March, 1980] © 1980 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **53**, 611—615 (1980) 611

# Electrophoresis and Diffusion Studies of the Solubilization of Polar and Nonpolar Oily Compounds with Sodium Dodecyl Sulfate. II

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The solubilization of polar and nonpolar oily materials into an aqueous sodium dodecyl sulfate (SDS) solution with and without sodium chloride was studied. Normal paraffins and their derivatives, with carbon numbers of $C_7$, $C_8$, and $C_{10}$, were used as solubilizates, the extents of solubilization, the relative viscosities of the solutions, the diffusion coefficients, and the electrophoretic mobilities of the micelles in the solutions were observed, and the effective specific volumes, the effective radii, the $\zeta$-potentials, and the effective charge of the micelles were derived assuming that the micelles were spherical. The micelles of SDS showed increasing mobilities when they incorporated octanoic acid, 1-octanol, and decanoic acid, while the mobilities decreased when they incorporated heptane, octane and 1-decanol. On the basis of these results, we discussed the mechanism of the solubilization of polar and nonpolar oily compounds with SDS.

The behavior of the micelles of surfactants have been studied extensively by many investigators for SDS,[1] mixed ionic-nonionic surfactants,[2] polyether sulfate, and other surface-active agents,[3] but only a few investigations have been devoted to the micelles incorporating solubilizates in them.

In a previous paper[4] we observed the electrophoretic mobilities of micelles of SDS, $|U_M|$ in aqueous solutions, and showed that the $|U_M|$ increased with an increase in the concentration of octanoic acid and decreased with that of octane. We further studied the behavior of the micelles of SDS including polar or nonpolar oily materials in an aqueous medium in the presence or absence of electrolytes in order to elucidate the mechanisms of the solubilization of the oily materials. We suggest that strongly polar compounds are adsorbed on the outer surface, weakly polar compounds penetrate deeply into the palisade layers, and nonpolar compounds are occluded in the hydrocarbon cores of the micelles.

## Experimental

*Materials.* *Surface-active Agent*: Sodium dodecyl sulfate (SDS) of a reagent grade was purchased and was purified by extraction with petroleum ether, followed by recrystallization from ethanol.

*Solubilizates (Oily Materials)*: Octanoic acid, decanoic acid, 1-octanol, and 1-decanol were used as polar oily materials, and heptane and octane as nonpolar ones, all obtained in a purity of better than 99% from Wako Pure Chemical Industries.

*Apparatus and Conditions.* Sodium dodecyl sulfate was dissolved into a 0.2 M NaCl solution or into water at the concentrations of 0.3 and 1.5% (wt), which were higher than the critical micelle concentration (CMC) of SDS. The solubilization limits of the oily materials into the SDS solutions were determined as follows. Into 100-ml glass-stoppered Erlenmeyer flasks containing 50 ml of SDS solutions (0.3% and 1.5%), various amounts of one of the oily materials were added; the mixtures were stirred for 12 h at 25 °C and then left standing for 24 h until the solubilization equilibria were established. Then, the turbidities of the mixtures were measured with a spectrophotometer of the Hirama Type-2B at the wavelength of 655 nm. The turbidities of the solutions were plotted against the concentrations of the solubilizates, and the solubilization limits were determined from the break points of the relating curves. After that, the solubilizates were added until the solubilizing limit was reached and then submitted to dialysis by the use of cellulose tubing for 36 h at 25 °C.

The electrophoretic mobility and the diffusion coeffecient for the SDS solutions saturated with the oily materials were determined at 25 °C by a Schlieren method using a Hitachi Model HTB-2A Tiselius apparatus in combination with a Tsukasa Neurath cell, with the usual precautions.[2,3] The concentrations of both the upper and lower layers were chosen to be higher than the CMC in order to eliminate the contribution of the monomers to the diffusion coefficient; the initial concentration difference between layers was 1.2 g/dl. Then, a pair of 0.3 and 1.5% SDS solutions were set as the upper and the lower layers in the cell to minimize the boundary disturbance often encountered in electrophoresis and diffusion measurements. The electrophoretic measurements were performed under the following conditions: voltage the 50 V; current, 10 mA; migration time, 30—50 min. The calculation of diffusion coefficient was based on the maximum ordinate-area method.

