R&D NOTES

Effect of Micellar Life-Time on the Bubble Dynamics in Sodium Dodecyl Sulfate Solutions

Seong-Geun Oh, Scott Paul Klein, and D. O. Shah
Center for Surface Science & Engineering, Dept. of Chemical Engineering and Anesthesiology,
University of Florida, Gainesville, FL 32611

The dynamic surface tension of surfactant solutions plays a very important role in the dynamic processes, such as surface rheology, bubble size, textile wetting and coating of solids (Rosen, 1989). The dynamic surface tension can be measured by the drop weight (Jho et al., 1983), oscillating jet (Thomas et al., 1975), capillary wave (Austin et al., 1967), and maximum bubble pressure methods (Mysels, 1989). Rosen et al. (1988) showed that the dynamic surface tension of surfactant solutions decreases more rapidly as the concentration of surfactant or the temperature increases. Ward et al. (1989) reported that the dynamic surface tension of sodium dodecyl sulfate (SDS) solution increases as the frequency of bubble formation increases due to the decreased adsorption of monomers from the bulk to the surface below CMC (critical micelle concentration).

During the bubble growth, the surfactant monomers adsorb from the bulk to the expanding surface (Figure 1). The bubble detaches itself from the tip when the buoyancy force exceeds the surface tension force at the tip/bubble interface. The following expression relates the dynamic surface tension (γ) with the radius of capillary (r), radius of bubble (R), and the density difference between the liquid and gas (ρ) (Bikerman, 1973).

$$R^3 \alpha \frac{3r\gamma}{2g\rho} \tag{1}$$

The bubble size decreases as the dynamic surface tension decreases. Also the frequency of bubble increases as the dynamic surface tension decreases if the flow rate of air is kept constant. The various bubble shapes such as spherical, ellipsoidal, spherical cap, or wobbling have been observed (Clift et al., 1981). They showed that the bubble shape depends on the dynamic surface tension of the bubble surface as well as on the viscosity and density of the solution.

The growth of a bubble in the surfactant solution below and above CMC can be viewed as follows. Below CMC, the surfactant monomers diffuse to the bubble surface as the bubble grows. Above CMC, however, the diffusion of monomers is augmented by the spontaneous breakdown of micelles as the monomers are depleted from the vicinity of the micelles. The bubble dynamics is controlled mainly by the diffusion process below CMC (Joos, 1982). In the case of diffusion-controlled process, the adsorption kinetics at the surface of a growing bubble can be described by a modified Ward and Tordai equation (Hunsel et al., 1989):

$$\Gamma(t) = \Gamma_o$$

$$+ 2C_o\left(3\,\frac{Dt}{7\pi}\right)^{\frac{1}{2}} - \left(\frac{D}{\pi}\right)^{1/2} t^{-2/3} \int_0^{3/7\; t^{7/3}} \frac{C_s\left(\frac{7}{3}\,\lambda^{3/7}\right)}{\left(\frac{3}{7}\,t^{7/3} - \lambda\right)^{1/2}}\, d\lambda \tag{2}$$

where $\Gamma(t)$ is the surfactant concentration at the surface at time t, Γ_o is the initial surfactant concentration, C_o is the bulk

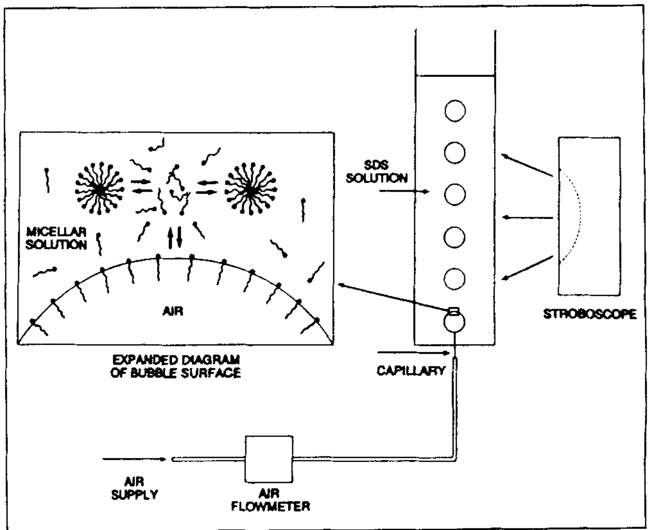

Figure 1. Experimental apparatus for adsorption of surfactant monomers from micellar solution to expanding interface by disintegrating micelles during the bubble formation.

