# Relationship between Micellar Lifetime and Foamability of Sodium Dodecyl Sulfate and Sodium Dodecyl Sulfate/1-Hexanol Mixtures

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The interface between air and surfactant solution expands rapidly during the foam generation process. Surfactant molecules in the solution should adsorb onto the newly created surface to stabilize foam. As surfactant monomers adsorb on the surface, micelles disintegrate to provide additional monomers to adsorb on the expanding interface of foam. If micelles are very stable, they cannot rapidly provide monomers to the newly created surface. Hence, the kinetics of disintegration of micelles should influence the foaming ability of surfactant solutions. This study attempts to test this hypothesis and to establish the framework of knowledge on the micellization kinetics and the foamability of surfactants. In this study the relationship between the micellar lifetime and foaming ability of aqueous surfactant solutions was elucidated by the pressure-jump technique and air-generated foam columns, respectively, at 25 °C. The results showed that the average lifetime (i.e. the stability) of micelles reached a maximum value at a specific surfactant concentration. At the same surfactant concentration, we found the minimum foamability. With this approach, a correlation between micellar relaxation time and foamability of the surfactant solutions was established.

## Introduction

Foam is produced when gas is injected into the solution containing surfactants due to the adsorption of surfactants on the newly created surface.[1] The foamability and foam stability of the surfactant solutions are primarily dependent on the chemical composition and properties of the adsorbed surfactant molecules and are influenced by numerous factors such as the rate of adsorption from solution to the liquid–gas interface, the rheology of the adsorbed layer, gaseous diffusion out of and into bubbles, size distribution of bubbles, surface tension of liquid, bulk viscosity of liquid, microstructure of foaming solution, the presence of electrolyte as well as external temperature and pressure.[2-5]

The foam stability is increased as the bulk viscosity of foaming solution and surface viscosity of the adsorbed surfactant layer at the air/water interface are increased.[6] In contrast, the foam stability tends to decrease as the size distribution of bubbles, surface tension of solution, area/molecule of surfactant molecule, and diffusion coefficient of gas through the liquid film increase.[7-11] Also the foam stability decreases in the presence of electrolytes because the electrical repulsion between the ionic surfactant molecules at the interface decreases.[12,13]

Wasan et al.[14] observed stratification during the thinning of liquid films formed from micellar solutions of anionic surfactants. They explained that the stepwise thinning occurs due to the layer-by-layer removal of an ordered structure of micellar layers from the film. The thickness of each thinning step is of the order of the diameter of a micelle together with the Debye atmosphere around it. The gradient of the chemical potential of micelles at the film periphery causes the stepwise thinning of the film.[15] The foamability (i.e. the volume of foam generated) is reported to increase with the temperature and decrease with the surface tension of the surfactant solutions.[16,17]

We have shown in this paper that the foamability of the micellar solution is influenced by the average lifetime of micelles. This happens because the micelles must be broken into the monomers for adsorption onto the newly created surface of bubbles (Figure 1). Without this process, foam cannot be generated. If the micelles in solution are very stable, they cannot rapidly provide surfactant monomers to the newly created surface. Hence foaming ability would be poor. But if the micelles are relatively unstable, their disintegration provides the surfactant monomers which can rapidly adsorb to the newly created surface. This should enhance the foamability of micellar solutions, but the effect of micellar lifetime on foamability of micellar solutions has never been considered or established.

In this study, the effect of micellar lifetime on foamability of sodium dodecyl sulfate and mixtures of SDS and 1-hexanol was studied by the pressure-jump technique

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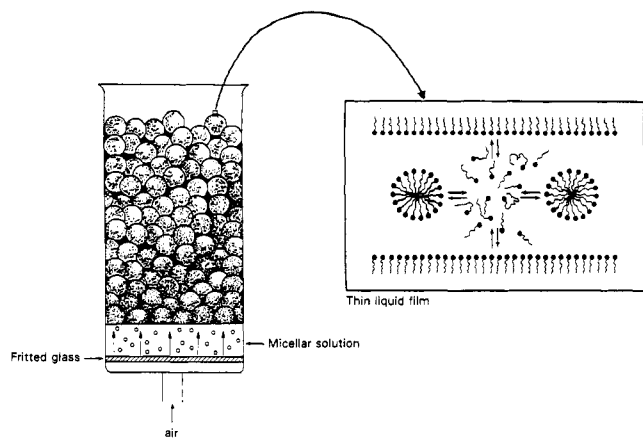(17) Sharma, M. K.; Shah, D. O.; Brigham, W. E. *AIChE J.* 1985, *31*, 222.

**Figure 1.** Schematic representation of adsorption of surfactant monomers to the expanding interface due to the disintegration of micelles during the foam generation.

and air-blowing foam column to establish the mechanism of foam generation process.

