greatly enhanced by the addition of long-chain alcohols or cationic surfactants. In summary, relaxation time data of surfactant solutions enable us to predict the performance of a given surfactant solution. Moreover, results suggest that one can design appropriate micelles with specific stability, or τ_2 , by controlling surfactant structure, concentration, and physicochemical conditions, as well as by mixing anionic/cationic or ionic/nonionic surfactants for a desired technological application, e.g., detergency.

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KEY WORDS: Detergency, dynamic surface tension, emulsification, foaming, micellar relaxation time, mixed micelles, nonionic surfactant, sodium dodecyl sulfate, solubilization, wetting.

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The emphasis on consumer needs, ecologically compatible surfactants, energy savings, and economics continue to be focal issues in the development of laundry detergents for the twenty-first century. Governmental regulations limit the use of nonbiodegradable ingredients in detergent formulations. Surfactants obtained from natural raw materials have found applications in the consumer market in recent years (1,2). In addition, significant improvements were made with regard to manufacturing enzymes for the detergent industry (3). Biotechnological advances introduced genetically modified enzymes which exhibit increased activity, efficiency, and compatibility with other components of detergent formulations. Various approaches including aqueous vs. nonaqueous systems have been ongoing for the past 15 yr and are the focus of considerable patent art and some commercial sales in European heavy-duty liquids (4).

The Center for Surface Science & Engineering at the University of Florida performed extensive studies on micellar relaxation kinetics in relation to technological processes for the last 18 yr (5). The importance of surfactant relaxation kinetics was emphasized in several interfacial processes, such as foaming, antifoaming, wetting, emulsification, solubilization, and detergency. This article gives a brief overview of the significance of micellar relaxation kinetics in interfacial processes involved in detergency.

Micellar relaxation time. Surfactants or surface-active agents are molecules active at the interface of two immiscible phases (6). They show an abrupt change in physical properties, such as surface tension, osmotic pressure, conductivity, etc., at a characteristic concentration named the critical micelle concentration (CMC). Figure 1 schematically shows three environments in which surfactant molecules reside in a typical surfactant solution above the CMC. Surfactant molecules, in general, disperse as monomers in the aqueous phase, form aggregates (micelles), and adsorb as a film at the air/water interface. The surfactant is in dynamic equilibrium among all these compartments. Thus, at a given temperature, pressure and concentration, the number of monomers, micelles, and number of monomers adsorbed at the air/water interface are fixed under equilibrium conditions.

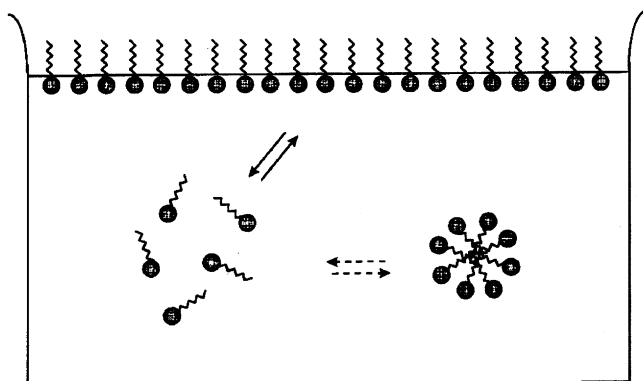


FIG. 1. Schematic representation of the three environments in which surfactant molecules reside in water.

Micelles are often drawn as static structures of spherical aggregates of oriented surfactant molecules. However, micelles are in dynamic equilibrium with individual surfactant molecules that are constantly being exchanged between the bulk and the micelles. Additionally, micelles themselves are continuously disintegrating and reforming. The kinetics of micellization have been studied by various techniques such as stopped-flow, temperature-jump, pressure-jump, and ultrasonic absorption (7–11), and the theoretical implementation of micelle formation and disintegration was developed by Aniansson and coworkers (12). Two relaxation processes are involved in micellar solutions. The first is a fast relaxation process with relaxation time τ_1 (generally of the order of microseconds), which is associated with fast exchange of monomers between micelles and the surrounding bulk phase. This process is considered as the collision between surfactant monomers and micelles. The second relaxation time τ_2 (usually on the order of milliseconds to minutes) is attributed to micelle formation and the dissolution process. Figure 2 shows two characteristic relaxation times, τ_1 and τ_2 , associated with micellar solutions. Micellar relaxation kinetics show dependence on temperature, pressure, and concentration.