The relative viscosities of the solutions containing the oily materials were measured at 25 °C with an Ubbelohde viscometer.

The specific gravity was determined using a pycnometer with a capacity of about 25 ml.

## Results and Discussion

*The Solubilized Amounts and the Susceptibilities to Solubilization.* Figure 1 shows the solubilized amounts of the oily materials in the aqueous solutions of SDS with or without 0.2 M NaCl. The solubilized amounts widely changed according to the kinds of solubilizates in the aqueous solutions without NaCl, but it remained around a constant value in the presence of NaCl. The results also show that octanoic acid, 1-octanol, and decanoic acid are solubilized to greater extents, whereas 1-decanol, octane, and heptane are present to smaller extents in water than in 0.2 M NaCl solution. From the results presented in Fig. 1, the susceptibilities of the substances to the solubilization are determined as the moles solubilized by the mole of SDS in the solutions. The susceptibilities depend on the structures of the compounds much as they depend on the solubilized amounts. Klevens[5] found that the solubilized amounts of nonpolar compounds in aqueous surfactant solutions increased when electrolytes were added, and that some polar compounds

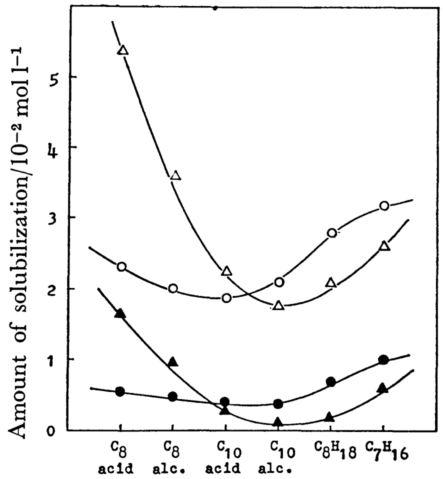

Fig. 1. Amount of solubilization in 0.2 M NaCl and pure water at 25 °C.
○: SDS 1.5% in 0.2 M NaCl, ●: SDS 0.3% in 0.2 M NaCl, △: SDS 1.5% in pure water, ▲: SDS 0.3% in pure water.

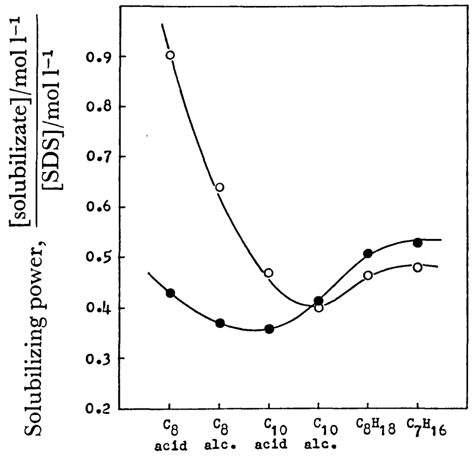

Fig. 2. The susceptibility to the solubilization of the solubilizates in 0.2 M NaCl and pure water at 25 °C.
○: In pure water, ●: 0.2 M NaCl.

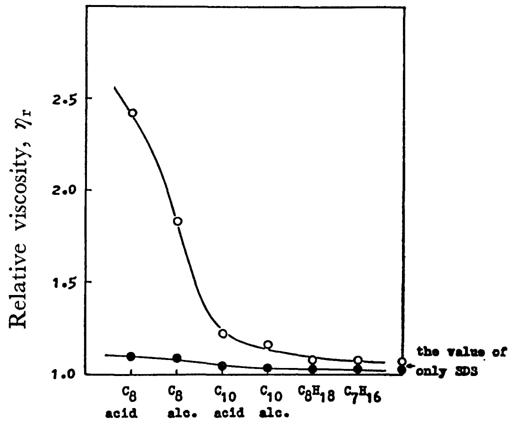

Fig. 3. Relative viscosty of the solubilized solution in 0.2 M NaCl at 25 °C.
○: SDS 1.5%, ●: SDS 0.3%.

with large alkyl groups and only weakly polar groups, such as 1-decanol, showed a solubilization similar to these of nonpolar compounds.

