The Effect of Micellar Lifetime on the Rate of Solubilization and Detergency in Sodium Dodecyl Sulfate Solutions

S.G. Oh and **D.O. Shah***
Center for Surface Science and Engineering, Departments of Chemical Engineering and Anesthesiology,
University of Florida, Gainesville, Florida 32611

The slow relaxation time (τ_2) of sodium dodecyl sulfate (SDS) micelles, measured by the pressure-jump technique, was maximum at 200 mM concentration at 25°C, indicating that the most stable micelles are formed at this concentration. This is presumably related to the optimum molecular packing in the micelle. The rate of solubilization of benzene and Orange OT dye into SDS solutions was also maximum at 200 mM concentration. The results are explained as follows: The distance between micelles (*i.e.*, intermicellar distance) decreases as the surfactant concentration (or the number of micelles) increases, resulting in a stronger electric repulsion between micelles. Therefore, the micelles become more rigid, due to the compressive force of intermicellar repulsion, as the concentration increases up to 200 mM SDS. With further increase in the SDS concentration, the micellar shape changes from spherical to cylindrical to accommodate more surfactant molecules in the solution and to minimize the free energy of the system. The interior of the tightly packed micelles is more hydrophobic than that of loosely packed micelles and, therefore, the tightly packed micelles induce rapid solubilization of nonpolar molecules (*e.g.*, benzene, Orange OT) into these micelles.

KEY WORDS: Detergency, electrical conductivity, intermicellar distance, micellar lifetime, pressure-jump technique, rate of solubilization, rigidity of micelles.

Solubilization is defined as the spontaneous formation of a thermodynamically stable isotropic solution of a substrate (the solubilizate), normally insoluble or only slightly soluble in a given solvent, by the addition of a surfactant (1). Solubilization into aqueous media is of major practical importance in the formulation of products containing water-insoluble ingredients, where it can replace the use of organic solvents or cosolvents; in detergency, where solubilization is believed to be one of the major mechanisms involved in the removal of oily soil; and in the separation of materials for manufacturing or analytical purposes. Solubilization into nonaqueous media is of major importance in dry-cleaning (2). The solubilization of materials in biological systems sheds light on the mechanisms of the interaction of drugs and other pharmaceutical materials with lipid bilayers and membranes (3).

The location in the micelle where solubilization occurs varies with the nature of the solubilized materials and is important in that it reflects the type of interaction that occurs between surfactant and solubilizate. Solubilization is believed to occur at a number of different sites in the micelle: (i) on the surface of the micelle, at the micelle-solvent interface; (ii) between the hydrophilic head groups; (iii) in the so-called palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise the outer core of the micellar interior; (iv) more deeply in the palisade layer; and (v) in the inner core of the micelle (4). These loci of solubilization are determined mainly from studies on the solubilizate before and after solubilization, through X-ray diffraction (5), ultraviolet (UV) spectroscopy (6) and nuclear magnetic resonance (NMR) spectrometry (7). Diffraction studies measure changes in micellar dimensions on solubilization, whereas UV and NMR spectra indicate changes in the environment of the solubilizate on solubilization.

The amount of solubilizate that can be solubilized in the micellar solution depends on such conditions as the structure of surfactant, structure of solubilizate, temperature and additives. Nonionic surfactants are better solubilizing agents than ionic in dilute solutions because of their lower critical micelle concentration (CMC) (8). For hydrocarbons and long-chain polar compounds that are solubilized in the interior of the micelle or deep in the palisade layer, the amount of material solubilized generally increases with an increase in the size of the micelles. Therefore, an increase in the chainlength of the hydrophobic portion of the surfactant generally results in increased solubilization capacity for hydrocarbons (9). Klevens (10) pointed out that, in most cases, increasing the length of the alkyl chain, either in a straight chain or substituted on a benzene ring, decreases the solubility in a micellar solution and that unsaturated compounds are more soluble than their saturated counterparts. In most cases, the amount of solubilization increases with temperature due to changes in the aqueous solubility of the solubilizate and changes in properties of the micelles (11). For ionic micelles, the addition of electrolyte causes an increase in micellar size and a decrease in the CMC. Therefore, the addition of electrolyte generally increases the amount of solubilization (12).