The importance of micelle breakup on processes involving an increase in interfacial area was first reported by

Mijnlieff and Ditmarsch (13). Subsequently, Shah and coworkers (5) showed in several research publications a strong correlation of τ_2 with various dynamic processes such as foamability, wetting time of textile, bubble volume, emulsion droplet size, and solubilization rate of benzene in micellar solutions. Figure 3 shows schematically the importance of micelle breakup in foaming processes. When air is blown through a surfactant solution, a substantial amount of new interfacial area is created. The increased interfacial area has to be stabilized by an adsorbed film of surfactant molecules. These molecules come from the bulk solution, which contains monomers and micelles. As monomers diffuse to the newly created surface, micelles must breakup in order to provide additional monomers to the surface. Very stable micelles will not be able to augment the flux necessary to stabilize the newly created interface, and therefore foamability will be less. Micelle breakup is also important in fabric wetting. When a piece of fabric is placed on a surfactant solution, the solution begins to penetrate the interfiber spaces of the fabric. The monomers deposit on the hydrophobic sites of the surface to decrease the interfacial tension between the water and fabric. More stable micelles will cause less monomer flux, which slows down the wetting process and hence a longer wetting time is obtained (Fig. 4). Figure 5 shows the relevance of micelle breakup in the emulsification process. When mechanical energy is applied to increase the interfacial area between oil and water to produce oil droplets, the newly created interface must be stabilized by adsorption of monomers from the aqueous phase. More stable micelles cause less monomer flux, which leads to a higher interfacial tension at the oil/water interface. The relation between surface tension or interfacial tension and the amount of interfacial area created in foams or emulsions can be given by Reference 14:

$$W = \gamma \cdot \Delta A \quad [1]$$

where W is the work done, γ is the surface or interfacial tension at the air/water or oil/water interface, and ΔA is the change in interfacial area. Obviously, when the same

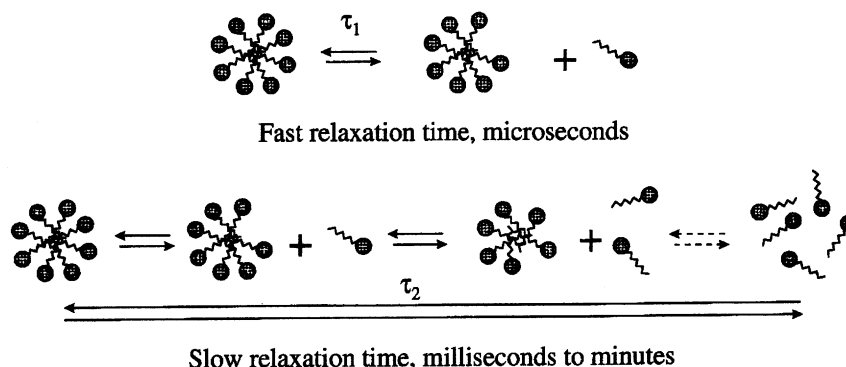


FIG. 2. Mechanisms for the two relaxation times, τ_1 and τ_2 , for a surfactant solution above critical micelle concentration (CMC).

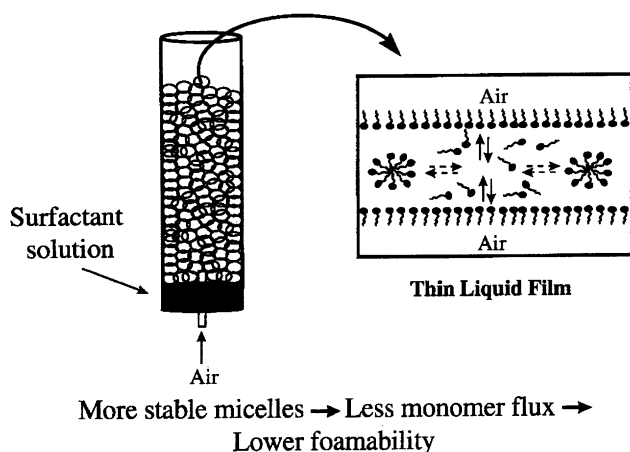


FIG. 3. Schematic representation of adsorption of surfactant on the newly created air/water interface during foam generation.

