1880 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (6), 1880—1882 (1978) [Vol. 51, No. 6

Study on Solubilization by Electrophoresis and Diffusion

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(Received August 1, 1977)

The difference in solubilization phenomena exhibited when polar and nonpolar oily materials are solubilized by Sodium dodecyl sulfate (SDS) has been investigated by measuring the electrophoresis, the diffusion, and the viscosity. Based on the assumption that the micelle is spherical the effective specific volume, the effective radius, the ζ-potential and the number of effective charges have been calculated. At the limit of solubilization all four quantities were larger for octanoic acid than for octane. The electrophoretic mobility of the micelle, $|U_M|$, increased when octanoic acid was solubilized, in contrast to a decrease observed in the solubilization of octane.

In the literature, we find a number of reports dealing with the electrophoresis, diffusion and light scattering of micelles composed of pure surfactant including SDS,¹⁾ mixed ionic-nonionic surfactants²⁾ and polyether sulfate.³⁾ However, only a few are concerned with solubilizate-containing micelles. Among the ways of incorporating the solubilizate into the micelles are (a) adsorption on the surface of the micelles; (b) deep penetration in the palisade layer and (c) dissolution in the hydrocarbon core.

In this study, the mechanism of solubilization has been investigated. SDS micelles containing octanoic acid, a polar oily material, or octane, a nonpolar oily material, have been examined in terms of electrophoretic properties. The results indicate that octanoic acid is solubilized by deep penetration into the palisade layer whereas octane is solubilized by dissolution in the hydrocarbon core.

Experimental

Materials. Sodium dodecyl sulfate (SDS) of reagent grade was extracted with ether and recrystallized from ethanol. The octanoic acid and octane were supplied by Wako Pure Chemical Industries, LTD and were more then 99% pure.

Apparatus and Conditions. 0.3 and 1.5% SDS solutions, of above critical micelle concentration (CMC), were prepared with 0.2 mol dm^{-3} NaCl solutions. The procedure for the determination of the limits of solubilization was as follows. Into several 100-cm^3 glass-stoppered Erlenmeyer flasks, 50-cm^3 portions of 0.3 or 1.5% SDS solutoin were placed; varying amounts of oily materials were added to them, and the mixtures were stirred for 12 h in a thermostat at 25 °C, followed by settling for 36 h until equilibrium was established After equilibrium had been established, the turbidity of the solution was measured with an Electro photocolorimeter of Hirama 2B type at wave length 655 nm, using a cell of 10.0 mm light path. The limit of solubilization was determined from the break point of the turbidity *vs.* solubilizate concentration curve. An amount of solubilizate, corresponding to 10, 30, 50, 80, 90, or 100% of the above-determined limit of solubilization in 0.3 and 1.5% SDS solutions. Two series of solutions with different degrees (10—100%) of solubilization were prepared by dissolving. The electrophoresis and diffusion measurements were carried out with a Hitachi, model HTB-2A Tiselius apparatus and a Tchukasa, Neurath cell immersed in a thermostat at 25 °C. A pair of 0.3 and 1.5% solutions with the same degree of solubilization were used as upper and lower layers, thus minimizing the boundary disturbance often encountered in electrophoresis and diffusion.

The relative viscosities of the solutions including solubilized oily substances were measured at 25 °C with an Ubbelohde viscometer with appropriate auxiliary equipment. The flow time was measured with a stopwatch of 0.1-s precision; the over-all fluctuations were within ±0.1-s. The specific gravity gravity was determined using a pycnometer of 25-cm^3 capacity.

Results and Discussion

Relative Viscosity and Effective Specific Volume of the Micelle. Figure 1 shows the relative viscosity, η_r, of the solutions which were prepared by solubilizing octanoic acid using given concentrations of SDS.

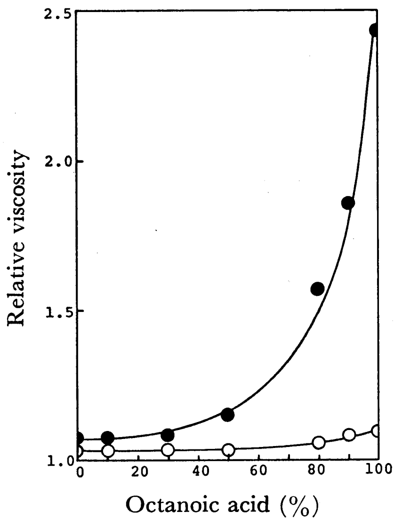

Fig. 1. Relative viscosity, η_r, of the solutions which were prepared by solubilizing octanoic acid using SDS of given concentrations.
○: 0.3% SDS, ●: 1.5% SDS.

