Effect of Chain Length Compatibility on Micellar Stability in Sodium Dodecyl Sulfate/Alkyltrimethylammonium Bromide Solutions

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The effect of chain length compatibility on the micellar stability was investigated for mixtures of sodium dodecyl sulfate (SDS) and alkyltrimethylammonium bromides (C_nTAB, $n = 8, 10, 12, 14, 16$) at a 20/1 molar ratio. It was observed that the surface properties of surfactant solutions were influenced by the chain length compatibility of the surfactant molecules. The slow micellar relaxation time (τ_2), which directly correlates to the micellar stability, was determined using the pressure-jump technique. The addition of C_nTAB to SDS solutions results in a significant increase in the relaxation time compared to SDS alone, showing a maximum for the SDS/$C_{12}TAB$ system. The high micellar stability results in minimum surface tension, maximum surface viscosity, maximum micellar lifetime, maximum foam stability, and minimum foamability. The higher micellar stability as observed for SDS/$C_{12}TAB$ is attributed to both the chain length compatibility and the Coulombic interaction of the surfactant head groups, resulting in an optimum packing of molecules in micelles and at the air/water interface.

Introduction

The association of many classes of surface active molecules into micellar aggregates is a well-known phenomenon.[1] Micelles are often drawn as static structures of spherical aggregates of oriented surfactant molecules. However, micelles are in dynamic equilibrium with individual surfactant molecule monomers that are constantly being exchanged between the bulk and the micelles. Additionally, the micelles themselves are continuously disintegrating and re-forming. The kinetics of this process has been evaluated by Aniansson,[2–4] and the relevance of micellar relaxation time to various technological processes for single surfactant systems such as sodium dodecyl sulfate (SDS) in water has been extensively studied by Shah and co-workers.[5]

The kinetics of micellization has been studied by various techniques such as stopped flow,[6] temperature jump,[7] pressure jump[8] and ultrasonic absorption.[9,10] There are two relaxation processes involved in micellar solutions. The first one is the fast relaxation process with relaxation time τ_1 (generally of the order of microseconds), which is associated with the fast exchange of monomers between micelles and the surrounding bulk phase. The second relaxation time τ_2 (usually of the order of milliseconds or longer) is attributed to the micelle formation and dissolution process. Interestingly, the two relaxation times can be used to calculate two important parameters of a micellar solution: (1) the residence time of a surfactant molecule in a micelle and (2) the average lifetime or stability of micelles.[11–14]

Stability of micelles plays an important role in various technological processes such as foaming, wettability, emulsification, and detergency.[5] It has been shown earlier that micellar stability depends on surfactant concentration. Oh[15] et al. showed a maximum micellar stability for SDS solutions at 200 mM due to the small intermicellar distance, resulting in a strong repulsion between the micelles. Therefore, the micelles become more rigid as the surfactant concentration increases. However, the micellar stability can also be influenced by the addition of an alcohol.[12] It has been shown that the maximum micellar stability for SDS/alcohol mixtures exists for the system SDS/$C_{12}OH$, where the chain lengths of the surfactant and the alcohol are the same and thus where the van der Waals interaction between the hydrophobic tails is maximum (hydrophobic interaction).[16–18] In general the chain length of surfactants used in a given mixture of surfactants must be the same to maximize lateral molecular interactions. It has been reported[19] that as the difference in chain lengths of mixed surfactants increases, the spacing between the adjacent surfactant molecule increases. Although these changes are very small, they have a very large effect upon the interfacial and bulk properties of the solutions, e.g., foamability, foam stability, surface tension, surface viscosity, contact angle, bubble size, fluid displacement in porous media, and microemulsion stability.[15,19–23]

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In this paper we have investigated the influence of a cationic surfactant on the micellar stability of SDS solutions. The micellar stability of SDS/C_nTAB ($n = 8$, 10, 12, 14, and 16) mixtures was determined by the pressure-jump technique. We have also shown the correlation of increased micellar stability with surface tension, surface viscosity, foamability, and foam stability.

Experimental Section

Sodium dodecyl sulfate (99% purity) was supplied by Sigma Chemical Co. (St. Louis, MO). The following chemicals were also used without further purification: C_8TAB (Lancaster Inc., Windham, NH), C_{10}TAB (Acros Organics, Pittsburgh, PA), C_{12}-TAB, C_{14}TAB (Sigma), and C_{16}TAB (Aldrich Chemical Co., Milwaukee, WI). Deionized, distilled water was used for all solutions.

All test solutions contained 100 mM SDS and 5 mM C_nTAB (a very low ratio C_nTAB/SDS (1/20) was used in all experiments in order to avoid precipitation). Surface tensions were measured from freshly prepared solutions by the Wilhelmy plate method at 22 °C. The platinum plate was always cleaned and heated to a red/orange color with a Bunsen burner before use.