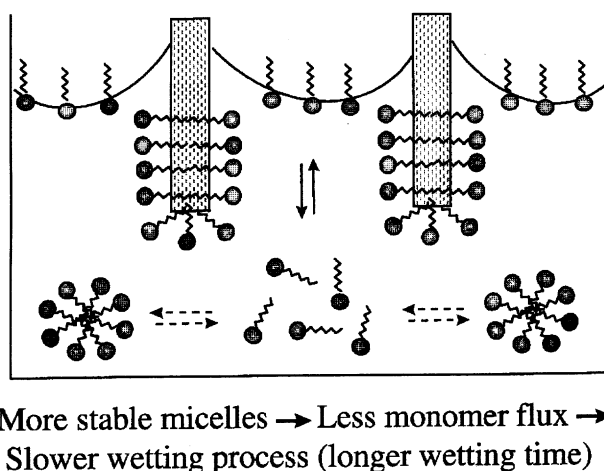


FIG. 4. Schematic representation showing the importance of micelle breakup in fabric wetting.

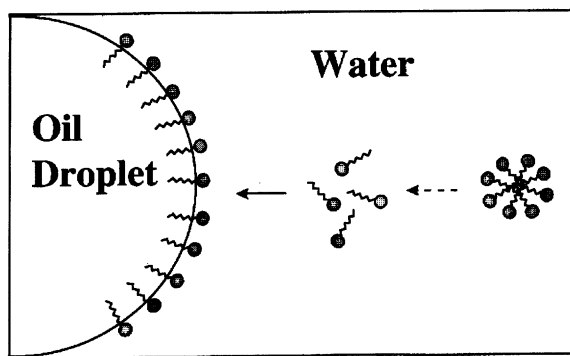


FIG. 5. Schematic representation showing the importance of micelle breakup in emulsification.

amount of work is done, a lower surface tension results in more interfacial area. Thus, one would expect a larger emulsion droplet size when micelles are very stable.

EXPERIMENTAL PROCEDURES

Materials. Sodium dodecyl sulfate (SDS) (purity 99%) was supplied by Sigma Chemical Co. (St. Louis, MO). C_8OH was supplied by Fisher Scientific (Fair Lawn, NJ). $C_{10}OH$ and $C_{12}OH$ were 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 Co. All solutions were prepared using water that was deionized and distilled. Benzene was supplied by Fisher Scientific (Fair Lawn, NJ). Synperonic A7, A50, and Brij 35 were supplied by ICI Americas (Wilmington, DE). All experiments were done at 25°C.

Pressure-jump. The slow relaxation time τ_2 of SDS micelles was measured using a pressure-jump apparatus from Dia-Log Corporation (Düsseldorf, Germany) by means of change in conductivity, resulting from micelle formation or disintegration. The surfactant solution was pressurized to 100–120 atmospheres, 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. The formation of new micelles 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 (15).

Stopped-flow. The slow micellar relaxation times of nonionic surfactants Synperonic A7, A50, and Brij 35 were determined by the stopped-flow dilution technique. A number of dyes or fluorescent compounds, such as Merocyanine, eosin, rhodamine and Sudan, show an appreciable change of extinction coefficient depending on whether the dye resides in- or outside the micelle. This effect is often used to determine the CMC, but it also provides a way of following relaxation kinetics upon a fast temperature, pressure or concentration jump by employing spectrophotometric detection methods. Eosin Y in water shows a maximal absorbance (λ_{max}) at 518 nm. However, increasing the surfactant concentration causes the dye to partition between the water and micelles, causing the maximal absorbance to shift to approximately 538 nm. This shift is caused by a change in the dye microenvironment. The concept of change in absorbance due to the presence of micelles can be used in the determination of the slow relaxation constant, τ_2 , for nonionic surfactants using the stopped-flow dilution technique. Stopped-flow is a method designed to measure the kinetics of fast reactions. The apparatus employs two separate syringes which can be filled with reactants, which are pushed instantaneously into a transparent cell. A change in absorbance can be detected with a very sensitive photomultiplier detector as the reaction progresses. When one solution containing micelles

and dye is instantaneously diluted with another solution containing water and dye at the same dye concentration, the absorbance of dye in micelles will decrease as micelles breakup, indicating the relaxation time of micelles. The exponential decay can be fitted to a first-order reaction, resulting in the associated time constant τ_2 .

Textile wetting. A fabric piece of 1 in.² was placed on the surface of SDS solutions. The surfactant solution displaces air in the cotton surface by a wetting process, and when sufficient air has been displaced, the cotton starts sinking. The residence time of cotton fabric on the solution surface was measured as wetting time in this study.

Emulsion droplet size. Four mL of hexadecane was added to 20 mL of SDS solution at various concentrations and shaken vigorously by a vibrator for 30 s at constant frequency. Pictures were taken of the emulsion droplets using an optical microscope (Nikon, Tokyo, Japan) at 400 magnification just after the formation of the emulsion to avoid coalescence.

