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NOTE

Effect of Surfactant Concentration and Film Area on the Stability of Films of Surfactant Solutions

The effect of surfactant concentration and film area on film stability was investigated in thin liquid films of sodium dodecyl sulfate (SDS) solutions. Film stability was evaluated at various concentrations of SDS solutions and various film areas. In this study, a maximum film stability was observed for the SDS concentration of 200 m*M*. Interestingly, this concentration also corresponds to the maximum micelle lifetime or long relaxation time (τ_2). The results also show that film stability decreases with increasing film area, and that the larger films appear to be more sensitive to the micelle stability and structuring effect in the film than films with smaller surface areas.

Key Words: **film stability; micelle lifetime; film surface area; thin liquid films.**

INTRODUCTION

Thin liquid films are essential to the understanding of emulsion and foam systems, both of which are common to many industrial applications today. The properties of emulsions and foams are closely related to the stability of thin liquid films (1). The stepwise thinning phenomena in thin liquid films have been linked to the structuring associated with layers of particles or micelles within these films (2–8, 20). Experimental observations have shown that layer-by-layer removal of micelles or particles inside the liquid films causes the film thickness to change in a stepwise manner (2–8). The step (change in thickness) is approximated as a constant and corresponds to the effective diameter of particles or micelles inside the film (2–4). The aggregation of vacancies, represented by the spaces between the particles or micelles inside the liquid films, causes the formation and expansion of thin spots that follow a stepwise thinning mechanism (7). Recently, a Monte Carlo simulation method was used to study the structuring phenomenon inside thin liquid films (9). The results verified the presence of particle layering inside free thinning films. Also shown was an ordered 2-D hexagonal structure that can exist within the layers depending on the film thickness and particle volume fraction (9). The transition from layers to bulk type disorder was shown to be dependent on the film thickness and the position of the layer inside the film (9). Also, the layering of the micelles or particles within the film becomes more pronounced as the concentration of these particles is increased (9). There have been a large number of studies in the literature (19) indicating that the aggregation number for sodium dodecyl sulfate (SDS) micelles remains constant as the concentration is increased above the critical micelle concentration (CMC) from 10 to 300 m*M* SDS. For 10 and 300 m*M* SDS, the aggregation numbers are 60 and 64, respectively. Thus, in view of the published results by several researchers, it is reasonable to assume that there are no liquid crystalline structures at 200 m*M* SDS.

The long relaxation time, τ_2, of micelles reaches a maximum at 200 m*M* SDS and is related to the micelle lifetime. It plays an important role in various technological processes (10). The emulsion droplet size for the SDS/hexadecane/water system reaches a maximum at a SDS concentration of 200 m*M* (11). The maximum rate of solubilization for benzene and Orange OT dye into SDS solutions also occurs at 200 m*M* SDS (12). At the same concentration, the foamability is at a minimum and the bubble size is at its maximum (13, 14). The wetting time of textile is also maximum at 200 m*M* SDS (15). This paper attempts to show that the structuring phenomenon for SDS micelles within the thin liquid films is also related to the micelle stability or micelle relaxation time, τ_2 (12). In addition, the effect of film area on film stability of SDS solutions at various concentrations is investigated.

MATERIALS

Sodium dodecyl sulfate (99% purity) used in the following investigation was obtained from Sigma Chemical Co. The platinum wire used to make the spherical loop was obtained from Fisher Scientific Co. A glass vial with an inner diameter of 1 inch and a length of 4 inches was also used in the experimentation. All the experiments were carried out in a constant temperature bath (Haake Corp.). A stopwatch was used to record the film stability for each experiment. See Fig. 1 for a sketch of the experimental setup.

