Effect of Antifoaming Agents on the Micellar Stability and Foamability of Sodium Dodecyl Sulfate Solutions

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The effect of antifoaming agents on the foamability of sodium dodecyl sulfate (SDS) solutions was investigated and correlated with their effect on the micellar relaxation time τ_2. The slow micellar relaxation time τ_2 of SDS micelles, which is directly related to micellar stability, was determined by the pressure-jump method in the presence of the antifoaming agents 2-ethylhexanol (EH), tributyl phosphate (TBP), and tetrabutylammonium chloride (TBAC). Pressure-jump studies show an increase in τ_2 up to a critical concentration of the antifoaming agent. Further addition of antifoaming agent results in a decrease in τ_2. Such behavior has been observed for all three antifoaming additives. The increase in τ_2 is attributed to the stabilization of SDS micelles by the additives, which essentially minimizes the repulsion between headgroups of SDS molecules at the micellar surface or at the interface. The antifoaming efficiency of EH, TBP, and TBAC was tested by simply generating the foam by the shaking method. The results of antifoaming experiments showed a strong correlation with the micellar relaxation time τ_2.

Introduction

Micelles are often considered as aggregates of surfactant molecules that are in dynamic equilibrium with individual surfactant monomers.[1] The kinetics of micellization of surfactants has been studied extensively by methods such as stopped-flow,[2] temperature-jump,[3] pressure-jump,[4] ultrasonic absorption,[5] and so forth. Essentially, micellar solutions are characterized by two relaxation processes. 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 breakup. The two relaxation times are used to calculate the residence time of a surfactant molecule in a micelle and the average lifetime or stability of micelles.[6−8]

The stability of micelles has been found to play an important role in various technological processes such as foaming, wettability, emulsification, and detergency.[9,10] It has been well established that the stability of micelles depends on the type of counterions, the electrolyte, and the concentration of surfactants.[11] Earlier, Oh et al.[12] showed a maximum micellar stability for SDS solutions at 200 mM due to the small intermicellar distance resulting in closely packed SDS micelles. Recently it has been shown by Shah and co-workers[13,14] that the stability of micelles can be tuned by additives such as alcohols and tetraalkylammonium salts. The difference in chain length of mixed surfactant systems has also been found to influence the micellar stability, leading to a dramatic effect on the interfacial and bulk properties of the solutions.[15] Stabilization of foam films containing high surfactant concentrations, caused by stratification of long range ordered microstructures in thin films, has been shown by Ivan and Dimitrov.[16] Wasan and co-workers[17] have theoretically and experimentally shown that the stepwise thinning of a foam film formed from micellar solutions of SDS is governed by a long range electrostatic repulsion by ionic micelles and a restricted volume effect in the film. Bergeron and Radke[18] determined disjoining pressure isotherms for single isolated foam films stabilized by SDS above the critical micelle concentration (cmc). Studies of the oscillatory form of the disjoining pressure permitted quantitative interpretation of the stepwise thinning behavior. The stabilizing action of liquid crystals in foam systems has been established by Friberg and co-workers.[19]

A typical list of antifoaming agents includes 2-ethylhexanol (EH), tributyl phosphate (TBP), poly(dimethylsiloxane) (PDMS), amides, mineral oil, fatty acids and their derivatives.[20] With such a wide range of foam-inhibiting chemicals, it is not surprising that there are so many alternative theories to explain the antifoaming action.[21] In the past the antifoaming mechanism has been associated with the interfacial properties such as increase

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in surface tension, decrease in elasticity, decrease in surface viscosity, and so forth.[22] The study by Blute et al.[23] was aimed at revealing the molecular mechanism of antifoaming agents. It was demonstrated that tetraalkylammonium cations (TAA^+) are more effective antifoaming agents in SDS systems than a well-known antifoaming agent, tributyl phosphate (TBP). The recent work by Manev et al.[24] showed that the presence of tetraalkylammonium counterions in aqueous foams and thin film lamella stabilized by SDS can act either to increase or to decrease the foam stability.

In the present work an attempt has been made to correlate the antifoaming efficiency of the antifoaming agents 2-ethylhexanol (EH), tributyl phosphate (TBP), and tetrabutylammonium chloride (TBAC) with the slow micellar relaxation time or stability of SDS micelles. We measured the relaxation time of pure SDS and SDS/antifoaming agent mixtures by the pressure-jump technique.[25] The antifoaming efficiency was tested by simply generating the foam by the shaking method.

Experimental Procedure

Sodium dodecyl sulfate (99% purity) was supplied by Sigma Chemicals Co. (St. Louis, MO). The different antifoaming agents (2-ethylhexanol (EH) and tetrabutylammonium chloride (TBAC) purchased from Eastman Kodak Company, Rochester, NY, and tributyl phosphate (TBP) obtained from Lancaster, Windham) were used as received. Deionized, distilled water was used for preparing each solution.

