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A Study of the Solubilization of Polar Oily Materials by Sodium Dodecyl Sulfate

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The difference due to carbon-chain lengths and kinds of polar groups in the solubilizing phenomenon caused by Sodium Dodecyl Sulfate (SDS) of polar normal fatty acids and polar normal alcohols has been studied in terms of the amount of solubilization, the viscosity, and the surface tension. The amount of solubilization decreased with an increase in the number of carbon atoms in the molecules of oily materials, and it was larger for normal fatty acids than for normal higher alcohols with the same number of carbon atoms in the molecule. It was found that the oily materials of a greater amount of solubilization exhibited a small viscosity and a small rate of the reduction of surface tension.

Solubilization is a phenomenon in which a solution of a surfactant in concentrations beyond the critical micelle concentration (CMC) dissolves a variety of organic compounds to yield a transparent solution. This results from the solution of the substances into the micelles. The structure of the micelles has been described by McBain[1] and by Hartley and coworker,[2] but it is still a matter of controversy. Among the ways of incorporating the solubilizate into the micelles, which are closely related to the structure of the micelles, are (a) adsorption on the surface of the micelles; (b) deep penetration of the palisade layer and (c) dissolution in the hydrocarbon core, these methods have been described by Kolthoff,[3] Riegleman,[4] and Mulley respectively.[5]

In this study normal fatty acids and normal higher alcohols with different polarities were solubilized by SDS, and the mechanism of the solubilization was investigated by measuring the amount of solubilization, the values of the CMC, the relative viscosities, and the surface tension. We found that the amount of solubilization decreased with an increase in the number of carbon atoms in the molecules of polar oily materials, and was larger for fatty acids than for alcohols with the same number of carbon atoms in the molecule.

As regards the CMC, the smaller the number of carbon atoms in the molecules of polar oily materials, the greater the reduction in CMC compared with that of SDS alone. It has been found that the CMC of SDS solubilizing an oily material is given by:

$$\mathrm{CMC} = A\sqrt{N_c} + B$$

where A and B are experimental constants and N_c is the number of carbon atoms in the molecules of the oily materials.

The relative viscosities of SDS solutions of oily materials increased with an increase in the number of carbon atoms in the molecules of oily materials, and they were larger for normal higher alcohols than for normal fatty acids with the same number of carbon atoms in the molecules.

The rate of the reduction of surface tension increased with an increase in the number of carbon atoms in the molecules of polar oily materials; it was greater for alcohols than for fatty acids with the same number of carbon atoms in the molecules. The surface tension at the saturation of solubilization exhibited a constant value, regardless of the kinds of oily materials added.

To summarize, it was found from this experiment that the oily materials of greater amounts of solubilization exhibited a smaller viscosity and a smaller rate of reduction in the surface tension.

Experimental

Materials. *Surfactant*: Sodium Dodecyl Sulfate (SDS) of a regent grade was extracted with ether and recrystallized from ethanol.

Polar Oily Materials: The octanoic acid (C_8), decanoic acid (C_{10}), dodecanoic acid (C_{12}), and tetradecanoic acid (C_{14}) were the purest grade products of Wako-Junyaku and were more 99% pure; The octyl alcohol (C_8, bp 179.5 °C), decyl alcohol (C_{10}, bp 228—232 °C), dodecyl alcohol (C_{12}, bp 86.5 °C), tetradecyl alcohol (C_{14}, bp 255—259 °C), and hexadecyl alcohol (C_{16}, bp 190 °C) were the purest grade products of Wako-Junyaku.

Apparatus and Conditions. When polar oily materials are added to a SDS solution, beyond the saturation point they are emulsified and the solution becomes turbit. The following procedure was used for the determination of the limits of solubilization. Into several 100 ml glass-stoppered flasks, 50 ml portions of a solution of a given concentration of SDS were placed; then varying amounts of polar oily materials were added to them, and the mixtures were shaken while being stirred for 12 h in a thermostat at 40 °C, followed by setting until a solubilization equilibrium was established. After the equilibrium had been established, the turbidity of the solution was measured with an Electro photocolorimeter, Hirama 2B type, with a cell 10.0 mm in length at 655 nm. The turbidity concentration obtained was extrapolated to zero in order to obtain the amount of solubilization. The CMC of SDS was determined from the solubilities of the polar oily materials in SDS solutions of various concentrations.