Correspondence concerning this work should be addressed to D. O. Shah.

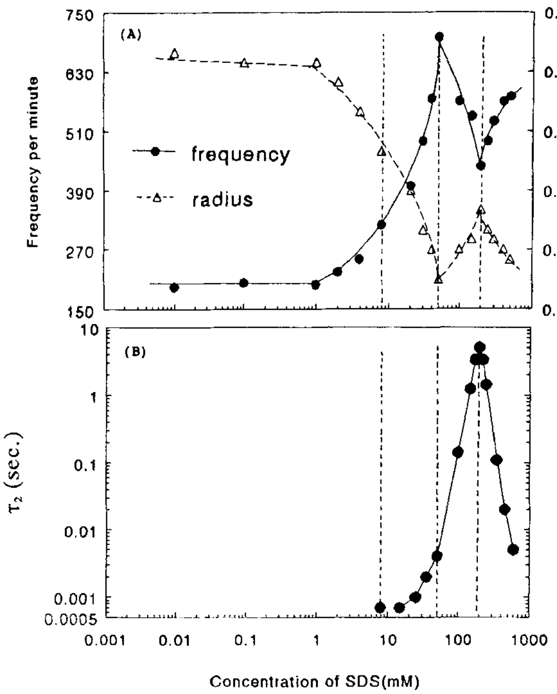

Figure 2. Effect of micellar relaxation time on the frequency of bubble formation and bubble size in SDS solution.

concentration of surfactant, D is the diffusion coefficient, C_s is the subsurface concentration of surfactant, and λ is a dummy variable.

As the concentration of surfactant increases, the micellar stability also increases as indicated by the relaxation time τ_2 up to a specific concentration (for example, 200 mM for the SDS solution) (Shah et al., 1986). Beyond this concentration, τ_2 decreases. We have reported that the life-time of micelles correlates with the foaming ability of surfactant solutions (Shah et al., 1991).

The present study reports on the diffusion effect of monomers on the bubble dynamics in the presence or the absence of micelles in the SDS solutions, as well as the effect of micellar stability on the bubble dynamics.

Experimental Procedure

Sodium dodecyl (C_{12}) sulfate, supplied by Sigma Chemical Company (purity 99%), and double-distilled water were used to make micellar solutions. The micellar life-time was measured by pressure-jump apparatus with conductivity detection from Dia-Log Corporation (Dusseldorf, Germany), as described by Shah et al., (1986).

The frequency of bubble formation was measured in a column with a diameter of 4.7 cm and a liquid height of 11.7 cm at 25°C as shown in Figure 1. The air flow rate was controlled by a flowmeter (Matheson Inc., tube size R-2-15-AAA) at 230 mL/min. The diameter of capillary was 1 mm. The stroboscope supplied by Cenco Company was used to measure the frequency of bubble formation. When the frequency of the blinking light in the stroboscope is the same as the frequency of bubble formation in column, bubbles appear to be stationary. But, bubbles may appear to be stationary at several frequencies of stroboscopic light. The frequency of stroboscopic light was taken as the bubble frequency when the number of bubbles in the column with and without stroboscopic light is the same.