The slow micellar relaxation time τ_2 which corresponds to the micelle formation/breakup 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.

Foaming experiments were carried out in a 100 mL volumetric cylinder using 10 mL of the foaming solution. The cylinder was gently shaken by hand 10 times as uniformly as possible, and the foam height was noted immediately. The foam height was measured in both the absence and presence of antifoam additives. All experiments were performed at least five times at ambient temperature, 23 ± 1 °C. Quoted results in this study are the average of five measurements.

Results and Discussion

The chemical structures of the antifoaming agents used in this study are shown in Figure 1. The effect of the addition of the antifoaming agents EH, TBP, and TBAC to 150 mM SDS solutions on the micellar lifetime or relaxation time τ_2 is shown in Figure 2, where τ_2 is plotted against the molar ratio of antifoaming agent and surfactant. A surfactant concentration far above the cmc (cmc = 8.2 mM) was chosen, because at SDS concentrations close to the cmc the relaxation time is too small (on the order of milliseconds) to observe a significant change in the presence of antifoaming agents. Moreover, above the cmc of SDS the presence of antifoaming agents results in transparent solutions, and hence, presumably other mechanisms of foam-inhibiting action of antifoaming agents such as spreading of the insoluble droplets or emulsion droplets on the surface do not exist in this situation.

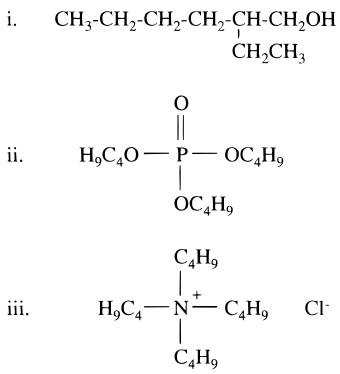

Figure 1. Structures of the antifoaming agents used. (i) 2-ethylhexanol (EH); (ii) tributyl phosphate (TBP); (iii) tetrabutylammonium chloride (TBAC).

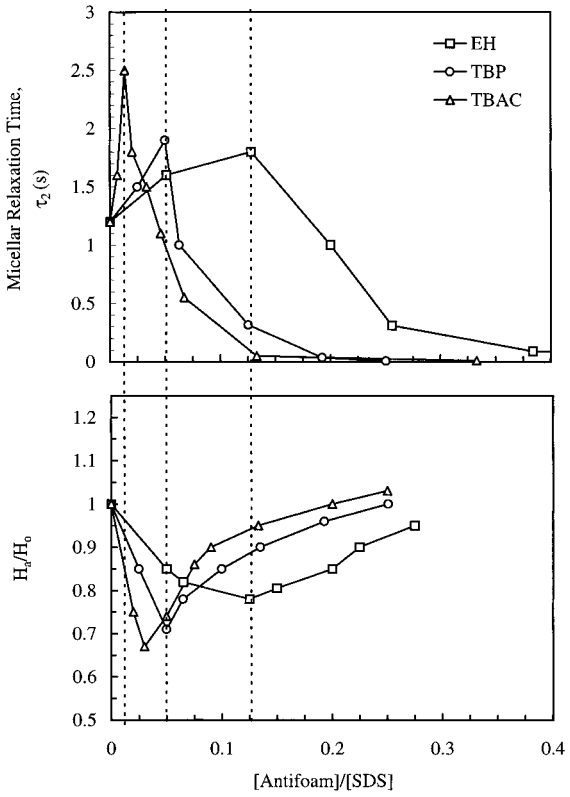

Figure 2. Effect of antifoaming agents on the slow micellar relaxation time τ_2 and foamability of SDS micellar solutions: [SDS], 150 mM; H_o, foam height in the absence of antifoaming agent; H_a, foam height in the presence of antifoaming agent.

It has been shown previously that a surfactant concentration considerably higher than the cmc gives a relaxation time where one can observe a significant effect of additives.[13,14] The τ_2 value obtained for 150 mM SDS without additives is 1.2 s, in good agreement with the values reported by Oh et al.[12] It is evident from Figure 2 that an increase in antifoaming agent content results in an increase in τ_2. However, beyond a critical concentration τ_2 decreases with increasing antifoaming agent concentration. The curves for the addition of antifoaming agents indicate that the maximum τ_2 is related to a specific antifoaming agent concentration rather than a specific surfactant concentration. The effectiveness in increasing SDS micellar stability by the antifoaming agents follows the order TBAC > TBP > EH. TBAC has a more significant stabilizing effect than TBP and EH, indicating the strong molecular interactions due to electrostatic attractions between the SDS headgroup and the tetrabutylammonium

