

NOTE

The Effect of Micellar Lifetime on the Droplet Size in Emulsions

The effect of micellar lifetime on the droplet size of an emulsion of hexadecane/sodium dodecyl sulfate (SDS) and hexadecane/cesium dodecyl sulfate (CsDS) solution was studied at various surfactant concentrations. The slow relaxation time (τ_2) measured by a pressure-jump technique attained a maximum at a specific concentration of the surfactant (200 mM for SDS, 100 mM for CsDS) at 25°C, the emulsion droplet size was also at a maximum, at which the most stable micelles were formed for both surfactants. The results are explained as follows: the stable micelles cannot augment the flux of monomers from the bulk to the oil/water interface in the solution. The lower flux of monomers causes the higher dynamic interfacial tension. The work done in expanding the interface during the emulsification is given by $\gamma \cdot \Delta A$. If γ is large, ΔA is smaller for the same amount of work, which results in the larger droplet size of the emulsion. Therefore, the more stable micelles lead to the larger droplet size of the emulsions. © 1993 Academic Press, Inc.

INTRODUCTION

Emulsions have been defined as heterogenous systems of one liquid dispersed in another in the form of droplets usually exceeding 0.1 μm in diameter, and each droplet is coated with a monolayer of the surfactant or emulsifier molecules (1). The two liquids are generally immiscible, chemically unreactive, and form systems characterized by a thermodynamic instability. Studies about formation, stability, and characteristics of emulsions have been done extensively due to their wide applications, such as paints, polishes, pesticides, metal cutting oils, food, cosmetics, and textile processing (2).

The emulsions may consist of droplets of oil in water (o/w) or water in oil (w/o), depending upon the water:oil ratio, emulsifier structure and concentration, temperature, addition of electrolyte, and pressure. The structure of an emulsion (e.g., oil-in-water or water-in-oil) can be determined by electrical conductivity measurement, dilution of the emulsion in water or oil, viscosity variation with added oil or water, and dye-uptake methods (3).

During the emulsion formation, the surfactant molecules adsorb at the oil/water interface from the solution. The surfactant film decreases the interfacial tension, forms a barrier delaying the coalescence of the droplets by changing steric, viscous, and elastic properties of the interface, and provides the electrostatic charge to the droplets (4).

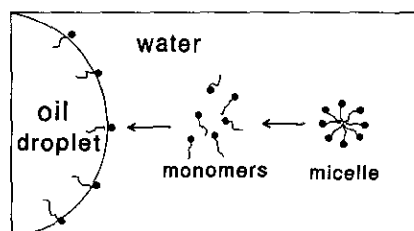


FIG. 1. Schematic diagram for the adsorption of surfactant monomers from the bulk to the oil/water interface during the emulsion formation.

An emulsification process needs energy to disperse one liquid into a continuous phase as droplets. The interfacial area is dramatically increased during this dispersion process. The work required (W) to expand the interfacial area is given by (5);

$$W = \gamma \cdot (\Delta A), \quad [1]$$

where γ is the interfacial tension and ΔA is the increase in the interfacial area. For constant W , a higher value of γ yields smaller ΔA . Thus, the emulsion droplet size increases as the interfacial tension increases. The interfacial tension between oil/water during the emulsification process is determined by the effectiveness of the surfactant monomers to adsorb at the interface from the bulk solution (from the water phase for o/w emulsion, from the oil phase for w/o emulsion). The rate of surfactant monomer adsorption from the bulk to the interface is determined by the following processes: (i) rate of adsorption and desorption at interface, (ii) rate of diffusion of monomers from the bulk to the oil/water interface (6), and (iii) augmentation of flux of surfactant monomers due to the disintegration of micelles. We propose that the short-lived micelles (i.e., small relaxation time) can effectively augment the flux of monomers from the bulk to the oil/water interface in the solution. Therefore, the adsorption of surfactant monomers at the oil/water interface is influenced by the rate of disintegration of the micelles (Fig. 1). The dynamic interfacial tension at the oil/surfactant solution interface will be higher when the micelles are relatively stable (i.e., long relaxation time). Higher dynamic interfacial tension results in smaller ΔA and hence a larger droplet size. But the systematic research about the effect of this micellar lifetime on the emulsion droplet size has not been studied previously.