Results and Discussions

Figure 2A shows the effect of SDS concentration on the bubble radius and frequency. The CMC of SDS is reported to be 8 mM. Thus, the bubble size was fairly large ($\approx$ 0.64 cm of radius) below CMC. However, as the SDS concentration approaches the CMC, the bubble size decreases and reaches a minimum radius at 50 mM. Then the bubble radius increases up to 200 mM and subsequently decreases. Figure 2B shows the relaxation time τ_2 of the micelles in this concentration range. It is interesting that the relaxation time τ_2 also exhibits a maximum at 200 mM of SDS concentration. There is no significant change in τ_2 in the range 8 to 50 mM of SDS (Inoue et al., 1978). The bubble dynamics and relaxation time τ_2 as a function of SDS concentration have been interpreted as follows.

From 10^{-3} mM to 1 mM SDS concentration, the bubble size is large because of high surface tension at the bubble surface. At the SDS concentration of 1 to 50 mM, the bubble size decreases because of the additional supply of SDS monomers due to spontaneous breakdown of micelles as the monomers diffuse to the bubble surface (Figure 3A). As the concentration of micelles increases, the flux of monomers to the bubble surface is also expected to increase (Figure 3B). It should be noted that the micellar stability or τ_2 in this range (8–50 mM) remains relatively constant (Figure 2B). However, at the SDS concentration of 50 to 200 mM, τ_2 increases strikingly due to the increase of micellar stability. Concomitantly, the bubble size also increases because relatively stable micelles do not augment the flux of monomers to the bubble surface (Figure 3C). Above 200 mM of the SDS concentration, both τ_2 and the bubble size decrease. This can be explained as follows.

Reiss-Husson et al. (1964) found the structural change of SDS micelles from spherical to cylindrical shape using X-ray

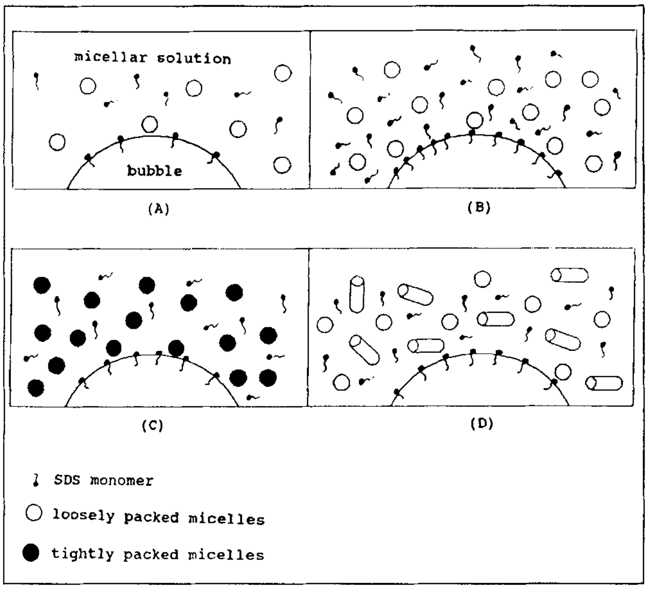

Figure 3. Monomer and micellar concentration near the bubble surface: (A) at 8 mM, (B) at 50 mM, (C) at 200 mM, and (D) at 400 mM.

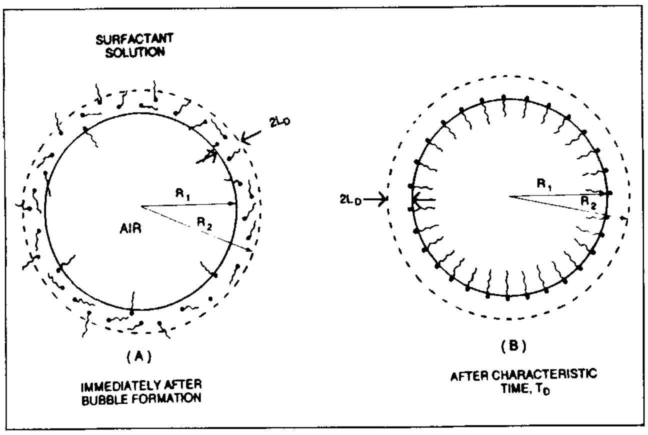

Figure 4. Characteristic diffusion length (L_D) around the bubble to saturate the bubble of 4.5-mm radius at CMC.