Previous research (13) indicated that, like the surfactant monomers, the solubilized molecules are not rigidly fixed in the micelle but have a freedom of motion that is dependent to some extent on the solubilization site. The residence time of benzene molecules in sodium dodecyl sulfate (SDS) micelles was measured by analyzing the NMR signal of SDS solutions saturated with benzene. However, the lifetime of the solubilized molecule within the micelles was too short to be determined by this technique, but was thought to be no longer than 10^{-4} s. Other studies showed that the lifetime of *t*-butyl-(1,1-dimethylpentyl)-nitroxide in SDS micelles was 3.3×10^{-6} s by electron spin resonance (14). Also, the lifetime of solubilizate in micelles increases with the increase of hydrocarbon chainlength in sodium octyl, decyl and tetradecyl sulfate solutions (15).

Micelles are in dynamic equilibrium with monomers in the solution; namely, micelles dissociate into monomers and monomers reaggregate into micelles continuously. These micellar kinetics have been studied by stopped-flow (16), temperature-jump (17), pressure-jump (18) and ultrasonic absorption (19) methods since Aniansson and Wall

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*To whom correspondence should be addressed.

(20) developed a theoretical model about the kinetics of micellization. There are two relaxation processes—the first one is the fast relaxation process with a relaxation time (τ_1, in the microsecond range) that is associated with the fast exchange of monomers between micelles and bulk aqueous phase. This process can be seen as the collision between surfactant monomers and micelles. The second relaxation time (τ_2, in the millisecond range) is related to micelle dissociation kinetics (Fig. 1). The average micellar lifetime is given by the following expression (21,22):

$$\frac{1}{\tau_2} = \frac{n^2}{A_1 R} \left\{ 1 + \frac{\sigma^2}{n} a \right\}^{-1} \tag{1}$$

$$T(m) = \tau_2 \frac{na}{1 + \frac{\sigma^2}{n} a} \tag{2}$$

where $T(m)$ is the average micellar lifetime, n is the aggregation number, σ is the distribution width of the distribution curve of micellar sizes and $a = (A_{tot} - A_1)/A_1$, where A_{tot} and A_1 are the total surfactant concentration and mean monomer concentration, respectively, as shown in the distribution curve of aggregates of surfactant molecules (Fig. 2). R is given by:

$$R = \sum_{s = s_1 + 1} 1/(k_s^{-1} A_s) \tag{3}$$

where s is the aggregation number of a particular aggregate, k_s^{-1} is the dissociation rate constant of this aggregate and A_s is the equilibrium concentration of aggregates of aggregation number s. The dependence of τ_2 on ionic strength, concentration and temperature can be interpreted in terms of their effect on R. When the surfactant concentration is much greater than the CMC, micellar lifetime is approximately equal to $n\tau_2$ (23).

In this paper, the effect of micellar lifetime on the rate of solubilization and detergency in SDS solutions was investigated by measuring the rate of movement of the interface between benzene and SDS solution, the rate of change in electrical conductivity after adding benzene into SDS solution and the rate of dye removal from cotton into SDS solution.

(1) Fast relaxation time, microseconds
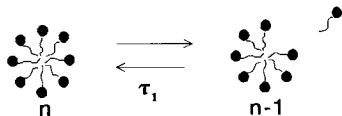
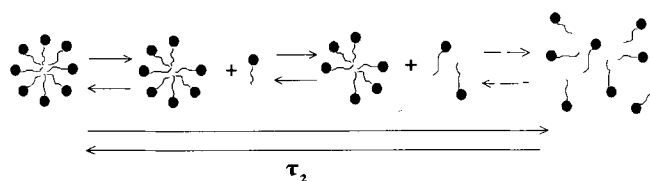(2) Slow relaxation time, milliseconds