Detergency: Removal of Orange OT. Orange OT (0.05 g) was dissolved in 5 mL of benzene; 0.4 mL of this dye solution was applied to cotton pieces (5" by 5"). Benzene was removed from the cotton by drying. The cotton pieces were submerged in 250 mL of SDS solution in a Tergotometer (United States Testing Co., Hoboken, NJ). A small amount of surfactant solution (3 mL) was withdrawn from the Tergotometer at different times to measure the absorbance of light at 505 nm in order to measure the concentration of Orange OT.

Solubilization of benzene by a moving interface. Benzene (5 mL) was added to 50 mL SDS solution in a flask. The SDS solution was agitated gently by a magnetic stirrer, and the rate of upward movement of the interface was measured.

Solubilization of benzene by electrical conductivity. The electrical conductivity of 50 mL of SDS solution was measured with a conductivity bridge (YSI model 31; Fisher Scientific) until there was no further change of conductivity while stirring, indicating that the system had reached the equilibrium state at ambient conditions. Consequently, benzene (1 mL) was added to the SDS solution, and the electrical conductivity was measured as a function of time. If there was no more change in conductivity, that time was considered to be the time required to solubilize benzene into the SDS solution up to its saturation limit.

Dynamic surface tension. The maximal bubble pressure apparatus was constructed using a differential pressure transducer purchased from Omega Engineering, Inc. (Stanford, CT), with a sensitivity of 0 to 10" H₂O (0 to 2500 Pa). A #23 steel needle was used as a capillary, with a nominal 0.025" (0.64 mm) external diameter, 0.013" (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. 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

Micellar stability of SDS solutions was determined by Oh and Shah (16) using pressure-jump with electrical conductivity detection (15). Figure 6 shows micellar relaxation time τ_2 as function of SDS concentration. Maximal micellar stability was found at 200 mM (5 s). These results are in agreement with those reported by Kahlweit (17). Figure 7 presents the various maxima and minima occurring at the liquid/liquid and solid/liquid interfaces at 200 mM in SDS solution. Wetting time and droplet size in emulsions show maxima at 200 mM. Wetting time is the time during which the fabric floats on a surfactant solution before it sinks. During this time, water penetrates the fabric structure to replace air until the gravitational force exceeds the buoyancy of entrapped air. When micelles are very stable, the flux of monomers decreases, and hence the wetting process slows down. Different types of fabric, such as polyester, dacron, nylon, cotton, and silk were investigated. Maximal wetting time of these fabrics occurs at 200 mM SDS (Fig. 8). Although the absolute magnitude of the wetting time depends on the fabric, the maximum occurring at 200 mM is a property of the SDS solution and not of the fabric. The liquid/liquid and solid/liquid phenomena can be explained based upon the monomer flux necessary to stabilize newly created interface. Very stable micelles result in high dynamic surface tensions and, hence, larger droplet sizes and longer wetting times (18,19). The solubilization rate of benzene in SDS solutions (Fig. 9) as well as the detergency or removal of orange OT dye from fabric surface show maxima at 200 mM concentration (16). This suggests that very stable micelles (i.e., tightly packed micelles) are more effective in oil solubilization. This can be explained based upon the micelle interior. The interior of rigid (i.e., tightly packed) micelles is more hydrophobic compared to loosely packed micelles, and hence the stronger hydrophobic core causes more rapid partitioning or solubilization of

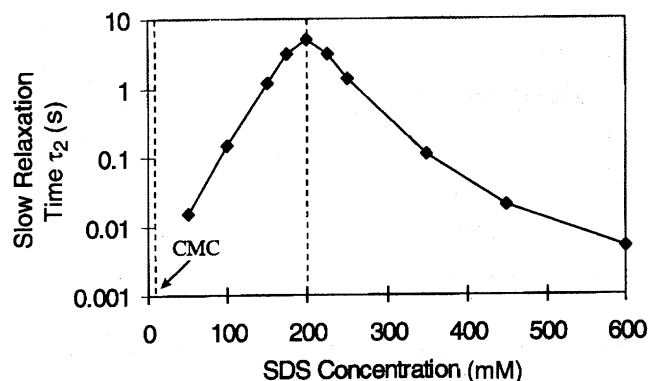


FIG. 6. Slow relaxation time, τ_2 , of sodium dodecyl sulfate (SDS) micelles at various surfactant concentrations (CMC = 8.3 mM). See Figure 2 for other abbreviation.