diffraction at 250 mM at 27°C. Our studies were carried out at 25°C, and hence this transition may occur at 200 mM. Moreover, Ekwall (1967) has shown that the transition from spherical to cylindrical micelles occurs in a wide concentration range as compared to the CMC. As this transition proceeds, the concentration of spherical micelles decreases, and hence intermicellar distance increases. This will lead to the decrease in the micellar stability and hence in the relaxation time τ_2. The cylindrical micelles are stabler than the spherical micelles. Thus, the decrease in τ_2 above 200 mM can be accounted for by the loosely packed spherical micelles (Figure 3D).

Since the flow rate of air was maintained constant, larger bubble size corresponds to a less frequency of bubble generation. Thus, our frequency of bubble is the reverse of the bubble size as a function of the SDS concentration (Figure 2A).

It is desirable to estimate the diffusion time of surfactant monomers from the bulk to the bubble surface during the bubble generation process as compared to the life-time of micelles.

Diffusion Length (L_D) and Characteristic Diffusion Time (T_D)

As shown in Figure 4, surfactant monomers near the bubble surface diffuse from the bulk to the surface. The number of monomers (N_1) needed to saturate the bubble surface of radius R_1 can be calculated by the following equation:

$$N_1=\frac{4\pi R_1^2}{A} \tag{3}$$

where A is the area/molecule of surfactant at the air/water interface. The number of molecules per mL of solution (N_2) at CMC (in unit of moles/liter) is CMC × (Avogadro number)/1,000. The volume around the bubble that contains N_1 monomers is given by N_1/N_2 mL. Therefore, the shell of radius R_2 (containing N_1 monomers) can be calculated from the following equation:

$$\frac{N_1}{N_2}=\frac{4}{3}\pi(R_2^3-R_1^3) \tag{4}$$

The only unknown quantity R_2 can be calculated by using the value of N_1, N_2, and R_1. For the bubble of radius of 0.45 cm (R_1) in the SDS solution, 4.8×10^{14} monomers (N_1) are needed to saturate the surface, because the surface area of the bubble is 2.54 cm^2 and the area/molecule at the air/water interface is 53 Å^2 (Dahanayake et al., 1986) using Eq. 3. The number of monomers per mL (N_2) at the CMC (8 mM) is 48.18×10^{17}. The R_2 value calculated by Eq. 4 is $0.45 + 4.0 \times 10^{-5}$ cm. The characteristic diffusion length (L_D) is $(R_2-R_1)/2$. Therefore, the average diffusion path length (L_D) is 2.0×10^{-5} cm. The diffusion time (T_D) calculated using the expression (Overbeek, 1977) $T_D = (L_D)^2/2D$, is 3.3×10^{-5}. This is the diffusion time when solution is assumed to be stationary. In fact, the diffusion time in real situation is much shorter than this value due to the convective motion of solution induced by bubble motion. The diffusion time even in the stationary solution (3.3×10^{-5} s) is negligible compared to the life-time of SDS micelles (0.6-65 s) in the experimental concentration range. However, the micellar kinetics can augment significantly the diffusion of monomers in determining the dynamic surface tension and the bubble dynamics in SDS solutions.

In Summary

The frequency of bubble formation in the SDS solution does not change below 1 mM; it increases from 1 to 50 mM because of the increase in the number of micelles of the same life-time, and then decreases. A minimum is reached at 200 mM where most stable micelles are formed. The frequency increases with concentration after 200 mM because of the structural transition from spherical to cylindrical micelles.

Acknowledgment

The authors are grateful to the Alcoa Foundation and the National Science Foundation (Grant NSF-CPE 8005851) for their support of this research.