FIG. 1. Schematic illustration of the mechanisms for fast and slow relaxation times of micelles in solution.
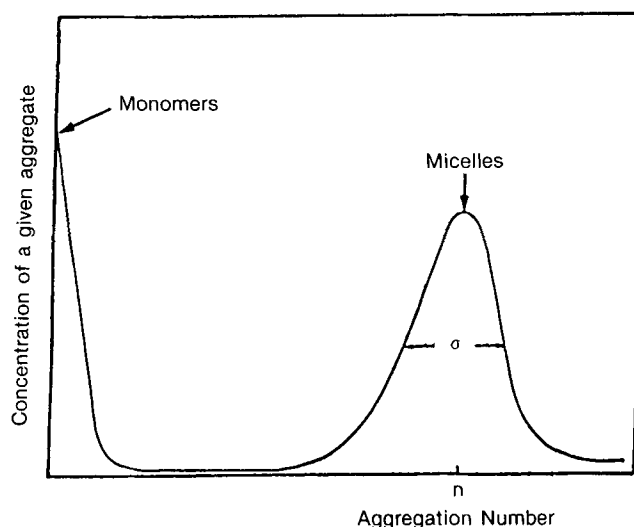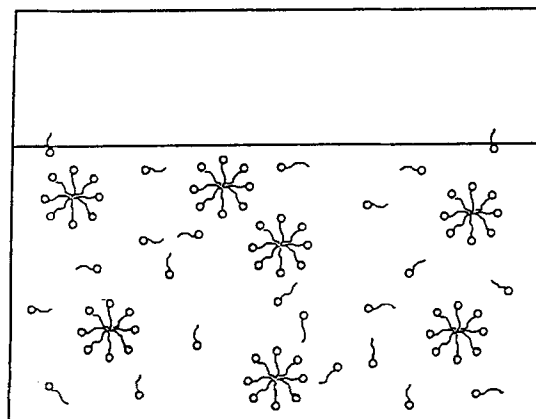

FIG. 2. A typical distribution curve for the aggregates of surfactant monomers above the critical micelle concentration.

EXPERIMENTAL PROCEDURES

Micellar lifetime. Sodium dodecyl (C_{12}) sulfate, supplied by Sigma Chemical Company (St. Louis, MO) (purity 99%), and double-distilled water were used to make micellar solutions. The micellar lifetime was measured with a pressure-jump apparatus with conductivity detection from Dia-Log Corporation (Düsseldorf, Germany), as described in the previous paper (24).

Relaxation amplitudes in the pressure-jump machine first decrease with increasing surfactant concentration to become rather small within a limited concentration range, but then they increase again with further increasing concentration to approach an apparently constant value that is proportional to $(\partial \ln m/\partial P)_T$, where m denotes the mean aggregation number of the proper micelles. As long as $(\partial \ln m/\partial P)_T$ is different from zero, the relaxation measurements can be extended to high concentration (25). Several studies have been reported with micellar relaxation times in the range of 100–500 mM SDS concentration (26).

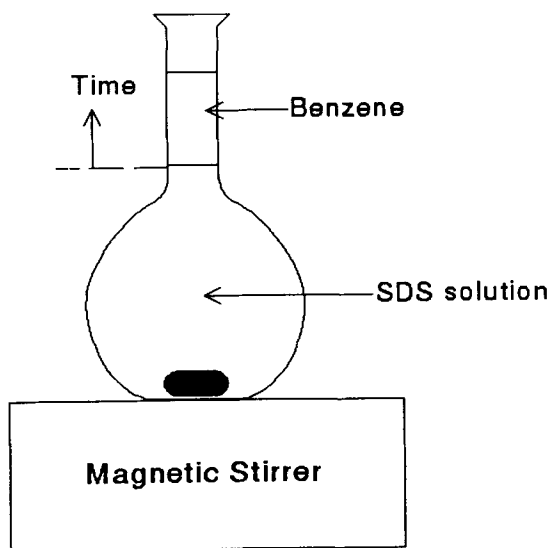*Movement of the benzene/surfactant solution interface.* Benzene (Fisher Chemical Co., Cincinnati, OH; 99%)

FIG. 3. Experimental set-up for the measurement of the rate of movement of the benzene/sodium dodecyl sulfate (SDS) solution interface by stirring.

FIG. 4. The slow micellar relaxation time (τ_2) vs. concentration of sodium dodecyl sulfate (SDS) at 25°C.

(5 mL) was added to 50 mL of SDS solution in a flask (Fig. 3). The SDS solution in the bottom was agitated gently by magnetic stirrer, and the rate of upward movement of the interface was measured.

Solubilization of benzene by electrical conductivity. The electrical conductivity of 50 mL of SDS solution was measured with a conductivity bridge (YSI model 31) (Fisher Scientific Co., Fairlawn, NJ) until there was no further change of conductivity while stirring, indicating that the system had reached the equilibrium state at ambient conditions. Benzene (1 mL) was added to the SDS solution. The electrical conductivity of the benzene/SDS solution mixture was measured as a function of time. If there was no more change in conductivity with time, we considered that time as the time required to solubilize benzene into SDS solution up to its saturation limit.