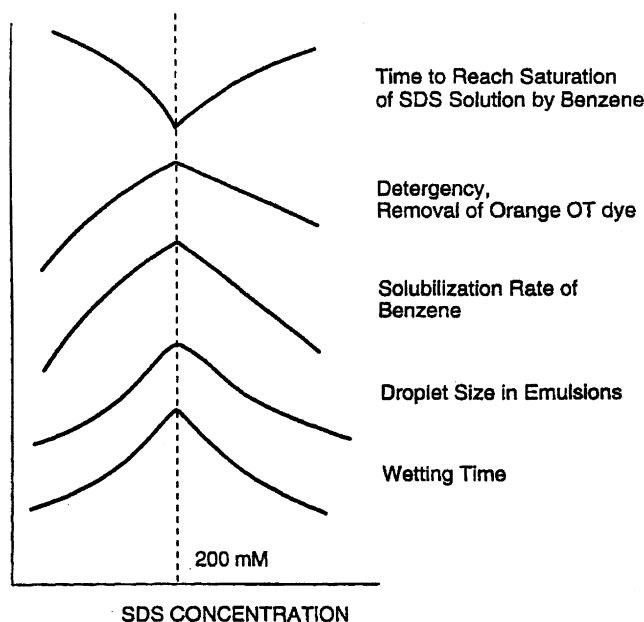


FIG. 7. Liquid/liquid and solid/liquid phenomena exhibiting minima and maxima at 200 mM SDS concentration. See Figure 6 for abbreviations.

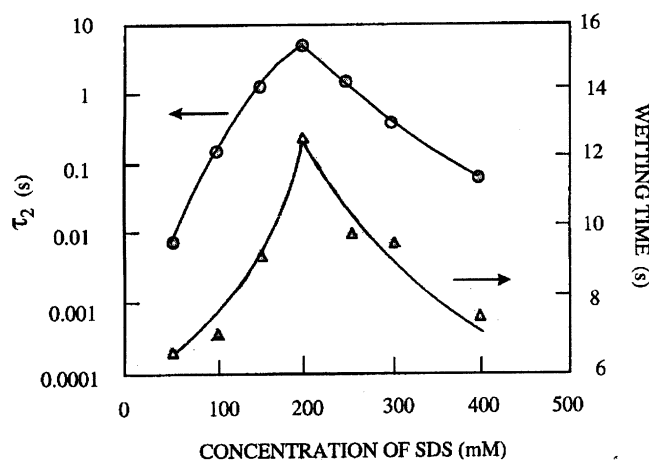


FIG. 8. Effect of micellar stability on fabric wetting.

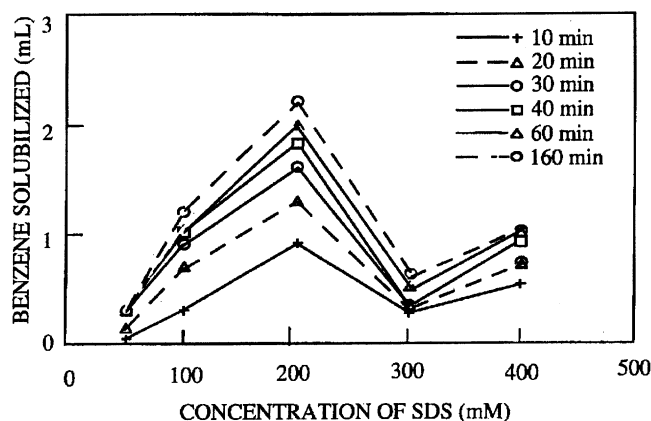


FIG. 9. Rate of solubilization of benzene in SDS solutions. See Figure 6 for abbreviation.

benzene and Orange OT into the micelles at 200 mM SDS. Droplet size in hexadecane/SDS emulsions was maximal at 200 M SDS, at which the most stable micelles are formed (Fig. 10). This is due to a minimal flux of monomers to the newly generated oil/water interface during emulsification. Because the micelles are most stable at 200 mM SDS, they can not effectively augment the flux of monomers by their disintegration when oil/water interfacial area is increased during emulsification.