METHODS

Platinum wire was used to make loops of 5, 6, 7, and 8 mm, respectively, that were made at the end of platinum wires that were in turn attached to corks (Fig. 1). Aqueous surfactant solutions of SDS were prepared at concentrations of 50, 100, 150, 200, 250, and 300 m*M*, respectively. The CMC for SDS is approximately 8.2 m*M* (16); thus, all of the SDS solutions used in this study were above the CMC. Each experiment was initiated by placing 10 ml of aqueous surfactant solution into a glass vial. Next, the film was shielded from external air currents by closing the vial by using the corks attached to the platinum loops. Platinum loops were suspended inside the vials so that they would not touch the solution. The loops were filled with solution by tilting the vial at 45°. Immediately after filling the loops, the vials were rotated back to their original position, leaving a thin vertical liquid film within the loop. The vials were then carefully lowered into a water bath (maintained at a constant temperature of 23°C), and the time required for the films to rupture were recorded using a stop watch. The experiments were repeated several times, and the average times and standard deviations were determined for each concentration and plotted as error bars in Fig. 2. The standard deviation was less than 5% of the measured stability times. Thus, the observed variation in the film stability is far greater than the standard deviation of the values.

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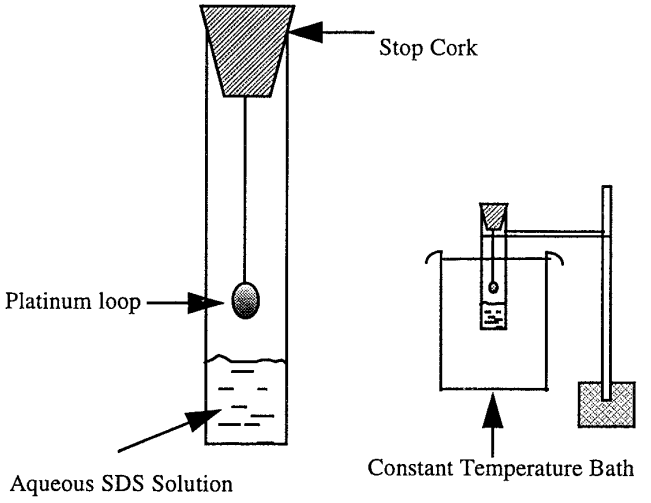

FIG. 1. Experimental design for the study of stability in thin liquid films.

RESULTS AND DISCUSSION

1. *Film Stability and Micelle Relaxation Time*

The film stability, for various film areas, and the micelle relaxation time, τ_2, as a function of SDS concentration are shown in Figs. 2A–2D (12). The results show that the film stability increases as the concentration is increased from 50 to 200 m*M*. A maximum film stability is observed at 200 m*M* SDS for the various loop diameters. Above 200 m*M* SDS, the film stability decreases slightly as the concentration is increased further. We believe that more stable micelles (having a long relaxation time) lead to a greater structuring effect in the thin liquid film which consequently leads to a greater film stability. Therefore, the structuring force arising from more stable micelles is important in describing the stability of single films. Our hypothesis is an extension of the pioneering work of Dr. Wasan's (2–9, 20) group on the structuring phenomena in thin liquid films containing micelles. Kralchevsky *et al.* (4) proposed a mechanism to describe the expansion and formation of black (thin) spots in liquid films which leads to the decrease in film thickness. They postulated that vacancies exist within the structure of the liquid films that are dependent on the packing of the

