

## Effect of Tetraalkylammonium Chlorides on Foaming Properties of Sodium Dodecyl Sulfate Solutions

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Received February 10, 1998. In Final Form: May 20, 1998

The effect of tetraalkylammonium chlorides (TC<sub>n</sub>AC for  $n = 1, 2, 3,$  and  $4$ ) on the micellar stability of sodium dodecyl sulfate (SDS) solutions was investigated and related to dynamic interfacial properties, such as foamability and foam stability as well as surface viscosity and surface tension. The slow relaxation time  $\tau_2$ , which is directly related to the micellar stability, was determined using the pressure-jump technique. It was found that upon increasing the concentration of TC<sub>n</sub>AC, the micellar stability increases, due to the ionic interactions between the oppositely charged TC<sub>n</sub>AC and the SDS headgroup. Beyond a critical concentration (depending on the alkyl chain length of TC<sub>n</sub>AC), the micellar stability decreases again, which is attributed to the disruption of the molecular packing in the micelles as well as at the air/water interface. The location of a maximum in the micellar stability corresponds to maxima in foam stability and surface viscosity and to minima in foamability and surface tension. These maxima and minima shift to lower concentrations as the alkyl chain length of TC<sub>n</sub>AC is increased. This indicates that alkylammonium chlorides with longer chain length are more effective in decreasing the molecular packing of SDS in micelles as well as adsorbed monolayers.

### Introduction

Foams are used for many different purposes, such as mineral flotation, food processing, purification (foam fractionation), processing of textiles, personal care, enhanced oil recovery, and fire fighting.<sup>1,2</sup> However, in some processes the formation of foam is not desired and its presence can cause serious problems.<sup>3,4</sup>

Foaming properties can be greatly modified by the addition of organic materials.<sup>5,6</sup> Previous investigations by Blute et al.<sup>7</sup> demonstrated that the foam destabilizing efficiency of tetraalkylammonium bromide salts is equivalent or superior to the traditional antifoamer agents tributyl phosphate and 2-ethylhexanol, which are used in many commercial foam-inhibiting formulations. Furthermore, unlike most antifoamers, the tetraalkylammonium salts are water soluble. This is very important, since solubility in water allows the addition of foam inhibitor into the solution prior to foaming.

We seek to establish that the influence of tetraalkylammonium salts on foam stability and foamability is a result of the effect of these compounds on the molecular packing at the air/water interface and in micelles and to demonstrate a correlation between dynamic interfacial properties and micellar stability.

It was shown earlier that the foamability of sodium dodecyl sulfate (SDS)/hexanol and SDS/alkyltrimethylammonium bromide mixtures is inversely related to micellar stability, and for certain anionic/cationic systems foamability and foam stability are inversely related.<sup>8-11</sup> Micelles play a role in foaming processes by influencing the adsorption of surfactants. During the generation of foam, surfactant monomer adsorbs onto the freshly created interface from the bulk solution. If the monomer is depleted (more likely in the case of a low critical micelle concentration (cmc)), the 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, resulting in less foam. However, if the micelles are relatively unstable, their disintegration resupplies the depleted monomer and foaming is enhanced. The kinetics of micellization and its relation to micellar stability have been evaluated by Aniansson,<sup>12-14</sup> and the relevance of micellar relaxation to technological processes, such as foaming, emulsification, detergency, fabric wetting, and oil solubilization for single surfactant systems has been investigated extensively by Shah and co-workers.<sup>15-17</sup>

The present paper reports the effect of tetraalkylammonium chloride (TC<sub>n</sub>AC, for  $n = 1, 2, 3,$  and  $4$ ) on the micellar stability of SDS solutions in relation to the slow

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micellar relaxation time ( $\tau_2$ ) and interfacial properties such as foamability, foam stability, surface tension, and surface viscosity.

### Experimental Procedure

All micellar solutions were prepared with sodium dodecyl sulfate (99%, Sigma Chemical Co., St. Louis, MO). Tetramethylammonium chloride (97%) was supplied by Fisher Scientific (Fair Lawn, NJ). Tetraethylammonium chloride, tetrapropylammonium chloride, and tetrabutylammonium chloride were supplied by Eastman Fine Chemical (Rochester, NY) and used as received. The tetraalkylammonium chloride concentration was varied from 0 to 50 mM in solutions of 150 mM SDS. Sodium perchlorate (99+% purity) was purchased from Acros (Fair Lawn, NJ). Deionized, distilled water was used for all solutions. All experiments were performed at 22 °C.