Dynamic surface tension is the transient interfacial tension associated with the deformation of fluid interfaces when a surface-active species is present in the liquid. The understanding of dynamic surface tension is important in any technological application where a new gas/liquid or liquid/liquid interface is rapidly being created in a surfactant solution. In most cases the equilibrium surface tension is never reached, and the surface tension experienced at the interface is much higher. Dynamic surface tension can be measured by the maximal bubble pressure method (20,21) and depends on several factors: monomer concentration (CMC), micellar stability, diffusion rate of the surfactant molecule to the interface, and surfactant concentration. Dynamic properties are relevant to technological processes, 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. During bubble formation, surfactant monomers adsorb onto the freshly created interface from the bulk solution. If the monomer is depleted by the adsorption process, micelles must breakup to provide additional monomers. If micelles in solution are very stable, they cannot provide monomer fast enough, and the dynamic surface tension remains high. This is schematically illustrated in Figure 11. To show the importance of micellar breakup in the dynamic surface tension measurement, a dimensionless parameter θ was introduced (22),

$$\theta = \frac{\gamma_D - \gamma_{eq}}{\gamma_w - \gamma_{eq}} \quad [2]$$

where γ_D is the dynamic surface tension, γ_{eq} is the equilibrium surface tension as measured by the Wilhelmy plate method, and γ_w is the surface tension of pure water at 25°C (72.96 mN/m). This equation normalizes surface tension with respect to solution surface activity. The denominator ($\gamma_w - \gamma_{eq}$) can be considered as the effectiveness of the surfactant (6). When $\gamma_D = \gamma_{eq}$ then $\theta = 0$, which indicates that the surfactant concentration at the bubble surface is the same as that under equilibrium conditions. However, when $\gamma_D = \gamma_w$ then $\theta = 1$, which indicates that no surfactant is present at the bubble interface. So, values between 0 and 1 are a measure of the surfactant concentration at the surface and hence, the stability of micelles, assuming the diffusion time of monomers to be negligible (23). The more stable the micelles, the less monomer flux and hence θ values closer to 1 are obtained.

In this study, the dynamic surface tension behavior of

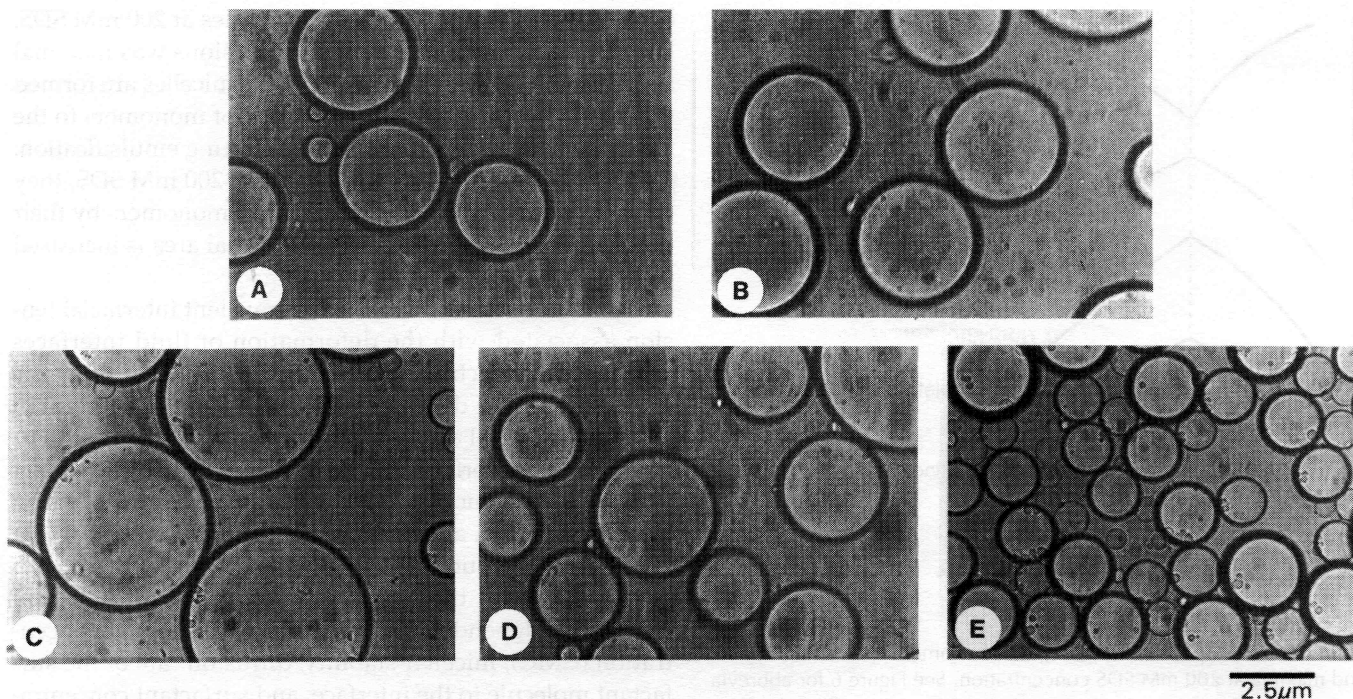


FIG. 10. Droplet size of SDS/hexadecane/water emulsions. A, 50 mM; B, 100 mM; C, 200 mM; D, 300 mM; and E, 400 mM of SDS concentration. See Figure 6 for abbreviation.