The relative viscosities of the solutions solubilizing oily substances were measured at 40.0 °C±0.1 with an Ubelohde viscometer with appropriate auxiliary equipment to keep atmospheric moisture off as far as possible. The time of flow was determined with a stop watch of a 0.1 s precision; the overall fluctuations of the time measured were within ±0.1 to 0.2 s. The specific gravity was determined by using a pycnometer with a capacity of about 25 ml.

The effective specific volume of 1 g of a SDS including a polar oily material was calculated from the values of the relative viscosity.[6]

The surface tensions of the solubilized solutions were measured at 40.0 °C±0.1 with a Wilhelmy tensiometer, Shimadzu ST-1 type, equipped with a glass plate.

Results and Discussion

Solubilizing Power and CMC of SDS. The difference due to the carbon-chain lengths and the kinds of polar groups in the solubilization caused by SDS solutions has been studied. Figure 1 shows the optical densities of various concentrations of SDS solutions with an increase in the amounts of dissolved octanoic acid. The rapid increase in I_0/I began when emulsion droplets first appeared. The point of the intersection of the curves representing the optical density with the horizontal axis is considered to give the solubility of octanoic acid in the SDS solution. Plots of the solubility of materials in SDS of various concentrations which were obtained in the manner described above are shown in Figs. 2 and 3. As is evident from the figures, the solubility remained constant near null until the critical concentration was reached, beyond which point it showed a sharp increase in the SDS micelles due to solubilization. The slopes of these lines and the intersections of the horizontal

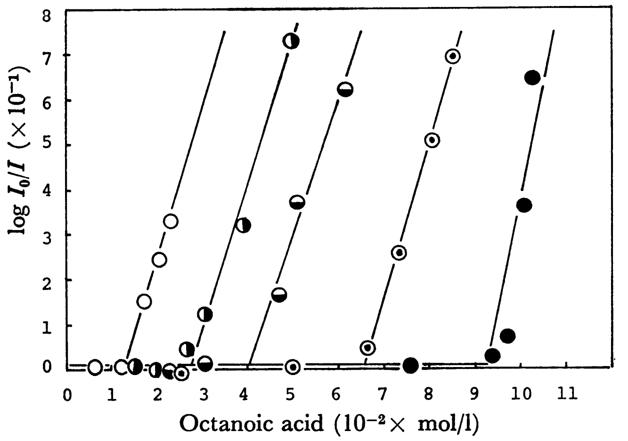

Fig. 1. Optical density of various concentrations of SDS solution with increasing amount of dissolved octanoic acid.
○=3.47×10^{-3} mol/l SDS; ◑=6.94×10^{-3} mol/l SDS; ◒=10.4×10^{-3} SDS; ⊙=17.4×10^{-3} mol/l SDS; ●=24.3×10^{-3} SDS.
I=intensity of permeable light; I_0=intensity of incident light.

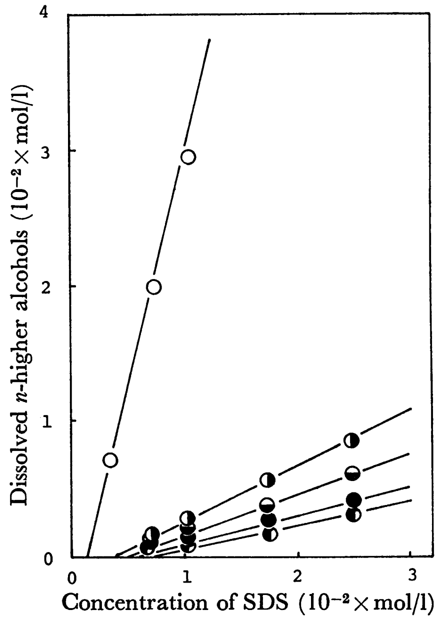

Fig. 3. Solubilizing power and critical micelle concentration of SDS.
○=Octyl alcohol; ◑=decyl alcohol; ◒=dodecyl alcohol; ●=tetradecyl alcohol; ◐=hexadecyl alcohol.