The slow relaxation time  $\tau_2$  was measured using a pressure-jump apparatus with conductivity detection from Dia-Log GmbH (Duesseldorf, Germany) with a pressure-jump of 120 bar. The conductivity of the surfactant solution held in the conductivity cell attached to the pressure chamber was compared to a reference cell loaded with a KCl solution of the same conductivity.

Foamability measurements were carried out by shaking 15 mL of the sample solution vigorously for 10 s, in a 100 mL graduated cylinder. A shaking time of only 10 s was chosen to ensure that not all the surfactant solution goes into the making of foam, and thus a certain amount of solution is still present after the foaming test at the bottom of the graduated cylinder. The foamability was recorded as the volume of foam produced immediately after shaking. Each solution was tested at least seven times.

A quartz cylinder, 3.5 cm in diameter, was used to acquire the foam stability measurements. At the base of the cylinder a single capillary, 2.5 mm in diameter, was used to generate the bubbles. A 50 mL portion 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 cm<sup>3</sup>/min. When the foam had reached a height of 40 cm, the air was shut off and the time was recorded for the foam to collapse to half of its initial height.

The deep-channel surface viscometer<sup>18,19</sup> was used to measure the surface viscosity of each solution. Two concentric cylinders form the deep channel of the 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. With this value, the surface viscosity can be determined using the following equation

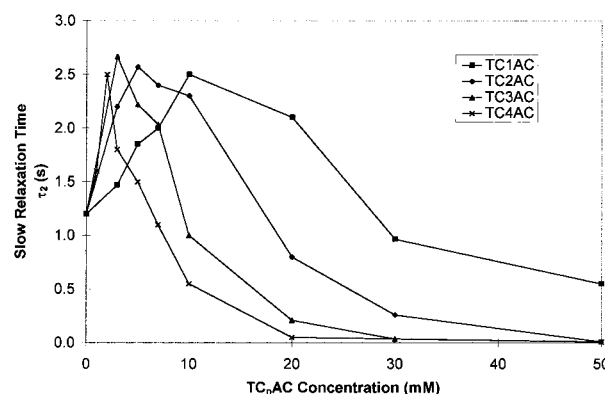
$$\epsilon = \frac{\eta y_0}{\pi} \left[ \frac{8 V_b}{\pi V e^{\pi D}} - 1 \right] \quad (1)$$

where  $\epsilon$  is the surface viscosity,  $\eta$  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 tensions were obtained from fresh 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.

### Results and Discussion

The effect of tetraalkylammonium chlorides (TC<sub>*n*</sub>AC for *n* = 1, 2, 3, and 4) on the micellar stability of 150 mM SDS solutions was measured by the pressure-jump technique. A surfactant concentration considerably higher than the cmc (cmc = 8.3 mM) was chosen, because at SDS



**Figure 1.** Effect of tetraalkylammonium chlorides (TC<sub>*n*</sub>AC for *n* = 1, 2, 3, and 4) on the slow micellar relaxation time  $\tau_2$  in 150 mM SDS solutions.

concentrations close to the cmc the relaxation time is too small (on the order of milliseconds) to observe a significant change after the addition of salt. Figure 1 shows the slow relaxation time  $\tau_2$  of SDS/TC<sub>*n*</sub>AC mixtures as a function of TC<sub>*n*</sub>AC concentration. The  $\tau_2$  of pure SDS was determined to be 1.20 s, in perfect agreement with the value measured by Oh et al.<sup>8</sup> and independently by Lessner et al.<sup>20</sup> All curves show the appearance of a maximum micellar stability depending on the alkyl chain length of the anti-foamer. When the TC<sub>*n*</sub>AC concentration is increased, the micellar stability increases. This indicates a greater stability of the micelles in this concentration range as compared to pure SDS, which can be explained by the Coulombic interactions between the ionic headgroups. The TC<sub>*n*</sub>AC concentration is large enough to partially screen the charges between the headgroups of the SDS molecules, reducing the area/molecule occupied by each headgroup, yet not sufficient to disrupt the molecular packing of the micelles. Besides ionic interactions (shielding of charges) the so-called salting out effect plays a role. When the monomeric form of a surfactant is salted out by the presence of an electrolyte, micellization is favored and the cmc is decreased.