SDS detergency rate for Orange OT adsorbed on cotton. Orange OT (0.05 g) was dissolved in 5 mL benzene; 0.4 mL of this dye solution was applied to cotton pieces (5" × 5"). The benzene was removed from the cotton by drying. The cotton pieces were submerged in 250 mL of SDS solution in a Tergotometer (United States Testing Co., Inc., Hoboken, NJ). The Tergotometer was operated at 25°C. A small amount of surfactant solution (3 mL) was withdrawn from the Tergotometer at different times to measure the absorbance of light at 505 nm in order to measure the concentration of Orange OT.

RESULTS AND DISCUSSION

The micellar lifetime of SDS solution has been reported by several investigators (21,26,27). The lifetime of SDS micelles increases as the concentration of SDS increases up to 200 mM, and then decreases. This result suggests that the most stable micelles are formed at 200 mM SDS at 25°C (Fig. 4). Lessner and Frahm (25) reported that the most stable micelles of cesium dodecyl sulfate (CsDS)
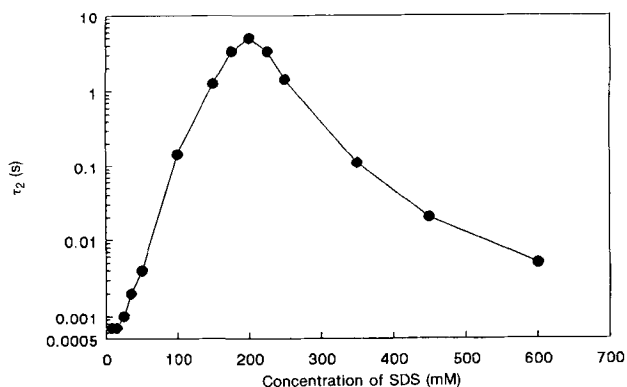
were formed at 100 mM surfactant concentration. The τ_2 values of CsDS micelles measured by the pressure-jump technique were in the range of 0.001–10 s, similar to those of SDS micelles (0.005–10 s).

Figure 5 shows the rate of upward displacement of interface between benzene and SDS solutions. The rate was maximum at 200 mM concentration, a level at which the most stable micelles are formed. Figure 6 shows the electrical conductivity change after adding benzene into SDS solution at 200 mM concentration. Electrical conductivities of mixtures at other concentrations also decay in a similar way, but it took a longer time to reach equilibrium than at 200 mM SDS concentration. The decay curve of conductivity can be used as a measure of the rate of solubilization because the solubilization of benzene decreases the CMC and, hence, monomer concentration (28). This results in a decrease of electrical conductivity. The electrical conductivity of the mixture of benzene and SDS solution reaches the equilibrium value in minimum time for 200 mM SDS concentration. This indicates that the highest rate of solubilization of benzene into SDS solutions occurred at 200 mM SDS concentration (Fig. 7).

In detergency, solubilization of soil from fabric into the detergent solution is one of the most important events. The rate of dye (Orange OT) removal from cotton to SDS solutions in the Tergotometer was maximum at 200 mM concentration (Fig. 8).

Chan *et al.* (29) proposed a theory of solubilization kinetics in micellar solution, based on an analysis of five steps. Surfactant molecules diffuse to the surface as micellar species (step 1). These molecules adsorb on the surface of the solubilizate (step 2), and the surfactant and solubilizate form mixed micelles (step 3). The mixed micelles are dissolved (step 4), and they diffuse away into the bulk solution (step 5). However, the most rapid solubilization and detergency at 200 mM SDS concentration in our study can be explained by the following proposed intermicellar coulombic repulsion model (ICRM).