Kinetics of micellization have been studied by stopped-flow,[18] temperature-jump,[19] pressure-jump,[20] and ultrasonic absorption[21,22] methods since Aniansson[23] developed a theoretical model for the kinetics of micellization.[24] There are two relaxation processes: The first one is the fast relaxation process with relaxation time ($\tau_1$, in the microsecond range) associated with the fast exchange of monomers between micelles and bulk aqueous phase. This process is considered as the collision between surfactant monomers and micelles. The second relaxation time ($\tau_2$, in the millisecond range) is related to micelle dissociation kinetics. The average micellar lifetime is given by the expressions[25,26]

$$\frac{1}{\tau_2} = \frac{n^2}{A_1 R}\left\{1 + \frac{\sigma^2}{n}a\right\}^{-1} \quad (1)$$

$$T(m) = \tau_2\frac{na}{1 + \frac{\sigma_2}{n}a} \quad (2)$$

where $T(m)$ is the average micellar lifetime, $\tau_2$ is the second relaxation time, $n$ is the aggregation number, $\sigma$ is the half-width of the distribution curve of micellar sizes and $a = (A_{tot} - A_1)/A_1$. Here $A_{tot}$ and $A_1$ are the total surfactant concentration and mean monomer concentration, respectively. $R$ is given by the equation

$$R = \sum_{s=s_1+1}^{s_2} 1/(k_s^{-1}A_s) \quad (3)$$

where $s$ is the aggregation number of a particular aggregate, $k_s^{-1}$ is the dissociation rate constant of this aggregate, and $A_s$ is the equilibrium concentration of aggregates of aggregation number $s$. The dependence of $\tau_2$ on ionic

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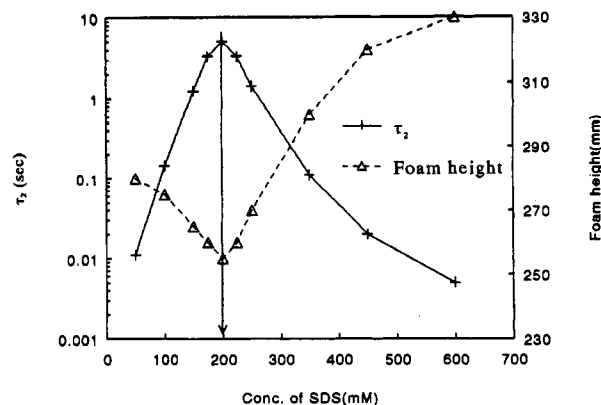(26) Leung, R.; Shah, D. O. *J. Colloid Interface Sci.* **1986**, *113*, 484.



**Figure 2.** Effect of concentration of SDS on the micellar relaxation time and foaming ability.

strength, concentration, and temperature can be interpreted in terms of their effects on $R$. When the concentration of surfactant is much greater than the critical micelle concentraation (cmc), micellar lifetime is approximately equal to $n\tau_2$.[27] The aggregation number of SDS changes from 63 to 91 as the concentration increases from 0.07 to 0.73 M.[28] The change of aggregation number ($n$) is negligible when it is compared with the change of $\tau_2$ value (0.01–10 s) as the concentration increases. Therefore, the slow relaxation time represents the lifetime (i.e. stability) of micelles.[26]

## Experimental Procedure

Sodium dodecyl ($C_{12}$) sulfate was supplied by Sigma Chemical Co. (purity 99%) and 1-hexanol with purity 98% by Eastman Kodak Company. These materials were used without further purification to make micellar solutions. The surfactant concentrations of sample covered from the cmc (8.2 mM at 25 °C) to 800 mM of SDS. The 1-hexanol was added to 50 and 100 mM SDS solutions until phase separation occurred, respectively. The phase separation occurred at 250 mM and 300 mM 1-hexanol, respectively, at 25 °C. The second relaxation time ($\tau_2$) of micelles in each sample was measured by the pressure-jump apparatus with conductivity detection from Dia-Log Corporation (Dusseldorf, Germany) with a pressure-jump of 140 bar (2030 psi). A KCl solution having the same electrical conductivity as that of the surfactant solution was used as reference cell in the pressure-jump experiments. The foam heights in the air-generated foam column with diameter 5 cm were read after 30 s of air flow at $P = 2$ psig. All measurements were carried out at 25 °C.

## Results and Discussions

The results of pressure-jump experiments for pure sodium dodecyl sulfate showed that the average lifetime (or relaxation time $\tau_2$) of micelles increased as the surfactant concentration increased up to 200 mM and then decreased with surfactant concentration (Figure 2). This suggests that the lifetime of SDS micelles in aqueous solution is maximum at 200 mM concentration. On the contrary, the foamability of SDS solutions in the air-blowing foam column was at a minimum at 200 mM concentration probably because surfactant monomers cannot be provided by relatively stable micelles. Thus, it seems that the more stable the micelles, the less is the foamability of the micellar solutions.