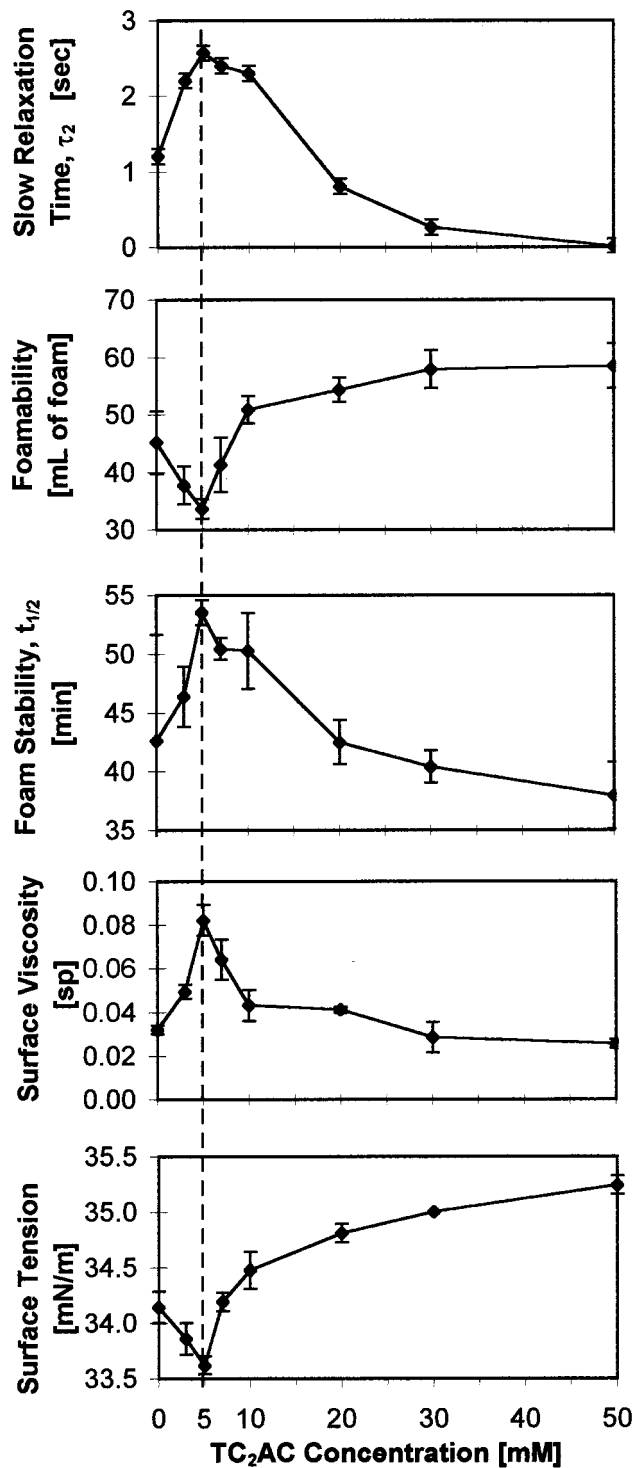
The effects discussed above are more effective when longer alkyl chain lengths are used and therefore the maxima in Figure 1 shift to lower concentrations as the alkyl chain length goes from methyl to butyl. Beyond a critical concentration the micellar stability decreases again, which is attributed to the bulkiness of the anti-foamer molecules. At this point the concentration is large enough to obstruct the close packing of surfactant molecules, thereby decreasing the micellar stability.