ICRM. The intermicellar distance in SDS solution decreases as the surfactant concentration increases, due to the increase in the number of micelles. The intermicellar distance was calculated as follows: Divide the solution into cells (or cubes) of the same volume, and the number of cubes is the same as the number of micelles. Each cube
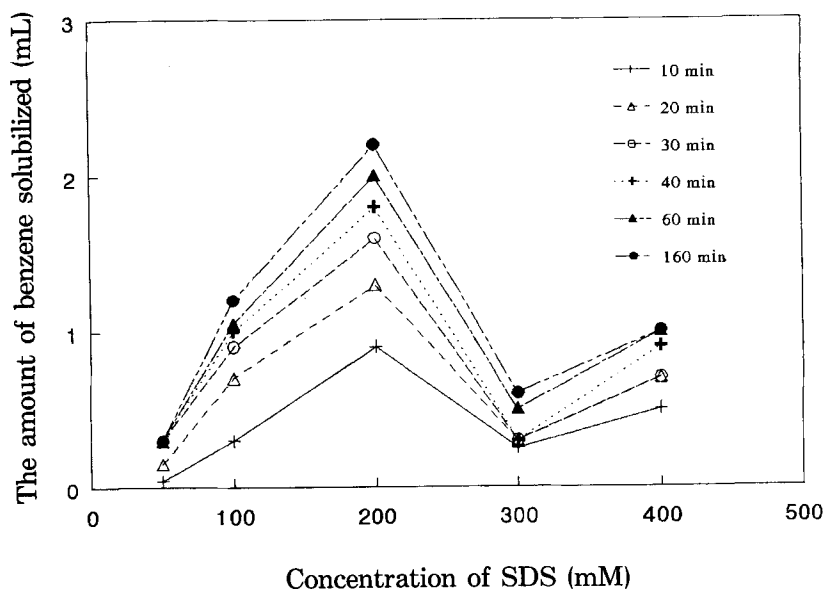
FIG. 5. The amount of benzene solubilized into sodium dodecyl sulfate (SDS) solutions at various times.

contains a micelle, as shown in Figure 9. The number of micelles (N_m) in the solution is given by Equation 4.

$$N_m = \frac{(C_{tot} - CMC) \times N_0}{n} \qquad [4]$$

where C_{tot} is the total concentration of surfactant (moles/L), N_0 is the Avogadro number and n is the aggregation number of the micelle. If the volume of surfactant solution (V) is 1 L (*i.e.*, $1000 \times 10^{24}\ Å^3$), then the volume of the cell occupied by each micelle is V/N_m. Therefore, the average intermicellar distance (ℓ) or the length of the cube is given by $(V/N_m)^{1/3}$. The intermicellar distances obtained from this procedure at various SDS concentrations are shown in Figure 9 for a micellar

aggregation number of 64 (30). The intermicellar distance at 50 mM SDS concentration is 130 Å, which is equivalent to 3.6 times the micellar diameter, but at 200 mM concentration it is 78.6 Å, equivalent to approximately twice the micellar diameter ($\approx$40 Å) (31). The micellar lifetime at 200 mM is more than 1,000 times larger than that at 50 mM. It is possible that binding of sodium ions to micelles increases to decrease the coulombic repulsion between micelles as they become closer, and the stability of micelles increases. It appears that micelles pack very closely in the SDS solution at 200 mM concentration. Above 200 mM SDS concentration, the structural transition from spherical to cylindrical shape occurs to
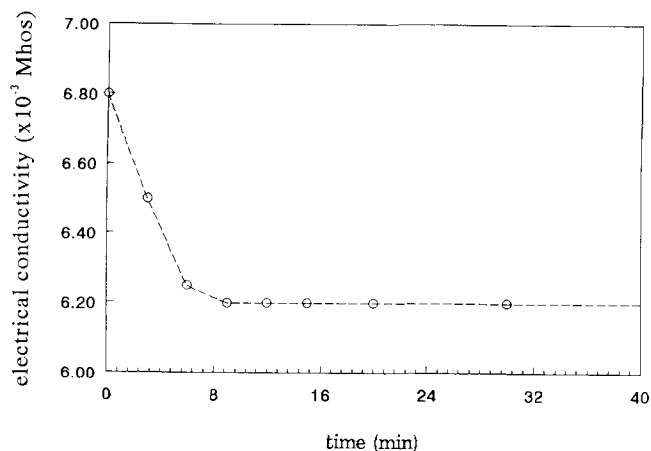