The plots in Figs. 1 and 2 indicate that carboxyl is a stronger solubilizing group than hydroxyl for the compounds of the same carbon number, probably because of its stronger depolarizing power. Furthermore, the electrolyte in the solution has effects not only on the solubilized amount, but also on the susceptibility to the solubilization of the materials in the SDS solution.

*Relative Viscosities and Effective Specific Volume of the Micelles.* The relative viscosities, $\eta_r$, of the solutions saturated with the solubilizates in 0.3 or 1.5% SDS solutions containing 0.2 M NaCl are plotted in Fig. 3. The relative viscosities of 0.3 and 1.5% SDS solutions both decreased in the following order of the dissolved compounds; octanoic acid>1-octanol>decanoic acid>1-decanol>octane>heptane. The viscosities changed over a wider range in the 1.5% SDS solution than in the 0.3% solution. The relative viscosities of the solutions showed a larger change than the solubilized amounts of the components in the SDS solutions containing NaCl; the change seems to be related to the structures of the solubilizates. The solutions containing octanoic acid showed the largest viscosity. This large viscosity due to octanoic acid may be attributed to the adsorption of octanoic acid on the surface of the micelles of SDS, which would cause the increase in the mutual interaction of the micelles. On the other hand, nonpolar compounds are deeply occluded into the palisade layers and are occluded in the hydrocarbon cores of the micelles; consequently, the mutual interaction of the micelles is not influenced, and the relative viscosities of the solutions do not change because of the dissolution of the solubilizates.

Based on the Guth and Simha equation (Eq. 1),[6–9] which is an extension of Einstein's equation to the higher concentration range of the micelles in aqueous solution,

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

the volume fraction of the spherical particles, $\phi$, can be calculated from the relative viscosity, $\eta_r$. The effective specific volume, $V$, of SDS containing an oily material is given by[7,10]

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

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

Figure 4 shows the effective specific volume, $V$, of the micelles of SDS containing solubilizates in 0.2 M NaCl solutions.

Nakagawa has suggested that the effective specific volume of micelles in various concentration ranges of the surfactant from 0.3 to 3.0% was nearly constant.[11,12] Our experimental results agreed approximately with this suggestion. For a solution of the surfactant alone, it can be said that, above the CMC, the number of micelles increases with an increase in the amount of the surfactant, whilst the size of the micelle remains almost unchanged (aggregates of 50—100).[13]

As is evident in Fig. 4, the effective specific volumes of the micelles containing octanoic acid and 1-octanol

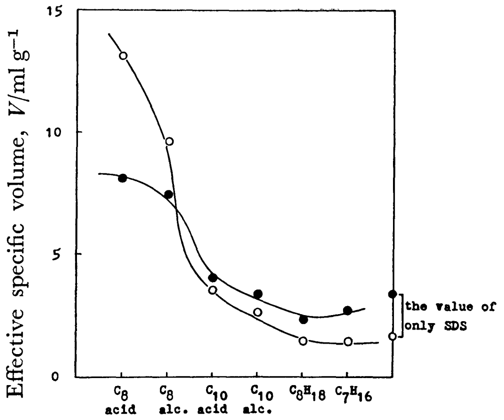

Fig. 4. Effective specific volume of the solubilized micelle in 0.2 M NaCl at 25 °C.
○: SDS 1.5%, ●: SDS 0.3%.

were larger than those of the micelles containing less polar or nonpolar compounds. Besides, the effective specific volumes of SDS micelles containing decanoic acid, 1-decanol, octane, and heptane were almost the same as that of SDS-single-component-micelles. The increase in the effective specific volume of the micelles upon the addition of polar solubilizates may be attributed to the adsorption of the solubilizate molecules on the surface of micelles, as if needles with bulky heads are inserted into a spherical needle pad.