The deep-channel surface viscometer[24] was used to measure the surface viscosity of the SDS/C_nTAB solutions. In the deep-channel surface viscometer the channel walls are stationary concentric cylinders, while the floor moves with a constant angular velocity. In order to measure the center-line velocity of the air/water interface, a small Teflon particle was placed at the interface, and the time for that particle to make one complete revolution under a specific angular velocity of the vessel was recorded from visual observations. After measuring the center-line velocity of the air/water interface, the surface viscosity can be calculated using the following equation.[24]

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

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 viscosity measurements were performed at 22 °C.

The slow micellar lifetime (τ_2) was measured using a pressure-jump apparatus with conductivity detection from Dia-Log Corp. (Duesseldorf, Germany) with a pressure jump of 120 bar. A KCl solution having the same electrical conductivity as that of the surfactant solution was used as a reference cell in the pressure-jump experiments. All experiments were carried out at 22 °C.

A quartz cylinder (3.5 cm diameter) was used for the foam stability measurements. The cylinder contained a single capillary (2.5 mm diameter) to generate the bubbles. A 50 mL solution was poured into the cylinder using a long tube reaching the bottom, thereby avoiding contact with the walls, since any solution on the walls could act as an additional supply of surfactant molecules increasing the foam stability. After the foam reached 50 cm, the air flow was stopped and the time recorded to collapse to half of its initial height. The experiments were performed at 22 °C.

Foamability measurements were carried out by shaking 15 mL of the surfactant solution vigorously for 10 s, in a 100 mL volumetric cylinder. Foam heights were recorded immediately after shaking. The experiment was repeated for at least 5 times at 22 °C.

The accuracy of the measurements is represented as error bars in the appropriate figures discussed in the next section.
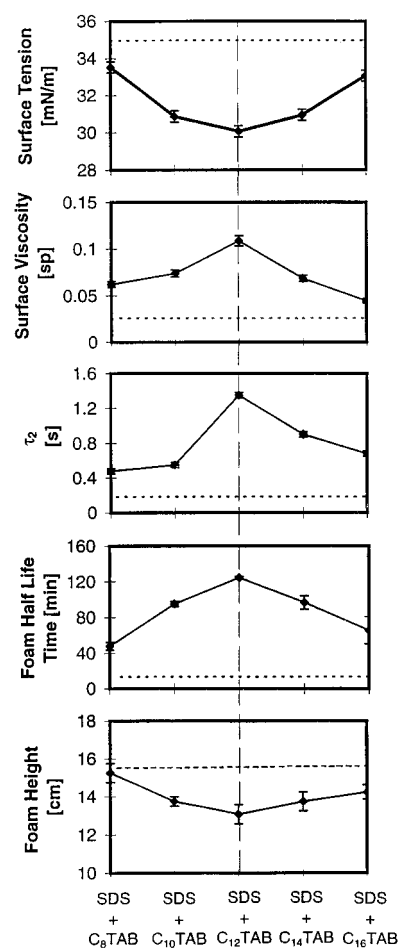
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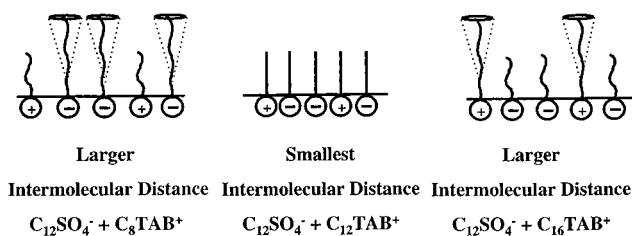(24) Chattopadhyay, A. K.; Ghaicha, L.; Oh, S. G.; Shah, D. O. *J. Phys. Chem.* **1992**, *96*, 6509.

Figure 1. Effect of chain length compatibility on surface tension, surface viscosity, micellar stability, foam stability, and foamability. The dashed lines represent 100 mM pure SDS solution.

Results and Discussion

In order to correlate the effect of chain length compatibility with surface properties of the foaming solutions, SDS and C_nTAB of various chain lengths (i.e., C_8TAB, C_{10}TAB, C_{12}TAB, C_{14}TAB, and C_{16}TAB) in the molar ratio of 20/1 were used as mixed surfactant systems. It was observed that the surface tension (γ) was lowest when the chain length of both surfactants was the same (SDS + C_{12}TAB, Figure 1). Mixtures of anionic and cationic surfactants show a lower surface tension than pure anionic or cationic surfactant solutions because of the Coulombic interaction between the ionic head groups. However, the lowest surface tension as observed for SDS + C_{12}TAB can be explained on the basis of chain length compatibility of both surfactant molecules. The hydrophobic interaction between the alkyl chains causes the molecules to pack closer, resulting in a lower area per molecule and thus a lower surface tension. Another parameter indicating the close packing of molecules at the air/water interface is the surface viscosity. The measurements have shown that the maximum surface viscosity is obtained when the foaming agents possessed similar chain lengths (Figure 1).