The slow relaxation times as measured by the pressure-jump technique were related to interfacial properties such as foamability, foam stability, surface viscosity, and surface tension for the system SDS/TC<sub>2</sub>AC. The results are shown in Figure 2. At 5 mM TC<sub>2</sub>AC, a minimum foamability, maximum foam stability, maximum surface viscosity, and minimum surface tension were observed. A minimum foamability at 5 mM coincides with a maximum micellar stability. This can be explained based on the ability of micelles to break up in order to provide monomers to stabilize the newly created interface. At 5 mM the micelles are very stable so that they cannot breakup fast enough to augment the flux of monomers necessary to stabilize the new air/water interface. Hence, foaming ability is low. A relation between micellar stability and foam stability is less pronounced. It is known

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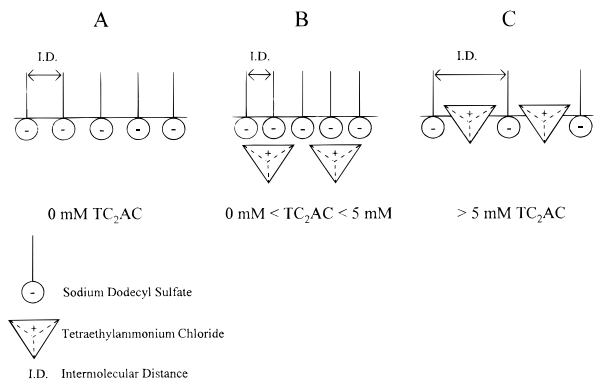
**Figure 2.** Effect of tetraethylammonium chloride on foaming properties of 150 mM SDS solutions.

that foam stability increases with bulk viscosity or surface viscosity.<sup>21–23</sup> Normally, the counterions decrease the repulsion between adjacent surfactant headgroups, causing a more condensed film of higher surface viscosity,<sup>1,2,19,21–23</sup> thereby increasing foam stability. Another important factor influencing foam stability is the micellar

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**Figure 3.** Schematic diagram showing the effect of tetraalkylammonium chlorides on the SDS molecular packing at interfaces (A, pure SDS; B, decrease in electrical repulsion due to adsorption of TC<sub>2</sub>AC below the SDS monolayer results in a smaller area per molecule; C, penetration of TC<sub>2</sub>AC into the SDS monolayer increases the area per molecule).

structure inside the thin liquid film, which has been investigated by Wasan and co-workers.<sup>24,25</sup> The stratification of thin liquid films can be explained as a layer by layer thinning of ordered structures of micelles inside the film. This structured phenomenon is affected by micellar effective volume fraction and micellar stability, interaction, and polydispersity. The presence of TC<sub>2</sub>AC above 5 mM affects the micellar volume fraction by decreasing the width of the electrical double layer, which inhibits the formation of layers inside the film, and hence decreasing foam stability is observed. So, at concentrations higher than 5 mM TC<sub>2</sub>AC a decrease in the thickness of the electrical double layer together with a decrease in surface viscosity leads to a reduction in foam stability.

Finally, a minimum surface tension was observed at 5 mM TC<sub>2</sub>AC. At concentrations lower than 5 mM the ion–ion interactions between the SDS headgroups and the tetraalkylammonium salt cause the surfactant molecules to pack closer, thereby lowering the surface tension. However, beyond 5 mM TC<sub>2</sub>AC the antifoamer salt starts disrupting the SDS molecular packing at the air/water interface resulting in a larger area per molecule, and hence, a higher surface tension is obtained. The effect of tetraalkylammonium salts on the molecular packing at interfaces and in micelles is schematically shown in Figure 3.

Since it is known that sodium counterions can also serve to increase micellar stability, it is interesting to compare the effect of Na<sup>+</sup> and TC<sub>n</sub>A<sup>+</sup> ions for the system used in this study. For this matter, the data obtained by Lessner et al.<sup>20</sup> were taken as comparison. They measured the effect of NaClO<sub>4</sub> on the micellar stability in SDS solutions. Their results can be fit to the following equations:<sup>26</sup>