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It is important to establish that the diffusion time of surfactant monomers from bulk to the surface in thin films during foam generation process is much shorter than the lifetime of micelles. Thus, the lifetime of micelles can be considered as the rate-limiting step in a foam-generation process. Overbeek[29] has derived an approximate equation for the diffusion time of molecules based on the Stokes–Einstein equation

$$t_{Diff} = \frac{(\text{diffusion path length})^2}{2D} \qquad (4)$$

where $D$ is the diffusion coefficient of molecules. When the film thickness is 1 $\mu$m, the average diffusion path length of surfactant inside the liquid film is 0.25 $\mu$m as explained below. The molecules diffuse toward both sides of the films. Hence, only half of the film (0.5 $\mu$m) is able to provide monomers to one side of the film. In half of the film the average path length traveled by molecules is 0.25 $\mu$m. In this case, the calculated average diffusion time of surfactant monomers is $10^{-4}$ s. This value is negligible when it is compared with the micellar lifetime ($n\tau_2$, 0.6–65 s) of SDS micelles. Therefore, the rate of diffusion of surfactant monomers inside the thin liquid film does not influence the foamability of surfactant solutions in the air-generated foam column. Thus, it can be concluded that the micellar stability plays a major role in foamability of micellar solutions.

It was reported that the short chain alcohols ($C_1$–$C_4$ chain length) labilize the SDS micelles (i.e. decrease $\tau_2$) in aqueous solutions as the concentration of alcohols increases.[26] In contrast, Inoue et al.[30] reported that the SDS micelles are stabilized by the addition of a small amount of dodecyl alcohol.

The effects of addition of 1-hexanol to 50 and 100 mM SDS solution on the micellar lifetime (i.e. relaxation time $\tau_2$) and the foaming ability are shown in Figures 3 and 4, respectively. The pressure-jump relaxation times indicated that the most stable micelles were formed when 70 mM 1-hexanol was added to 50 mM SDS solution and 50 mM 1-hexanol to 100 mM SDS solution. The foamability also showed a minimum at these concentrations.

From these results, it can be concluded that the surfactant solutions which exhibit greater relaxation time (i.e. longer lifetime or greater stability) yield poorer foamability. We postulate that the rate of adsorption of surfactant monomers onto the newly created surface during the foam generation process is primarily dependent upon the disintegration of micelles. These results are relevant to the processes encountered in detergency, enhanced oil recovery by foam flooding, wetting of textile fibers, ore flotation, etc.

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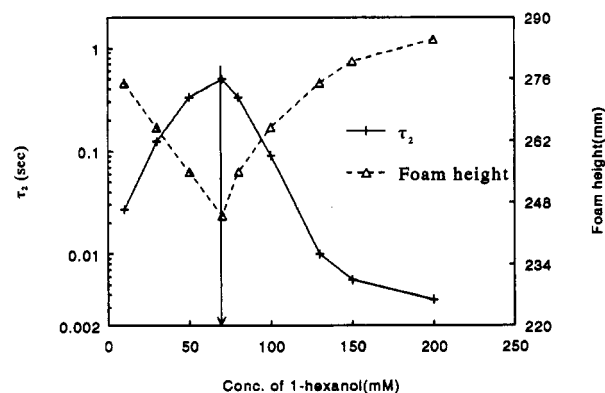(30) Inoue, T.; Shibuya, Y.; Shimozawa, R. *J. Colloid Interface Sci.* 1977, *65*, 370.



**Figure 3.** Effect of concentration of 1-hexanol on the micellar relaxation time and foaming ability of 50 mM SDS solution.
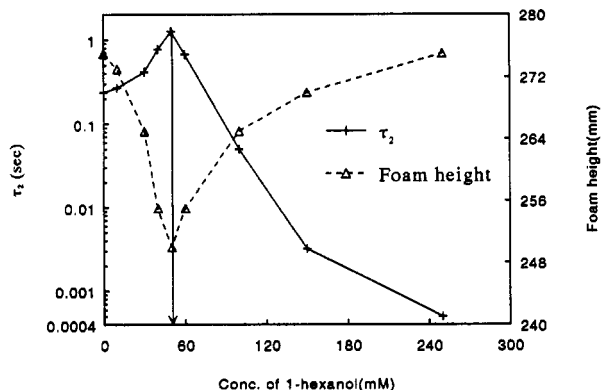


**Figure 4.** Effect of concentration of 1-hexanol on the micellar relaxation time and foaming ability of 100 mM SDS solution.

It should be emphasized that the present paper deals only with the foaming ability of surfactant solutions and not with foam stability. It is well recognized that the addition of long chain alcohols to the SDS solution increases the stability of foams.[31] This effect can be attributed to the shielding of the negative charges of SDS with hydroxy groups (–OH) of alcohol molecules and a possible stabilizing effect of ion–dipole interactions between sulfate and hydroxy groups.

In summary, the results described in this paper suggest that the stability (or relaxation time $\tau_2$) of micelles correlates with the foamability of the micellar solutions. The minimum foamability occurs when the micellar solution exhibits the maximum in the relaxation time (i.e. micellar stability).

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