three nonionic surfactants, Synperonic A7, Brij 35 and Synperonic A50, was studied. These three surfactants have comparable structures: REO_7 , REO_{23} , and REO_{50} (where $R = \text{C}_{12}$ to C_{15}), respectively. Figure 12 shows the dimensionless parameter θ vs. the bubble life time for 2 mM solutions of Synperonic A7, Brij 35, and Synperonic A50 (with relaxation times 150, 80, and 40 s and equilibrium surface tensions of 29, 38.7, and 49.5 mN/m, respectively). The slow micellar relaxation time was measured by the stopped-flow dilution technique. It is clear that Synperonic A7 shows the slowest rate of adsorption of surfactant molecules due to micelle stability, resulting in θ values closer to 1 at very short bubble life times. On the other hand, Syn-

peronic A50 shows a faster adsorption of surfactant molecules as indicated by the lower θ values due to the shorter micellar life time ($\tau_2 = 40$ s). It is also clear that micellar stability decreases as the degree of ethoxylation increases.

The ability to determine micellar stability of ionic as well as nonionic surfactants allows us to tailor micelles with specific stability. It was shown recently (22) that the stability of SDS micelles (at 25 mM) can be greatly enhanced by addition of 1-dodecanol (C_{12}OH). In fact, any long-chain alcohol will increase τ_2 , and hence the SDS micellar stability, due to the strong ion-dipole interaction between the SDS and the alkyl alcohol. At a concentration of 25 mM of SDS or at approximately three times the CMC

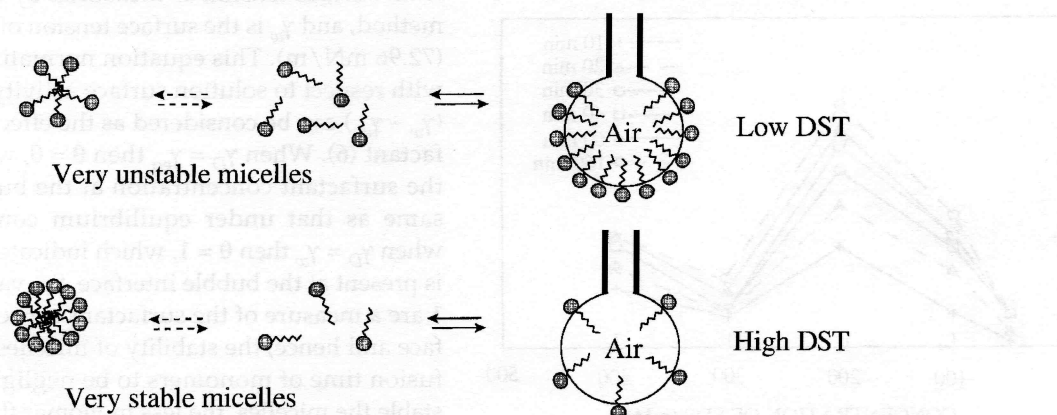


FIG. 11. Schematic diagram showing the influence of micellar stability on the dynamic surface tension (DST).

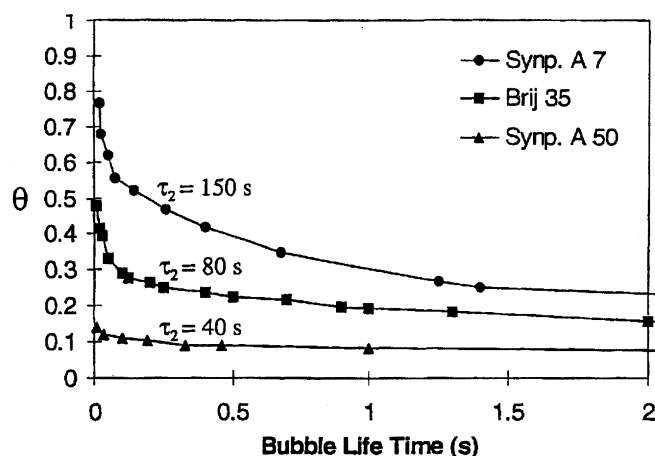


FIG. 12. Dimensionless dynamic surface tension (θ) vs. bubble life time for 2 mM solutions of Synperonic A7, Brij 35, and Synperonic A50.