From Guth and Simha's equation,⁴⁻⁷⁾ which is a form of Einstein's equation extended to more concentrated solutions,

$$\eta_r = 1 + 2.5\phi + 14.1\phi^2, \qquad (1)$$

the volume fraction occupied by the spherical particles, ϕ, may be calculated from the relative viscosity, η_r. The effective specific volume of 1 g of SDS containing oily materials, V, is given by⁵,⁸⁾

$$V = \phi/C, \qquad (2)$$

where C is the concentration of the solution in g/cm^3.

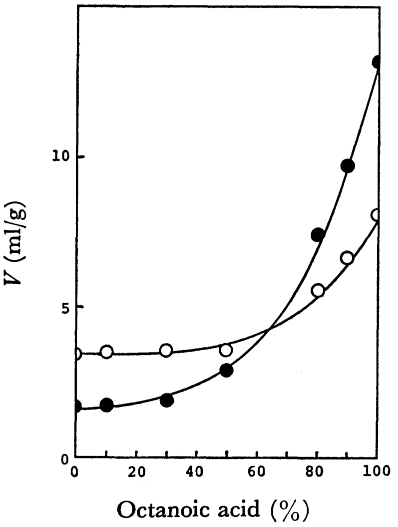

Fig. 2. Effective specific volume, V, plotted against the amount of octanoic acid.
○: 0.3% SDS, ●: 1.5% SDS.

Figure 2 shows the effective specific volume, V, plotted against the amount of octanoic acid. Nakagawa[9] suggested that the effective specific volume in various concentrations of the surfactant (0.3—3.0%) was approximately constant and did not tend to decrease or increase with increasing concentration of surfactant. For a solution of surfactant alone, it can be said that above the CMC the number of micelles increases with an increase in the amount of surfactant whilst the size of the micelle remains almost unchanged (aggregates of 50—100).[10] From Fig. 2, it is evident that the effective specific volume of 0.3 and 1.5% SDS solutions containing octanoic acid increases with an increase in the amount of octanoic acid.

TABLE 1. MICELLAR PARAMETERS FOR OCTANOIC ACID AND OCTANE

Octanoic acid (%)	$D\times10^7$ cm²/s	$a\times10^8$ cm	$-U_M\times10^4$ cm²/V s	$-\zeta$ mV	Q
0	9.33	25.2	2.56	45.3	23
30	8.76	26.9	3.01	52.9	30
50	6.22	37.9	3.06	52.0	54
80	3.88	60.7	3.15	51.0	126
90	2.78	84.7	3.22	50.3	233
100	2.15	109.5	3.26	49.7	376
Octane 100 %	5.59	42.1	1.49	25.1	32

Diffusion Coefficient and Effective Radius of the Solubilizate-containing Micelle. The diffusion coefficient of the SDS micelle containing solubilized octanoic acid was measured in 0.2 mol dm^{-3} NaCl. The diffusion of hydrophilic colloidal electrolyte usually becomes rapid, since the charged colloid is influenced by ionic atmosphere. This effect may be suppressed by keeping the concentration of the salt above 0.2 mol dm^{-3}.[10] Table 1 demonstrates the change in the diffusion coefficient and the effective radius of the micelle with an increase in the amounts of octanoic acid. This indicates that the diffusion coefficient of the micelle decreases with an increase in the amount of solubilized octanoic acid. Consequently, the effective radius of the micelle, a, increases as shown by the Stokes equation[11]

$$a = kT/6\pi\eta D, \tag{3}$$

where k is Boltzmann constant and η is the viscosity of the medium. The increase in the effective radius of the micelle is considered to be due to the deep penetration of octanoic acid into the micelle. This view is concordant with the results obtained for the relative viscosity and the effective specific volume measurements of the micelle. At the limit of solubilization of oily material, the diffusion coefficient of the micelle containing octanoic acid is smaller than that of octane-containing one. The effective radius of the micelle containing octanoic acid is larger than that of the micelle containing octane.

Electrophoresis. In the electrophoresis of the above mentioned surfactant solution, there exist Na^+, Cl^- and micelle, M^-, in both the upper and lower layers. Thus two boundaries appear when the current is applied.[12] (Since the concentrations of surfactant monomer and solubilizate are negligibly small compared with the concentration of the other ions, they may be neglected). One of the boundaries is an unmoving one named ζ and ε peak, which if the concentrations of NaCl and surfactant are correct do not appear.[13] With 0.2 mol dm^{-3} NaCl, the peak of the electrophoretic diagram was only one in both upper and lower sides. From the measurements at 25 °C of the velocities of the upper and lower boundaries, V_a and V_d, the electrophoretic mobility of the micelle, U_M, was calculated by the following equation:[2,12]