FIG. 6. The electrical conductivity change after adding benzene into sodium dodecyl sulfate solution at 200 mM concentration.
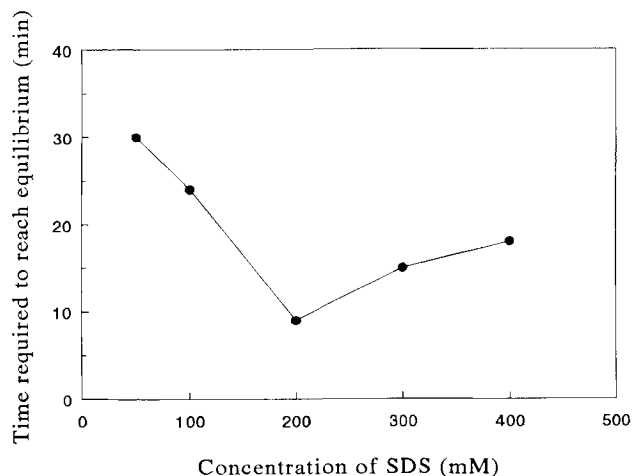

FIG. 7. Time required to solubilize 1 mL benzene into 50 mL of sodium dodecyl sulfate (SDS) solutions at different concentration as obtained by the electrical conductivity method.

EFFECT OF MICELLAR LIFETIME ON SOLUBILIZATION/DETERGENCY
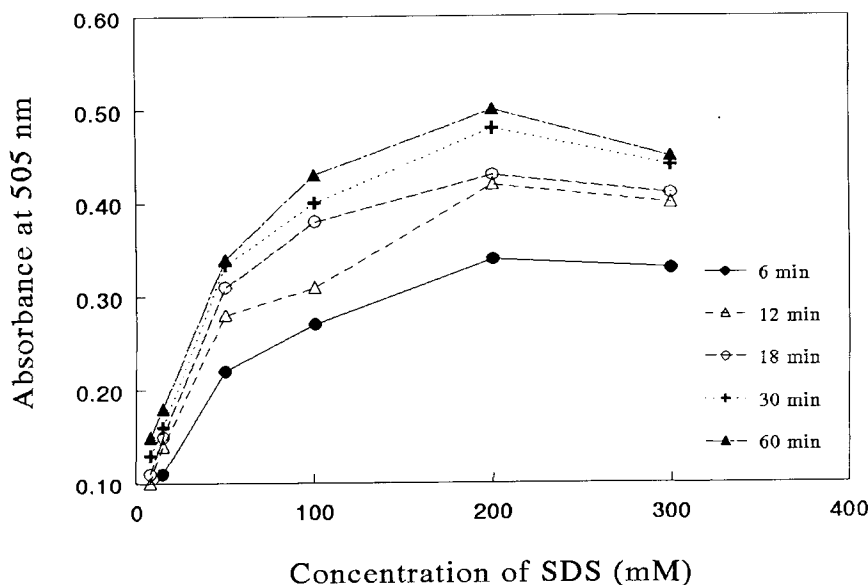

FIG. 8. The rate of solubilization of Orange OT from cotton into sodium dodecyl sulfate (SDS) solution in the Tergotometer.

accommodate more surfactant molecules into the solution and minimize the free energy of the system. Moreover, Ekwall (32) has shown that the transition from spherical to cylindrical micelles occurs over a wide concentration range. As this structural transition proceeds, the concentration of spherical micelles decreases, and the intermicellar distance between spherical micelles increases. Cylindrical micelles are likely to be more stable than spherical micelles. Hence, in solutions containing both spherical and cylindrical micelles, the relaxation time is predominantly determined by the spherical micelles because spherical micelles are more labile compared to cylindrical micelles. Because the intermicellar distance between spherical micelles increases in such systems (above 200 mM SDS; Fig. 9D), the relaxation time decreases due to less coulombic repulsion between the spherical micelles.

The micelles become more and more rigid and stable as the SDS concentration and, due to coulombic repulsion between them, increases up to 200 mM, and concomitantly increases in the binding of sodium ions to the micellar surface. Reiss-Husson and Luzzati (33) found the structural change of SDS micelles from spherical to cylindrical shape by X-ray scattering at 250 mM and 27°C. Our studies were carried out at 25°C, and this transition may occur at 200 mM. The interior of rigid (i.e., tightly packed) micelles becomes more hydrophobic compared to that of loosely packed micelles. The stronger hydrophobic core of the rigid micelles causes rapid solubilization of benzene and Orange OT into the micelles at 200 mM SDS concentration.

In conclusion, the relatively more stable micelles (longer relaxation time, τ_2) are formed at 200 mM SDS concentration at 25°C, and the rate of solubilization of benzene and Orange OT into the SDS micelles is maximum at 200 mM concentration. Therefore, we conclude that more stable micelles are more favorable for rapid solubilization of oil and efficient detergency.