In this study, the effect of the lifetime of the micelles on the emulsion droplet size of hexadecane/aqueous sodium dodecyl sulfate (SDS) solution and hexadecane/aqueous cesium dodecyl sulfate (CsDS) solution has been investigated by the pressure-jump technique for micellar relaxation time (τ_2) and by optical microscope for the droplet size.

EXPERIMENTAL PROCEDURE

Sodium dodecyl (C_{12}) sulfate, supplied by Sigma Chemical Company (purity 99%), and double-distilled water were used to make micellar solutions.

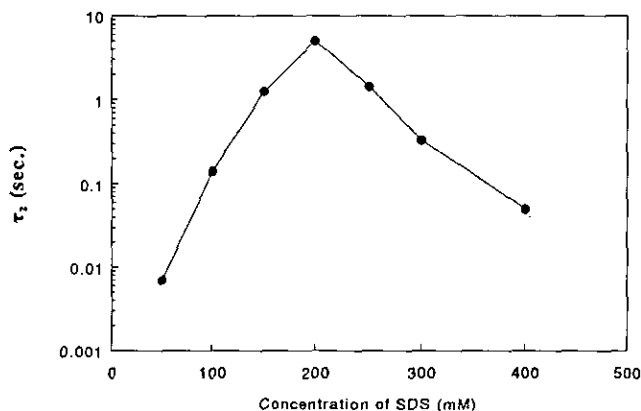


FIG. 2. The slow relaxation time (τ_2) of SDS micelles at various surfactant concentrations.