$$U_M = V_d\tau^\beta - (V_a\tau^\alpha - V_d\tau^\beta)/(T_M^\beta/T_M^\alpha) - 1, \tag{4}$$

where T_M is the transference number of the micelle, τ is the specific conductance of the solution, and the superscripts α and β refer to the upper and lower layers respectively. T_M^β/T_M^α in Eq. 4 is expressed as

$$T_M^\beta/T_M^\alpha = (C_M^\beta/\tau^\beta)/(C_M^\alpha/\tau^\alpha), \tag{5}$$

where C_M^α and C_M^β, which are the concentrations of M^- ions in α and β phases respectively, are given by

$$\begin{aligned} C_M^\alpha &= (C-\mathrm{CMC})_\alpha, \\ C_M^\beta &= (C-\mathrm{CMC})_\beta, \end{aligned} \tag{6}$$

where C is the concentration of the surfactant. Table 1 gives the data of the electrophoretic mobility of the micelle with corresponding amount of solubilized octanoic acid. The absolute value of the electrophoretic mobility of the micelle containing solubilized octanoic acid, $|U_M|$, increased a little with an increase in the amount of solubilized octanoic acid. The ζ-potential was calculated from U_M by the Henry equation[14]

$$\zeta = [6\pi\eta/\varepsilon f(\kappa a)] \times U_M, \tag{7}$$

where $f(\kappa a)$ is the Henry function; κ, the Debye-Hückel parameter; a, the radius of the micelle, and η and ε, the viscosity and dielectric constant of the medium respectively. Table 1 demonstrates that the ζ-potential of the micelle containing octanoic acid remained constant at about −50 mV, regardless of the amount of octanoic acid added. This may be responsible for the small changes in U_M. At the limit of solubilization of oily material, the ζ-potential for octanoic acid is larger than that for octane. The value of U_M for octanoic acid, 3.26, is larger than that of the solubilizate-free micelle, 2.56, as compared to octane, 1.49, which is smaller. The effective micelle charge, Q, may be estimated by the following equation:[14]

$$Q = (1/e) \times [(1+\kappa a+\kappa r_i)/(1+\kappa r_i)] \times \varepsilon a \varphi, \qquad (8)$$

where e is the elementary charge and r_i is the radius of the counter ion. (In the present study we have assumed 0.22 nm as its radius).[15] At the limit of solubilization of oily material, the effective charge of the octane-containing micelle is somewhat larger, and the octanoic acid-containing micelle much larger than that of the solubilizate-free micelle.

TABLE 2. DEGREE OF SOLUBILIZATION AND RELATIVE VISCOSITY FOR OCTANOIC ACID AND OCTANE

Concentration of SDS	Degree of solubilization (mol/l)		Relative viscosity	
	Octanoic acid	Octane	Octanoic acid	Octane
0.3%	0.53×10^{-2}	0.70×10^{-2}	1.09	1.03
1.5%	2.31×10^{-2}	2.80×10^{-2}	2.42	1.08

Table 2 demonstrates the degree of solubilization and relative viscosity of the solutions, prepared by solubilizing octanoic acid and octane up to the limit of solubilization. As is evident from Table 2, although the degree of solubilization of octanoic acid is smaller than that of octane, the relative viscosity of the solution containing octanoic acid is larger than that of the solution containing octane. This may be explained in terms that the effective specific volume is larger when the micelle is saturated with octanoic acid than when saturated with octane since octanoic acid carries a considerable amount of water of hydration, V (10.4), compared with octane, V (1.01). It is the carboxylic group that undergoes hydration. Since it is difficult energetically for this hydrated carboxylic acid to dissolve into the hydrocarbon core of the micelle, the carboxylic group of octanoic acid remains on the surface of the micelle, allowing the alkyl group of octanoic acid to penetrate into the palisade layer. Since octane does not undergo hydration, the whole molecule can dissolve into the hydrocarbon core of the micelle.

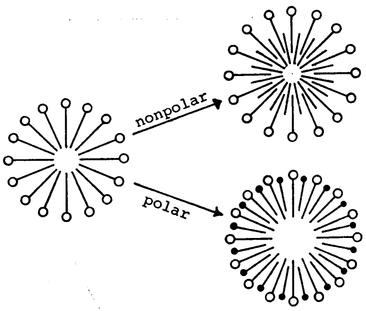

Fig. 3. Solubilization models of polar and nonpolar compounds.
○—— =Surfactant molecule, ●—— =polar molecule, —— =nonpolar molecule.

Thus, the solubilization model[16] shown in Fig. 3, which has been generally accepted, is consistent with the above results.

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