REFERENCES

1. Fendler, J.H., and E.J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, Inc., 1975, Chapter 3.
2. Rosen, M.J., Surfactants and Interfacial Phenomena, 2nd edn., John Wiley & Sons Inc., New York, 1989.
3. Florence, A.T., I.G. Tucker and K.A. Walters, Structure/Performance Relationships in Surfactants, edited by M.J. Rosen, ACS Symposium Series 253, American Chemical Society, Washington, D.C., 1984, p. 189.
4. Attwood, D., and A.T. Florence, Surfactant Systems: Their Chemistry, Pharmacy and Biology, Chapman and Hall, New York, 1984.
5. Philippoff, W., J. Colloid Interf. Sci. 5:169 (1950).
6. Mukerjee, P., and J.R. Cardinal, J. Phys. Chem. 82:1620 (1978).
7. Eriksson, J.C., and G. Gillberg, Acta. Chem. Scand. 20:2019 (1966).
8. Tokiwa, F., J. Phys. Chem. 72:1214 (1968).
9. Collett, J.H., R. Withington and L. Koo, J. Pharm. Pharmac. 27:46 (1975).
10. Klevens, H.B., Chem. Rev. 47:1 (1950).
11. Bates, T.R., M. Gibaldi and J.L. Kanig, J. Pharm. Sci. 55:191 (1966).
12. Stearns, R.S., H. Oppenheimer, E. Simon and W.D. Harkins, J. Chem. Phys. 15:496 (1947).
13. Nakagawa, T., and K. Tori, Kolloid-Z u. Z.-Polymere 194:143 (1964).
14. Nakagawa, T., and H. Jizomoto, Ibid. 250:594 (1972).
15. Nakagawa, T., and H. Jizomoto, Colloid Polymer Sci. 252:482 (1974).
16. James, A.D., B.H. Robinson and N.C. White, J. Colloid Interf. Sci. 59:328 (1977).
17. Tondre, C., J. Lang and R. Zana, Ibid. 52:372 (1975).
18. Hoffman, H., R. Nagel, G. Platz and W. Ulbricht, Colloid Polymer Sci. 254:812 (1976).