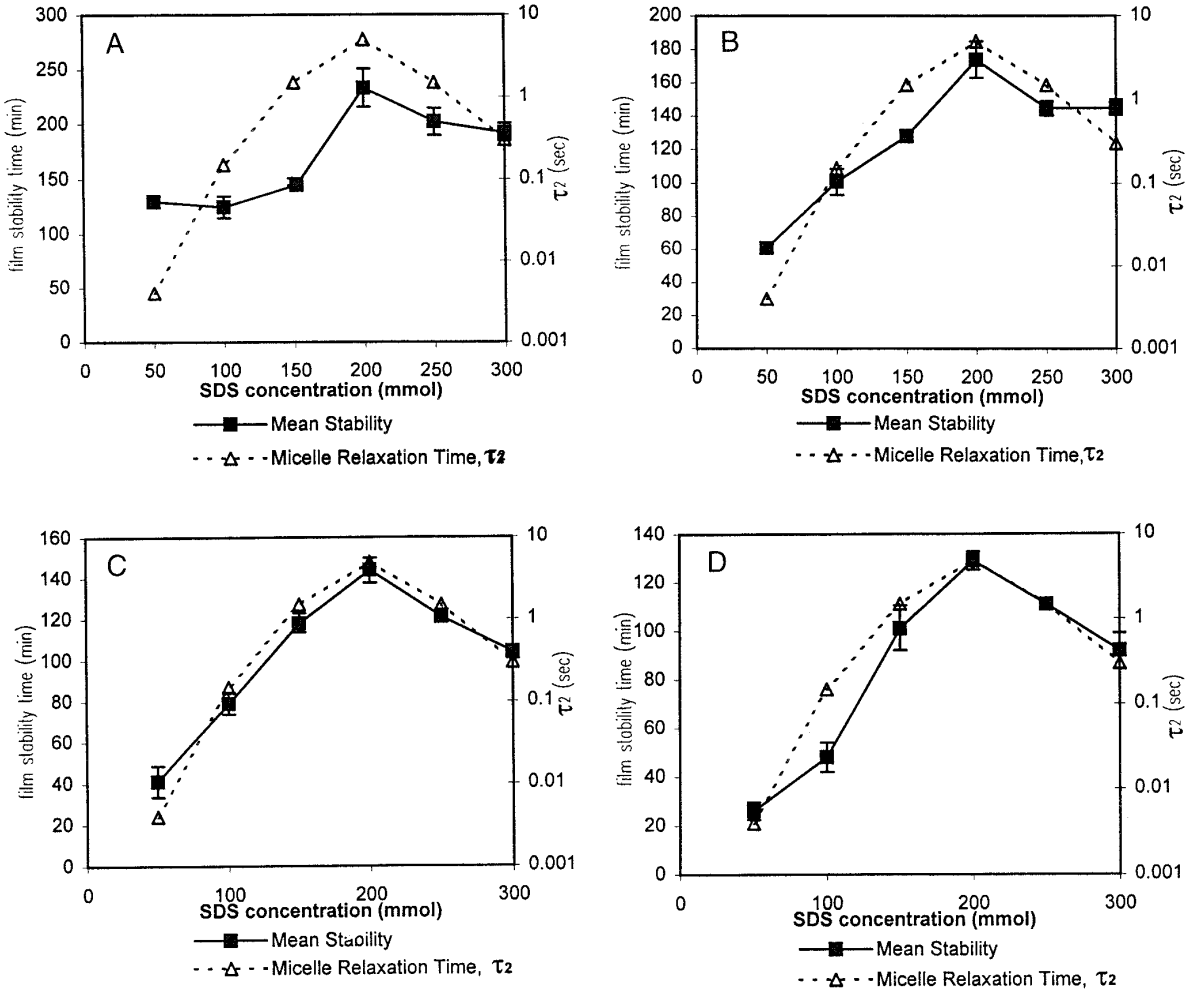

FIG. 2. (A–D). Film stability and micelle relaxation time as a function of SDS concentration. The diameter of platinum loop is (A) 5 mm, (B) 6 mm, (C) 7 mm, and (D) 8 mm.

TABLE 1
The Effect of Film Area on Film Stability at Concentrations of 50 and 200 m*M* SDS

Loop diameter (mm)	Film stability in minutes at 50 m*M* [SDS]	Film stability in minutes at 200 m*M* [SDS]	Film stability ratio [T_{200}/T_{50}]
5	130	233	1.8
6	61	174	2.9
7	41	144	3.5
8	26	129	5.0

particles or micelles. Therefore, they suggested that the vacancy density (number of vacancies per unit volume) is inversely related to the micelle concentration. The aggregation of vacancies is believed to cause an expansion of thin spots, within the film, leading to thickness transitions and eventual film rupture. These vacancies are dynamic in nature and are believed to be dependent on the diffusion rate of the micelles (4). However, we propose that the density of vacancies should also depend upon the micelle stability (or micelle relaxation time, τ_2), such that the higher the τ_2, the lower the vacancy density. Previous research has shown that the micelle relaxation time reaches a maximum and, hence, the molecular packing in SDS micelles is the closest at 200 m*M* (12). In addition, the intermicellar distance is at a minimum at a concentration of 200 m*M* (12). The favorable structuring of relatively stable SDS micelles at 200 m*M* inside the thin liquid films decreases the probability of aggregation of vacancies. This in turn slows down the transition in film thickness and causes greater film stability.