The slow relaxation time (τ_2) of mixed surfactants (SDS + C_nTAB) was determined using the pressure-jump technique. Oh et al.[15] reported a slow relaxation time of 0.15 s for 100 mM SDS solutions. It increases to 1.35 s when 5 mM C_{12}TAB is added to 100 mM SDS solutions, which indicates the formation of more stable micelles as compared to pure SDS micelles. The maximum relaxation

Larger Intermolecular Distance | Smallest Intermolecular Distance | Larger Intermolecular Distance

$C_{12}SO_4^- + C_8TAB^+$ $C_{12}SO_4^- + C_{12}TAB^+$ $C_{12}SO_4^- + C_{16}TAB^+$

Figure 2. Schematic diagram representing the effect of chain length compatibility on molecular packing at the interface.

time is observed when the chain lengths of both components of the foaming agents had the same chain length (SDS/C_{12}TAB mixtures, Figure 1). So, apparently the optimum packing of surfactant molecules does not only appear at the air/water interface but in the micelles as well. A schematic diagram showing the proposed explanation for the molecular packing at the air/water interface is presented in Figure 2. In mixtures of anionic and cationic surfactants there are two factors contributing to the micellar stability. First is the Coulombic interaction between the ionic head groups. This will results in a closer packing as compared to pure SDS micelles. Second is the chain length of the surfactants. Since the Coulombic interaction between the head groups plays a role in all of the solutions, only the difference in chain length can be observed.

When the chain length of both of the surfactants is equal, the molecular packing at the air/water interface is closer. However, when the chain length is different, the portion of the molecules above the height of the adjacent molecules will exhibit thermal motion. This thermal disturbance presumably propagates along the chain at a considerable length toward the polar group of the molecule, causing an increase in the area/molecule. The concept of thermal motion of hydrocarbon chains at the interface was advanced by Shah and Schulman.[25] According to the pressure-jump experiments a similar explanation can be held for the micellar interface. Micelles (irrespective of their shape) will pack closer when the chain lengths are equal. Different chain lengths result in a looser packing and thus a decrease in the break-up time of micelles.

Besides the surface measurements described above, foam stability and foam ability measurements were performed. Foam stability measurements have shown that stable micelles form stable foam. On the other hand, foamability was lowest for solutions containing SDS and C_{12}TAB. This happens because micelles must be broken up into monomers for adsorption onto newly created surface of bubbles (Figure 3). Without this process, foam
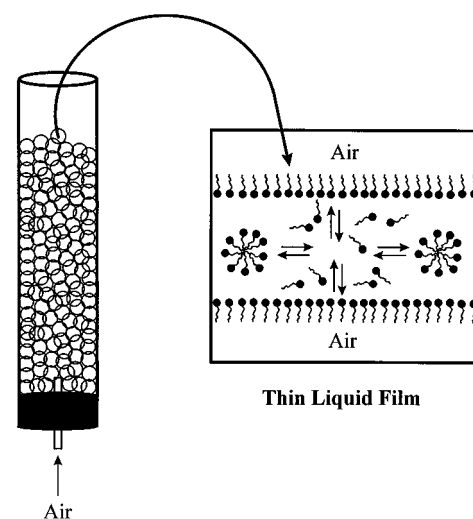
Figure 3. Schematic representation of adsorption of surfactant monomers on the expanding interface due to the disintegration of micelles during foam generation.

cannot be generated. If the micelles in solution are very stable, they can not rapidly provide surfactant monomers to the newly created surface. Hence, foaming ability would be poor.[26] However, if the micelles are relatively unstable, their disintegration provides the surfactant monomers which can rapidly adsorb to the newly created surface. This could enhance the foamability of the micellar solutions. A master diagram of all of the properties of SDS + C_nTAB systems is given in Figure 1.

Conclusions

1. For mixed solutions of anionic and cationic surfactants (SDS + C_nTAB), the surface properties depend upon the chain length of the individual surfactant molecules.

2. For mixed surfactant systems, minimum surface tension, maximum surface viscosity, highest micellar stability, maximum foam stability, and minimum foamability were observed when both surfactants in the system had the same chain length (SDS + C_{12}TAB).

3. The chain length compatibility and the Coulombic interaction in SDS/C_{12}TAB mixtures result in a closest packing of molecules in both micelles as well as at the air/water interface.

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