|← —— 130 Å —— →|

(A) at 50 mM

|← 100 Å —→|

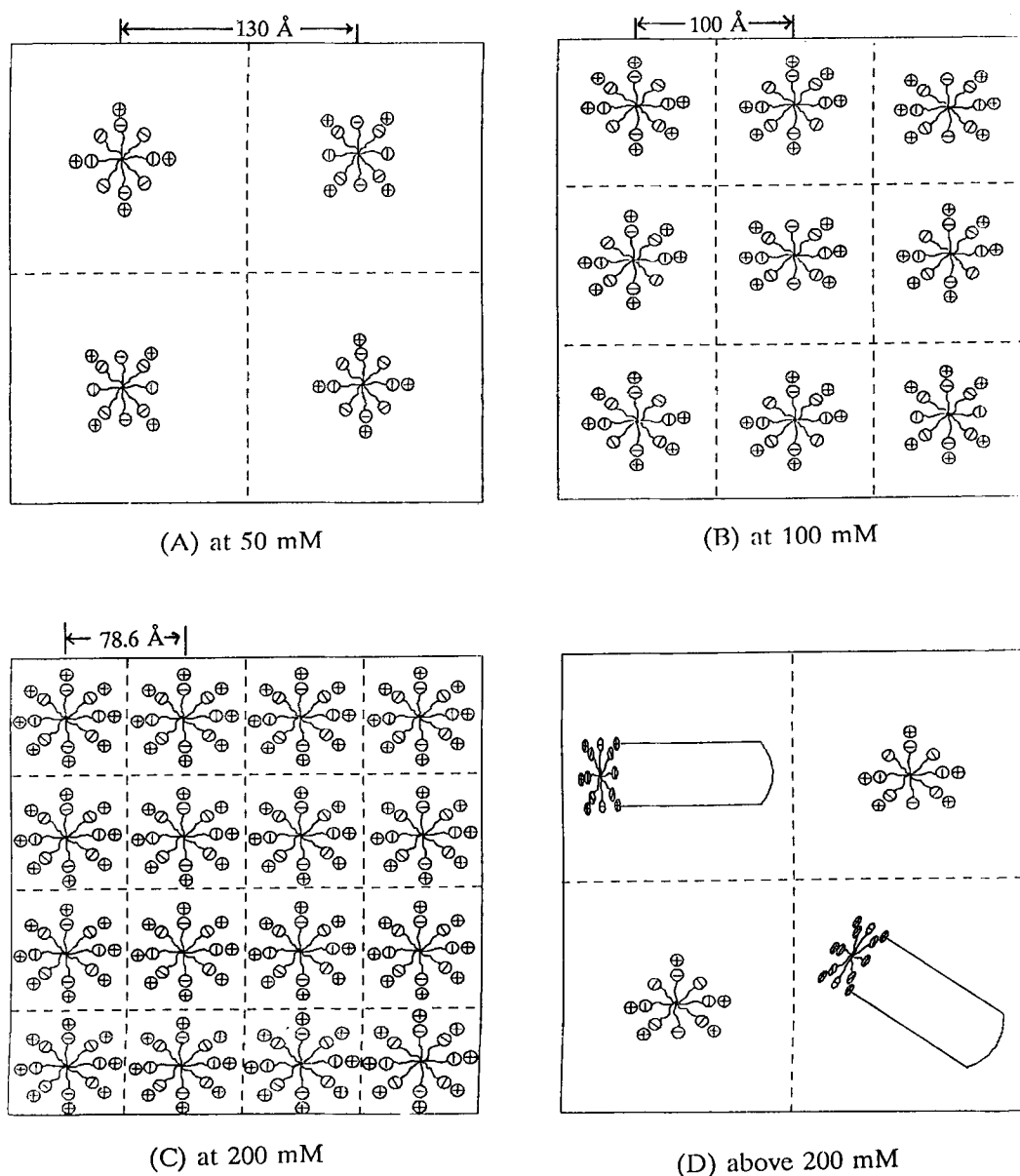(B) at 100 mM

|← 78.6 Å →|

(C) at 200 mM

(D) above 200 mM

FIG. 9. A schematic diagram for micellar packing at various sodium dodecyl sulfate (SDS) concentrations. The cubes and micelles in this figure are not scaled to real dimensions. The diagram simply indicates the decrease in the intermicellar distance with the increase in SDS concentration, which are calculated according to Equation 4.

19. Adair, D.A., V.C. Reinsborough, N. Plavac and J.P. Valleau, *Can. J. Chem. 54*:1162 (1976).
20. Aniansson, E.A.G., and S.N. Wall, *J. Phys. Chem. 78*:1024 (1974).
21. Leung, R., and D.O. Shah, *J. Colloid Interf. Sci. 113*:484 (1986).
22. Muller, N., *Solution Chemistry of Surfactant*, edited by K.L. Mittal, Plenum Press, New York and London, 1979, Vol. 1.
23. Gettings, W.J., J.E. Rassing and Wyn-Jones, *Micellization, Solubilization and Microemulsion*, edited by K.L. Mittal, Plenum Press, New York, 1977, Vol. 1.
24. Oh, S.G., and D.O. Shah, *Langmuir 7*:1316 (1991).
25. Lessner, E., and J. Frahm, *J. Phys. Chem. 86*:3032 (1981).
26. Kahlweit, M., *J. Colloid Interf. Sci. 90*:92 (1982).
27. Inoue, T., Y. Shibuya and R. Shimozawa, *Ibid. 65*:370 (1978).
28. Chan, K.S., Ph.D. thesis, The Molecular Mechanism of Achieving Ultra-Low Interfacial Tension in Surfactant-Oil-Brine-System, University of Florida, 1978.

29. Chan, A.F., D.F. Evans and E.L. Cussler, *Am. Ind. Chem. Eng. 22*:1006 (1976).
30. Lianos, P., and R. Zana, *J. Colloid Interf. Sci. 84*:100 (1981).
31. Hayter, J.B., and J. Penfold, *J. Chem. Soc., Faraday Trans. I 77*:1851 (1981).
32. Ekwall, P., in *Chemistry, Physics and Application of Surface Active Substance*, edited by J.Th.G. Overbeek, Gordon and Breach Science Publisher, New York, 1967.
33. Reiss-Husson, F., and V. Luzzati, *J. Phys. Chem. 68*:3504 (1964).