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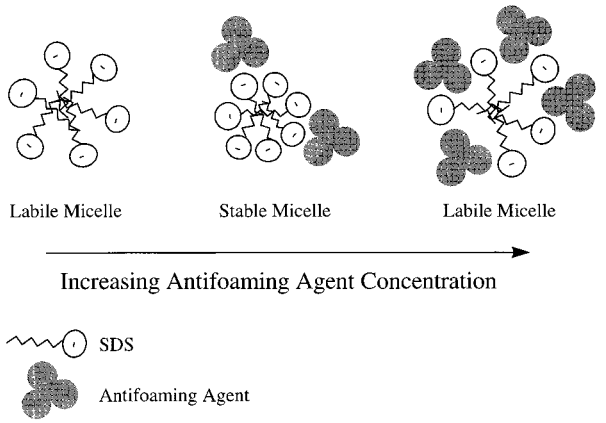

Figure 3. Schematic representation of the microstructural changes in the SDS micelles upon addition of antifoaming agents.

salt. On the other hand, the linking between TBP and SDS and between EH and SDS molecules is primarily due to hydrogen bonding or ion−dipole interactions, which probably shield the repulsion between the negatively charged SDS headgroups. The decrease in τ_2 after a critical concentration of antifoaming agents is attributed to the destabilization of micelles. In fact, at this point the concentration is large enough to obstruct the close packing of surfactant molecules, thereby decreasing the micellar stability. Such a trend or behavior is analogous to the electrolyte effect for which above a certain critical value the ionic attraction becomes greater than the double-layer repulsion, which leads to the destabilization of micelles.[26] Figure 3 schematically illustrates the possible changes in the SDS micelles due to antifoam additives. At low concentration of antifoaming agents, the micelles are labile. The addition of more antifoaming agents stabilizes the SDS micelles probably because of the closest molecular packing of SDS + antifoam mixed micelles. However, when the additive concentration exceeds the optimum concentration, destabilization of micelles occurs. It is known that the antifoaming agents with longer chain length are more effective in decreasing the molecular packing of SDS micelles.[13] Earlier Leung et al.[8] reported a decrease in τ_2 of the micelles in aqueous solutions by the addition of short chain (C_1−C_4) alcohols. The decrease in τ_2 was found to be a function of alcohol concentration. Other studies by Inoue et al.[27] and Patist et al.[14] demonstrated the significance of a small amount of lauryl alcohol on stabilizing the SDS micelles.

In Figure 2, H_a/H_o is a representative of the performance of the antifoaming agents at the particular dosage employed for the SDS micellar foaming solutions. H_o and H_a are the foam heights in the absence and presence of antifoaming agents, respectively. In mechanistic terms, H_a/H_o represents the degree to which the foamability has been reduced by the addition of antifoaming agent. Thus a H_a/H_o value equal to unity means the total ineffectiveness of an antifoaming agent, and H_a/H_o less than unity means effectiveness of the antifoaming agent in the inhibition of foam formation. We should emphasize that in the present study we are only considering the foamability and not the foam stability. The effect of antifoaming agents on the foam stability is not considered here. Essentially, the plots consist of two regions: one in which the antifoaming agents stabilize the pure SDS micelles and hence act as effective foam inhibitors and a second where they destabilize the pure SDS micelles and thus exhibit their ineffectiveness for foam inhibition. The curves for H_a/H_o show a minimum at maximum τ_2. This is in agreement with the finding of Oh et al.,[28,29] who found that minimum foamability occurs when the micellar solutions exhibit the maximum in the relaxation time (i.e. micellar stability). Usually, during the formation of a new air/water interface or bubble, the surfactant monomers adsorb from the bulk to the expanding surface. The foamability of micellar solutions depends on the ability of micelles to disintegrate into surfactant monomers, which in turn determines the efficiency of antifoaming agents. The decrease in the foamability of SDS solutions in the presence of antifoaming agents for a particular dosage is attributed to the lower flux of surfactant monomers coming to the newly created bubble surface from the relatively stable micelles. The effect of antifoaming agents on the foamability of SDS micellar solutions was reported earlier by Ross et al.[30] They observed a good correlation between the foamability and dynamic surface tension data. It was recently shown by Patist et al.[14] that foamability depends on the mode of foam generation. For the foamability of micellar solutions by the vigorously shaking method, which involves a very high shear rate process, the breakup of micelles controls the extent of foamability. The results of dynamic surface tension measurements by the maximum bubble pressure method provide further evidence that the micelle breakup time is the rate-limiting factor in the high-speed dynamic process.[14]

In conclusion, this study correlates the stability of micelles with antifoaming efficiency. The addition of antifoaming agents to SDS solutions shows two opposing effects depending on concentration. The antifoaming agents can stabilize the SDS micelles at lower concentrations and in turn act as foam inhibitors. On the other hand, beyond a critical concentration, the antifoaming agents destabilize the micelles (smaller relaxation time), which begins to improve the foamability of SDS solutions.

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