2. *Effect of Film Area on Film Stability*

A larger loop diameter exhibits greater sensitivity to SDS concentration for the film stability, as is indicated by the film stability ratio for SDS of 50 and 200 m*M* (Table 1). The film stability ratio is defined as the ratio of the film rupture times for 200 and 50 m*M* SDS solutions. The film stability ratio increases rapidly as the film surface area is increased. This indicates that the films with larger surface area are more sensitive to the micelle stability and the structuring effect in the film. The effect of film area on the stability has been noted by Wasan (2–9, 20), but the studies were done for very small film areas. The film area in their studies range from 0.06 to 0.1 cm. In our study, the film diameter was varied between 0.5 and 0.8 cm, almost an order of magnitude larger. Plateau (17) did extensive work related to the behavior of soap films. One particular experiment of significance to the work presented in this paper was his investigation into the effect of surface film area on film stability. In a simple experiment, Plateau showed that the film surface area is related to the film stability. He showed that a 7-cm-inner-diameter iron ring formed a stable liquid film for 1 h, while a film supported by a 2-cm ring was stable for 12 h (17). In related work, Dewar, as cited by Lawrence, found the same relationship between the stability of soap films and the area of the films (18). The film stability for SDS solutions at various concentrations as a function of the surface area of the films is shown in Fig. 3. The results show that the film stability for SDS solutions is inversely related to the film surface area. The results are conclusive over a wide concentration range from 50 to 300 m*M*. Moreover, the stability relationship appears to be linear for loop diameters of 6, 7, and 8 mm, and the only nonlinear behavior seems to occur below a 5-mm-diameter loop.

In summary, our results show that the film stability is related to the micelle stability (and hence to the micelle relaxation time, τ_2) and to the film area. Higher micelle stability leads to greater film stability, whereas higher film area leads to lower film stability.

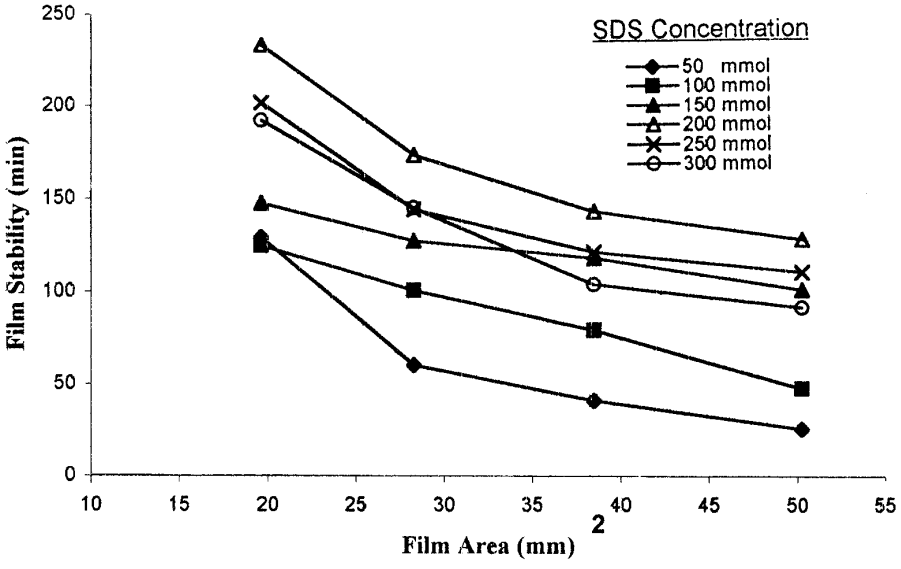

FIG. 3. Effect of film area on film stability for various SDS concentrations.

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