$$C_g = 0.325 C_{\text{SDS}} + C_{\text{NaClO}_4} \quad (2)$$

$$8 < C_g < 65 \quad -\log(\tau_2) = -4.41 \log(C_g) + 7.393 \quad (3)$$

$$65 < C_g < 115 \quad -\log(\tau_2) = 3.64 \log(C_g) - 7.201 \quad (4)$$

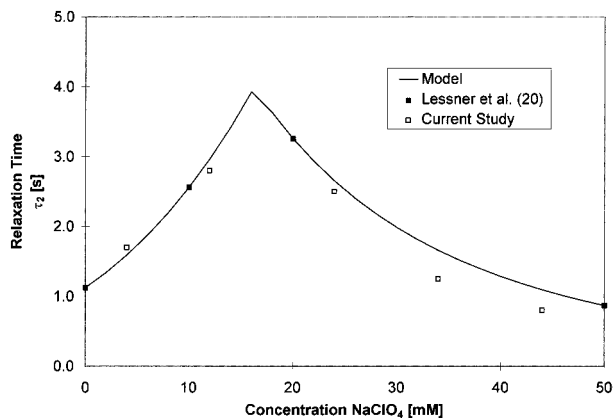
where  $C_g$  is the total counterion concentration (mM) and  $\tau_2$  the slow relaxation time (s). The data from Lessner et al.,<sup>20</sup> the model described in eqs 2, 3, and 4, and some

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**Figure 4.** Effect of  $\text{Na}^+$  counterions on the micellar stability of 150 mM SDS solutions (system, SDS/ $\text{NaClO}_4$ , Lessner et al.<sup>20</sup>).

additional points measured in the current study are plotted in Figure 4 for 150 mM SDS. It is clear that at concentrations higher than 10 mM (corresponding to the maximum  $\tau_2$  for  $\text{TC}_1\text{AC}$  in Figure 1), sodium ions still have a stabilizing effect on micelles, while all the  $\text{TC}_n\text{A}^+$  ions have a distinct destabilizing effect as observed in Figure 1. Eventually, at a concentration of about 17 mM, the sodium ions start destabilizing the micelles. Apparently beyond a critical concentration the sodium ions start also disrupting the micellar packing resulting in less stable micelles and, hence, smaller relaxation times. However, it is clear that the antifoamer molecules are much more effective in disrupting the molecular packing at interfaces, due to their bulkiness, as compared to sodium ions.

As pointed out by Koczko,<sup>27</sup> it is very important to distinguish between two ways of foam controlling: (i) antifoaming where the chemical is added in the liquid prior to foam formation in order to prevent foaming or (ii) defoaming where the chemical is added from outside to eliminate an existing foam. In the first case we have shown that at low concentrations the antifoam compound

actually serves to stabilize foams and decreases foamability, whereas at high concentrations the foamability increases and the stability of the foam decreases. When using  $\text{TC}_n\text{AC}$  as defoamer, the foam will break as the defoamer dissolves into the foam. This also shows the importance of the amount of tetraalkylammonium salt added to a solution in order to produce the antifoaming effect.

### Conclusions

The addition of tetraalkylammonium salts to SDS solutions as antifoaming agent shows two opposing effects depending on its concentration. The tetraalkylammonium counterions act to stabilize foams at lower concentrations. At concentrations lower than approximately 5 mM  $\text{TC}_2\text{AC}$  (varying from 2 mM for  $\text{TC}_4\text{AC}$  to 10 mM for  $\text{TC}_1\text{AC}$ ), the area per molecule of the SDS headgroup is decreased by the shielding of charge repulsion due to the addition of positive ions to the solution, together with a salting out effect. This results in more stable micelles, less foaming ability, higher foam stability, lower surface tension, and higher surface viscosity. At higher concentrations ( $>5$  mM for  $\text{TC}_2\text{AC}$ ), this stabilizing effect is countered by the increasing substitution of sodium counterions ( $\text{Na}^+$ ) by bulky tetraalkylammonium ions ( $\text{TC}_2\text{A}^+$ ), causing an increase in the area per molecule as the charge shielding is overwhelmed by the steric effect resulting in less stable micelles. The same ion effect on the packing of the headgroups occurs at the air/water interface, resulting in increased foaming ability and surface tension but decreased foam stability and surface viscosity. The maxima and minima in the (dynamic) interfacial properties shift to lower concentrations of  $\text{TC}_n\text{AC}$  as the alkyl chain length is increased, due to the decrease in molecular packing at the interface and a stronger salting out effect.

**Acknowledgment.** The authors wish to express their thanks and appreciation to the National Science Foundation (Grant NSF-CPE 8005851), the NSF-ERC Research Center for Particle Science & Technology (Grant EEC 94-02989), and ICI Surfactants for their partial support of this research.

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