*Diffusion Coefficients and Effective Radii of the Micelles Containing Solubilizates.* The diffusion coefficients, $D$, were calculated by means of the following equation, based on the maximum ordinate-area method,[14)]

$$D = \frac{A^2}{4\pi t(H_m)^2}\cdot\frac{1}{G^2}, \tag{3}$$

where $A$ is the area under the concentration gradient curve, $H_m$ is maximum ordinate, $t$ is the migration time, and $G$ is the optical magnification (here $G=1$)

Figure 5 shows the diffusion coefficients, $D$, and effective radii of micelles, $a$, in 0.2 M NaCl solutions. Since a charged colloid interacts with an ionic medium, the diffusion of a hydrophilic-charged colloid is usually retardated in the presence of electrolytes in solutions, but this effect is suppressed in the concentration range of electrolytes higher than 0.2 M.[3,13)]

The effective radii of micelles, a, can be calculated by means of the Stokes-Einstein's equation:[15,16)]

$$a = kT/6\pi\eta D, \tag{4}$$

where $k$ is the Boltzmann constant and $\eta$ is the viscosity of the medium. The diffusion coefficient of the micelles of SDS containing solubilized octanoic acid was the smallest, while that of SDS containing heptane was the largest, though the incorporated amounts in the micelles were almost the same for the two solubilizates, as has been mentioned above. On the other hand, the effective radii of the micelles of SDS containing octanoic acid were the largest, and those containing heptane was the smallest. These results are in accordance with the results of the relative viscosities and the effective specific volumes of micelles of the systems.

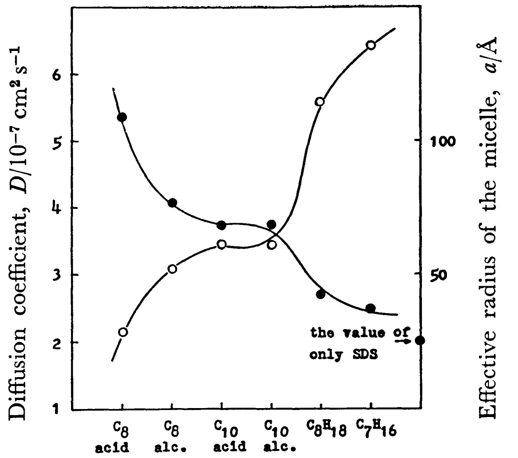

Fig. 5. Diffusion coefficient and effective radius of the solubilized micelle in 0.2 M NaCl at 25 °C.
○: Diffusion coefficient, ●: effective radius of the micelle.

*Electrophoresis.* From the measurements of the migration velocities of micelles from the upper layer to the lower layer ($V_a$) or in the reverse direction ($V_d$) in a cell of the Tiselius apparatus, the electrophoretic mobility of micelles, $|U_M|$, was calculated by means of following equation:[2,17–19)]

$$U_M = V_d\tau^\beta - \frac{V_a\tau^\alpha - V_d\tau^\beta}{(T_M{}^\beta/T_M{}^\alpha)-1}, \tag{5}$$

where $T_M$ is the transference number of micelles, and $\tau$ is the specific conductance of the solution, while the superscripts $\alpha$ and $\beta$ refer to the upper and lower layers respectively.

$T_M{}^\beta/T_M{}^\alpha$ in Eq. 5 is expressed as

$$T_M{}^\beta/T_M{}^\alpha = \frac{C_M{}^\beta/\tau^\beta}{C_M{}^\alpha/\tau^\alpha}, \tag{6}$$

where $C_M{}^\alpha$ and $C_M{}^\beta$, which are the concentrations of the $M^-$ ions in the $\alpha$ and $\beta$ phases respectively, are given by

$$C_M{}^\alpha/C_M{}^\beta = \frac{(C-\mathrm{CMC})^\alpha}{(C-\mathrm{CMC})^\beta}, \tag{7}$$

where $C$ is the concentration of the surfactant.