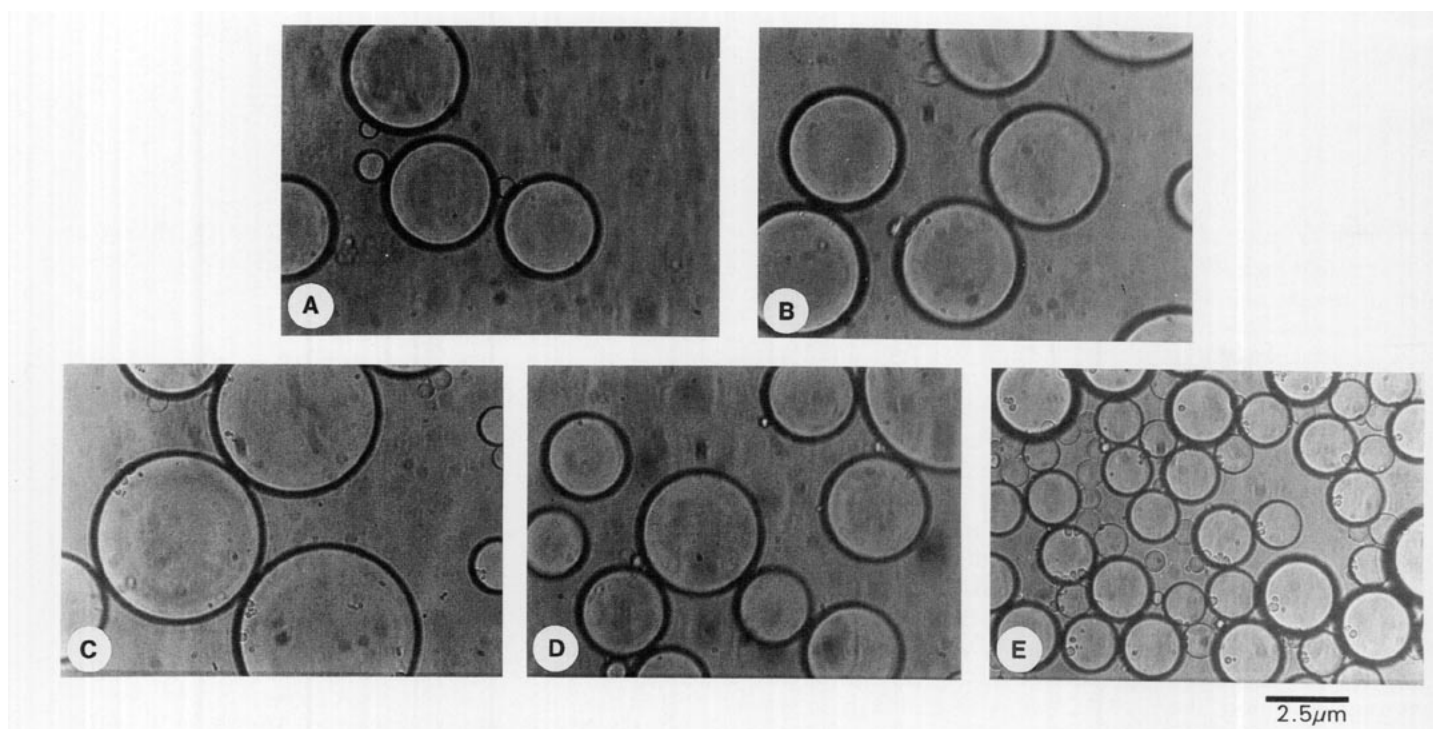


FIG. 3. The emulsion droplet size in the mixture of hexadecane/SDS solutions after 30 s emulsification: (A) at 50 mM, (B) at 100 mM, (C) at 200 mM, (D) at 300 mM, and (E) at 400 mM SDS solution.

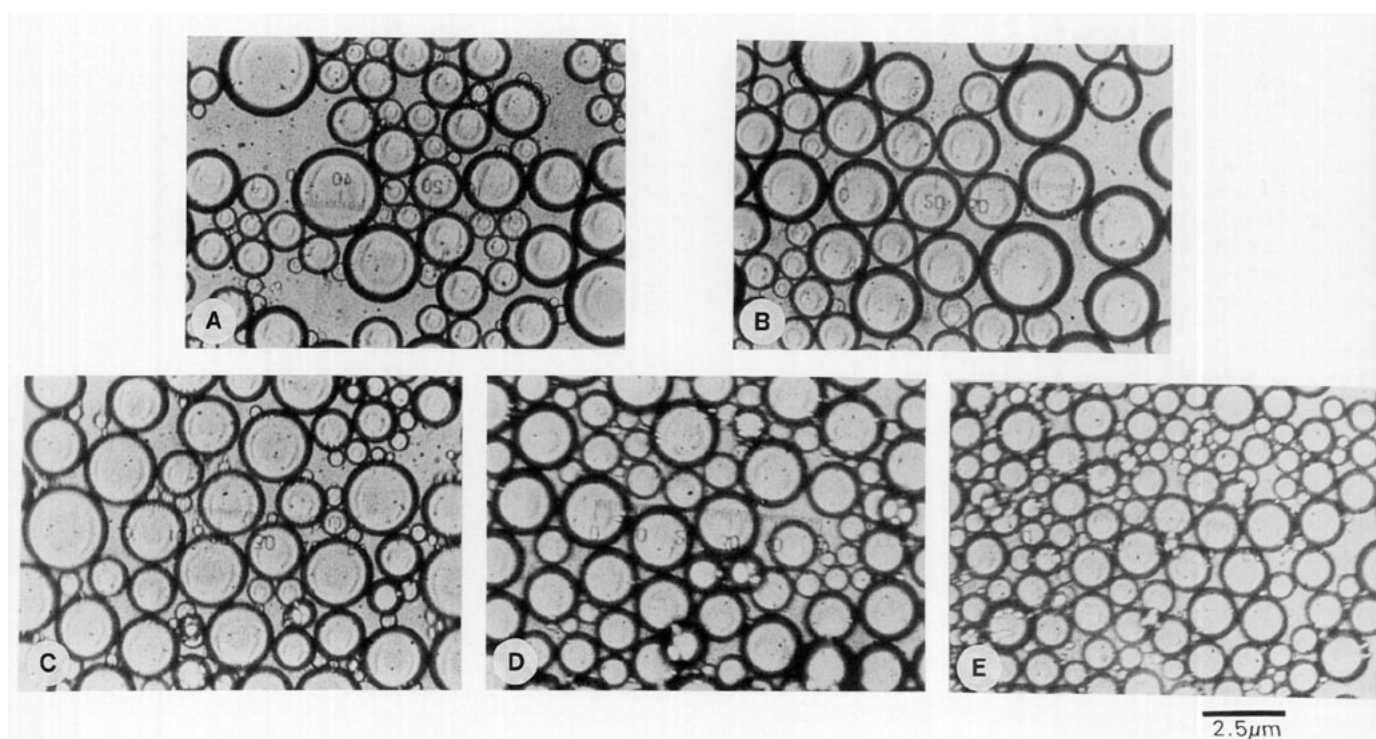


FIG. 4. The emulsion droplet size in the mixture of hexadecane/SDS solutions after 1 min emulsification: (A) at 50 mM, (B) at 100 mM, (C) at 200 mM, (D) at 300 mM, and (E) at 400 mM SDS solution.