Notation

A = area/molecule of surfactant at air/water surface
D = diffusion coefficient of SDS monomer, 6×10^{-6} cm^2/s
g = acceleration due to gravity
r = radius of capillary, cm
R = radius of bubble, cm
L_D = characteristic diffusion length, cm
T_D = characteristic diffusion time, s

Greek letters

Γ = concentration of surfactant at surface
γ = surface tension
λ = dummy variable
ρ = density difference between liquid and gas

Literature Cited

Austin, M., B. B. Bright, and E. A. Simpson, "The Measurement of the Dynamic Surface Tension of Manoxol OT Solutions for Freshly Formed Surfaces," *J. Colloid Interf. Sci.*, **23**, 108 (1967).

Bikerman, J. J., *Foams*, Springer-Verlag, New York (1973).

Clift, R., J. R. Grace, and M. E. Weber, *Bubbles, Drops and Particles*, Academic Press, New York (1978).

Dahanayake, M., A. W. Cohen, and M. J. Rosen, "Relationship of Structure to Properties of Surfactants," *J. Phys. Chem.*, **90**, 2413 (1986).

Ekwall, P., "Some Properties of Association Colloid Solutions above CMC," *Chemistry, Physics and Application of Surface Active Substances*, J. Th. G. Overbeek, ed., Gordon and Breach Science Publisher, New York (1967).

Hunsel, J. V., and P. Joos, "Study of the Dynamic Interfacial Tension at the Oil/Water Interface," *Colloid & Polym. Sci.*, **267**, 1026 (1989).

Inoue, T., Y. Shibuya, and R. Shimozawa, "Chemical Relaxation Studies in Micellar Solutions of Sodium Alkyl Sulfates," *J. Colloid Interf. Sci.*, **65**, 370 (1978).

Jho, C., and R. Burke, "Drop Weight Technique for the Measurement of Dynamic Surface Tension," *J. Colloid Interf. Sci.*, **95**, 61 (1983).

Joos, R. E., "Rate of Demicellization from the Dynamic Surface Tensions of Micellar Solutions," *J. Phys. Chem.*, **86**, 3471 (1982).

Mysels, K. J., "Improvement in the Maximum-Bubble-Pressure Method of Measuring Surface Tension," *Langmuir*, **2**, 428 (1986).

Overbeek, J. Th. G., "Recent Development in the Understanding of Colloid Stability," *J. Colloid Interf. Sci.*, **58**, 408 (1977).

Reiss-Husson, F., and V. Luzzati, "The Structure of the Micellar Solutions of Some Amphiphilic Compounds in Pure Water as Determined by Absolute Small-Angle X-Ray Scattering Techniques," *J. Phys. Chem.*, **68**, 3504 (1964).

Rosen, M. J,. *Surfactants and Interfacial Phenomena*, 2nd ed., Wiley, New York (1989).

Rosen, M. J., and X. Y. Hua, "Dynamic Surface Tension of Aqueous Surfactant Solutions," *J. Colloid Interf. Sci.*, **124**, 652 (1988).

Shah, D. O., and R. Leung, "Dynamic Properties of Micellar Solutions," *J. Colloid Interf. Sci.*, **113**, 484 (1986).

Shah, D. O., and S. G. Oh, "Relationship between Micellar Lifetime and Foamability of Sodium Dodecyl Sulfate and Sodium Dodecyl Sulfate/1-Hexanol Mixtures," *Langmuir*, **7**, 1316 (1991).

Thomas, W. D. E., and D. J. Hall, "Solution/Air Interface, II. Adsorption of Surfactants in Dilute Aqueous Solutions. Anomalous Oscillating Jet Phenomena," *J. Colloid Interf. Sci.*, **51**, 328 (1975).

Ward, D. R., and P. R. Garrett, "A Reexamination of the Measurement of Dynamic Surface Tensions Using the Maximum Bubble Pressure Method," *J. Colloid Interf. Sci.*, **132**, 475 (1989).

Manuscript received Aug. 23, 1991, and revision received Nov. 4, 1991.