Figure 6 shows the electrophoretic mobilities of the micelles containing various solubilizates. The absolute value of the electrophoretic mobilities of the micelles solubilizing octanoic acid, 1-octanol, and decanoic acid were larger than that of SDS alone (presented by the dotted line), while those of the micelles containing 1-decanol, octane, and heptane were smaller. The $|U_M|$ of the micelles containing 1-decanol was smaller than that of SDS alone in the presence of NaCl; this is a result of the behavior of 1-decanol, like that of normal paraffins in a medium containing electrolytes.

The $\zeta$-potential was calculated from $U_M$ by the use of Henry's equation:[20)]

$$\zeta = \frac{6\pi\eta}{\varepsilon f(\kappa a)}\cdot U_M, \tag{8}$$

where $f(\kappa a)$ is the Henry function, $\kappa$ is the Debye-Hückel parameter, $a$ is the radius of the micelle, and $\eta$ and $\varepsilon$ are the viscosity and dielectric constant of

Table 1. Electrophoretic and diffusion data for the solubilized micelles
(in a 0.2 M NaCl aq soln. at 25 °C)

| | Solubilizates | $-U_M$ / $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ | $D$ / $10^{-7}$ cm$^2$ s$^{-1}$ | $a$ / Å | $-\zeta$ / mV | $Q$ |
|---|---|---|---|---|---|---|
| Polar | $C_8$ acid | 3.26 | 2.15 | 109.5 | 49.7 | 376 |
| | $C_8$ alc. | 2.97 | 3.07 | 76.7 | 46.9 | 180 |
| | $C_{10}$ acid | 2.92 | 3.44 | 68.5 | 46.6 | 144 |
| | $C_{10}$ alc. | 2.28 | 3.44 | 68.5 | 36.4 | 113 |
| Nonpolar | $n$-$C_8H_{18}$ | 1.49 | 5.59 | 42.1 | 25.1 | 32 |
| | $n$-$C_7H_{16}$ | 1.02 | 6.44 | 36.6 | 17.4 | 17 |
| | SDS alone | 2.56 | 9.33 | 25.2 | 45.3 | 23 |

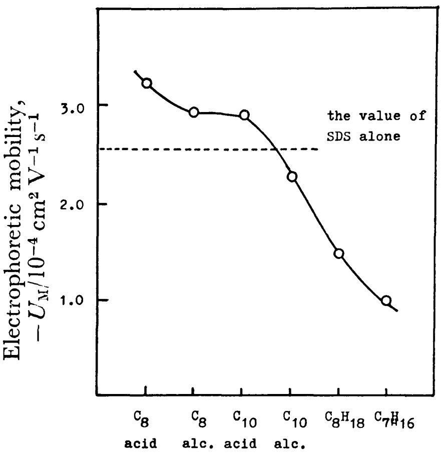

Fig. 6. Electrophoretic mobility of the solubilized micelles.
$|U_M|$ in 0.2 M NaCl at 25 °C.

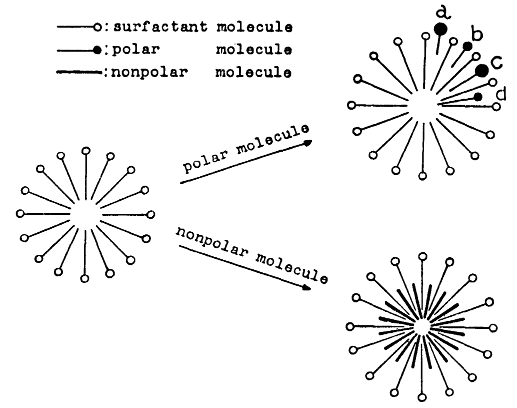

Fig. 7. Schematic solubilization model for the various solubilizates.

the medium respectively.