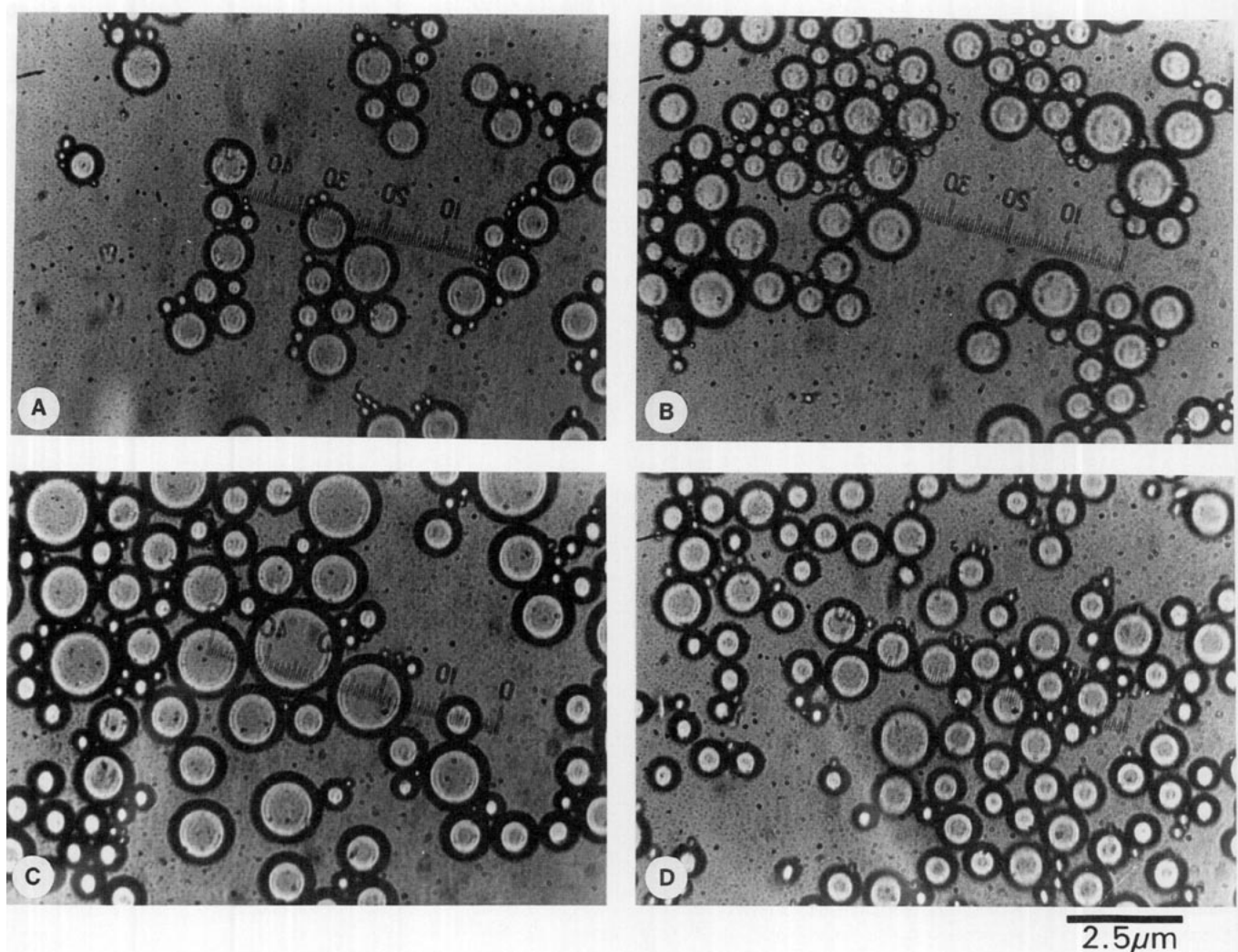


FIG. 5. The emulsion droplet size in the mixture of hexadecane/CsDS solutions after 30 s emulsification: (A) at 50 mM , (B) at 75 mM , (C) at 100 mM , and (D) at 150 mM CsDS solution.