(8.2 mM), the stabilizing effect of $C_{12}OH$ is much more significant than it is at 200 mM as shown in Figure 13. This indicates that the micellar stability of relatively low concentration SDS solutions can be greatly enhanced by addition of $C_{12}OH$ (at 25 mM almost 230 times). The stabilizing ef-

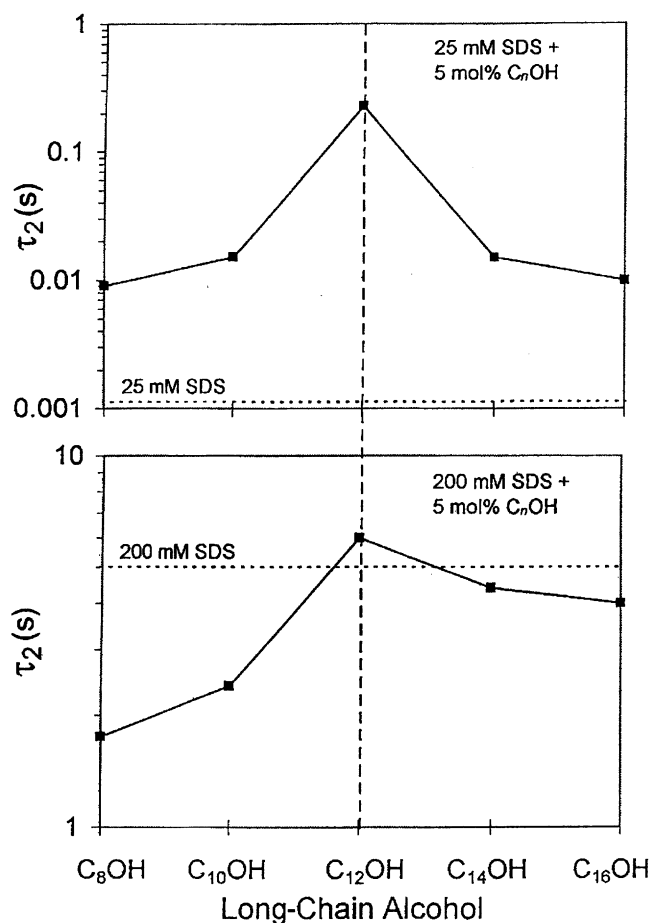


FIG. 13. Effect of long-chain alcohols (5 mol% C_nOH , where $n = 8, 10, 12, 14$, and 16) on SDS micellar stability at 25 and 200 mM. See Figure 6 for abbreviation.



25 mM SDS, $\tau_2 = 1$ ms



25 mM SDS + 5 mol% $C_{12}OH$, $\tau_2 = 230$ ms



100 mM SDS + 10 mol% $C_{12}TAB$, $\tau_2 = 5000$ ms

FIG. 14. Tailoring SDS micellar stability by addition of 1-dodecanol ($C_{12}OH$) or alkyltrimethylammonium bromide ($C_{12}TAB$). See Figure 6 for abbreviation.

fect of alcohol may be due to shielding of the negative charges of SDS with alcohol hydroxyl groups and a stabilizing effect of the hydrocarbon tails, resulting in tightly packed micelles. However, at 200 mM SDS, the increase in micellar stability from the addition of $C_{12}OH$ is very small, showing that the contribution of $C_{12}OH$ to already stable micelles is not significant. In fact, at 200 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 (22,23). In general, greater micellar stability leads to greater volume or size of bubbles in surfactant solutions due to higher dynamic surface tension (24).

Even more significant is the effect of alkylammonium bromides on the SDS micellar stability (25). In this case electrostatic interactions between anionic and cationic polar groups cause micelles to become even more stable. The effect of 5 mol% $C_{12}OH$ and 10 mol% dodecyltrimethylammonium bromide ($C_{12}TAB$) on 25 mM and 100 mM SDS solutions, respectively, is shown in Figure 14. The slow micellar relaxation time τ_2 increases from 1 to 230 ms after addition of 5 mol% $C_{12}OH$. In case of 10 mol% $C_{12}TAB$, a relaxation time of 5000 ms was found. Thus, the ability to induce ion-dipole or ion-ion electrostatic interactions allows us to control micellar stability and hence dynamic surface tension which in turn influences foaming, emulsification, wetting, solubilization, and detergency.

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