Furthermore, the number of the effective charge of micelles, $Q$, is estimated by means of the following equation:[20]

$$Q = \frac{1}{e}\cdot\frac{1+\kappa a+\kappa r_i}{1+\kappa r_i}\cdot\varepsilon a\zeta, \tag{9}$$

where $e$ is the elementary charge and $r_i$ is the radius of the counter ion, for which we adopted 0.22 nm in the present system.

Table 1 shows the results of electrophoretic and diffusion measurements for the micelles containing various solubilizates. The absolute value of the $\zeta$-potential follows the order of $|U_M|$. As is evident from Table 1, the numbers of the effective charges of micelles containing polar solubilizates are larger than those of the micelles containing nonpolar solubilizates or no solubilizates, with that of the micelles of SDS containing octanoic acid being the largest. These results suggest that the micelles containing octanoic acid aggregate with each other to form the larger micelles, whereas the micelles containing nonpolar solubilizates seem not to aggregate, showing a charge similar to that of the micelles of SDS alone.

The large number of the charge of the octanoic acid-containing micelles may be attributed to the hydration of carboxyl groups. From the point of view of energy, the hydrated carboxyls would better remain on the surface of the micelles than be incorporated into the hydrocarbon cores of the micelles. The alkyl group of octanoic acid is considered to penetrate into the palisade layer of the micelles. This mechanism of the solubilization of polar oily compounds is shown schematically in Fig. 7. In this figure, **a** indicates octanoic acid; **b**, 1-octanol; **c**, decanoic acid, and **d**, 1-decanol. Since nonpolar compounds, such as octane and heptane, are not hydrated, all the molecules are thought to be incorporated into the hydrocarbon cores of the micelles, like needles buried in a spherical pad. The generally accepted model of the solubilization of oily materials by the micelles of a surfactant was proved to be consistently true in the present systems.[21,22]

## References

1) J. N. Phillips and K. J. Mysels, *J. Phys. Chem.*, **59**, 325 (1955).

2) T. Nakagawa and H. Inoue, *Nippon Kagaku Zasshi*, **78**, 636 (1957).

3) F. Tokiwa and K. Ohki, *Bull. Chem. Soc. Jpn.*, **42**, 1216 (1969).

4) K. Ogino, M. Abe, and N. Takeshita, *Bull. Chem. Soc. Jpn.*, **51**, 1880 (1978).

5) H. B. Klevens, *Chem. Rev.*, **47**, 1 (1950).

6) E. Guth and R. Simha, *Kolloid-Z.*, **74**, 147 (1936).

7) D. C. Robins and I. L. Thomas, *J. Colloid Interface Sci.*, **26**, 415 (1968).

8) T. Ito and H. Mizutani, *Yakugaku*, **17**, 246 (1968).

9) K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York (1963), p. 115.

10) Y. Iwadare and T. Suzawa, *Bull. Chem. Soc. Jpn.*, **43**, 2326 (1970).

11) G. S. Hartley, "Aqueous Solution of Paraffin Chain Salts," Harman, Paris (1936).

12) T. Nakagawa and H. Inoue, *Nippon Kagaku Zasshi*, **79**, 345 (1958).

13) H. R. Bruins, *Kolloid-Z.*, **57**, 152 (1931).

14) I. Watanabe, *Kagaku*, **18**, 421 (1948).

15) A. Einstein, *Ann. Physik.*, **17**, 549 (1905).

16) F. Tokiwa and K. Ohki, *J. Phys. Chem.*, **71**, 1343 (1967).

17) V. P. Dole, *J. Am. Chem. Soc.*, **67**, 1119 (1945).

18) F. Tokiwa and K. Ohki, *Bull. Chem. Soc. Jpn.*, **41**, 2828 (1968).

19) L. G. Longsworth, *J. Phys. Colloid Chem.*, **51**, 171 (1970).

20) D. C. Henry, *Proc. R. Soc. London, Ser. A*, **133**, 106 (1931).

21) C. B. Monk, "Electrolytic Dissociation," Academic Press, New York (1961), p. 271.

22) S. Riegelman, N. A. Allawalla, M. K. Hrenoff, and L. A. Strait, *J. Colloid Sci.*, **13**, 208 (1958).