The micellar life-time was measured by a pressure-jump apparatus with conductivity detection from Dia-Log Corporation (Dusseldorf, Germany), as described in the previous paper (7). The relaxation time of SDS solution saturated with hexadecane (Fisher Chemical, 99%) was also measured to study the effect of hexadecane on the micellar lifetime. Hexadecane was added into SDS solutions and shaken for 30 min to bring the mixture to the equilibrium state. The shaken mixtures were centrifuged at 4000 rpm for 10 min to remove the foams generated during the mixing. CsDS, synthesized according to literature (8), was also employed to make emulsions using the same procedure as mentioned above. The 4 ml of hexadecane was added into the 20 ml of micellar solutions of various surfactant concentrations (50, 100, 200, 300, and 400 mM of SDS concentration, and 50, 75, 100, and 150 mM of CsDS concentration), and were vigorously shaken by vibrator for 30 s at constant frequency of vibration to make emulsions. The hexadecane/SDS solution mixtures of same concentration as before were made separately and emulsified for 1 min. The pictures of the emulsion droplets were taken through the optical microscope (Nikon, Japan) at 400 magnification just after the formation of the emulsions to avoid coalescence or flocculation of droplets.

RESULTS AND DISCUSSIONS

The micellar lifetime of SDS solution has been reported by several investigators (9, 10). The micellar lifetime of SDS increases as the concentration of SDS increases up to 200 mM , and then decreases with the surfactant concentration. This result suggests that the most stable micelles are formed at 200 mM of SDS concentration at 25°C (Fig. 2). Lessner and Frahm reported (11) that the most stable micelles of CsDS was found at 100 mM concentration of surfactant. The τ_2 values of CsDS micelles were in the range of 0.001–10 s, similar to those of SDS micelles (0.005–10 s).

The relaxation time of SDS solutions saturated with hexadecane was the same as those of pure SDS solutions, suggesting an insignificant solubilization of hexadecane in SDS solution (less than 4 μg per 100 ml SDS solution in experimental range of concentration).

Figure 3 shows the droplet size of emulsions of hexadecane/SDS solutions of various concentrations. The emulsion droplet size also increased as the concentration of SDS increased up to 200 mM SDS concentration, and then decreased with SDS concentration. The droplet size was maximum at 200 mM of SDS concentration, at which the most stable micelles are formed.

This is due to the minimum flux of monomers to the newly generated oil/water interface during the emulsification process. Because micelles are most stable at 200 mM SDS concentration, they cannot effectively augment the flux of monomers by their disintegration. The dynamic interfacial tension at oil/solution interface of hexadecane/200 mM SDS solution will be maximum due to the minimum flux of monomers from the bulk to the interface. Therefore, the largest droplet size is produced at 200 mM concentration of SDS when the same amount of work is applied to the mixtures.

Figure 4 shows the droplet size of the emulsion of hexadecane/SDS solutions after 1 min of emulsification. In this case, the droplet size of emulsion was almost same at all SDS concentrations, probably due to larger input of energy and longer emulsification time which would allow the disintegration of droplets and subsequent adsorption of surfactant monomers at the oil/water interface. Thus, it appears that the stability of micelles may not exert its influence on the droplet size if the emulsification is continued for a long time.

Figure 5 shows the droplet size of emulsion of hexadecane/CsDS solutions after 30 s emulsification. The droplet size of emulsion was maximum at 100 mM CsDS concentration, at which the most stable micelles were formed.

The studies about foamability and bubble dynamics in SDS solutions showed the minimum foamability and minimum rate of bubble generation at 200 mM SDS concentration due to a decrease in the flux of monomers (12, 13). We have also reported (14, 15) that the wetting time or penetration time of various fabrics in SDS solutions is maximum at 200 mM SDS concentration. The correlation between micellar lifetime and droplet size in emulsions raises some important implications for emulsion science in general.

In conclusion, the stable micelles of surfactants cannot augment the flux of surfactant monomers to the newly generated oil/solution interface during the emulsification process. The emulsion droplet size of hexadecane in the surfactant solution was found to be maximum at 200 mM SDS and 100 mM CsDS concentration respectively due to the above-mentioned mechanism. Micellar lifetime was also maximum at the corresponding concentration of SDS and CsDS.

ACKNOWLEDGMENTS

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