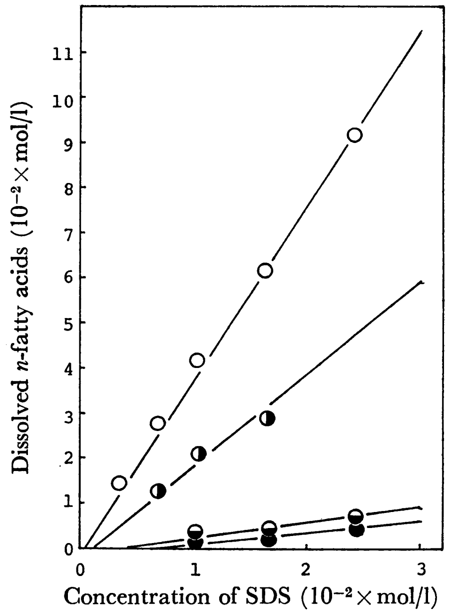

Fig. 2. Solubilizing power and critical micelle concentration of SDS.
○=Octanoic acid; ◑=decanoic acid; ◒=dodecanoic acid; ●=tetradecanoic acid.

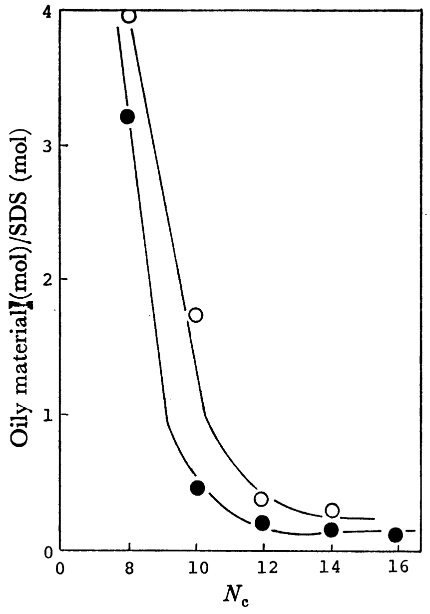

Fig. 4. The change of solubilizing power with increasing number of carbon atoms of oily materials.
N_c is the number of carbon atoms in the molecules of oily materials.
○=Normal fatty acids; ●=normal higher alcohols.

axis with these lines are the solubilizing power and the CMC respectively. Figure 4 shows the change in the solubilizing power with an increase in the number of carbon atoms in the molecules of oily materials. As is evident from Figs. 1, 2, and 3, the solubility and the solubilizing power decreased with an increase in the number of carbon atoms in the molecules of oily materials, and they were larger for normal fatty acids than for normal higher alcohols with the same number of carbon atoms in the molecule. This result is considered to be due to the decrease in the magnitude of the dipole moment with the increase in the number of carbon atoms in the molecule of the oily material and to the difference in polar groups between normal fatty acids and normal higher alcohols with the same number of carbon atoms in the molecule.[7]

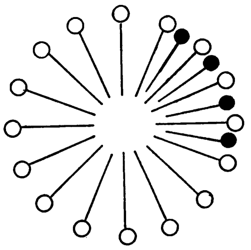

Fig. 5. Formation of palisade layer of mixing micelle between surfactant anion and polar molecule.
○——=Surfactant anion; ●——=polar molecule.

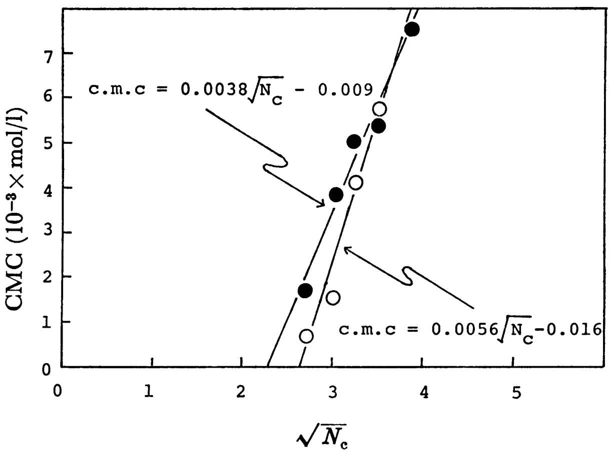

Fig. 6. Relationship between the CMC of SDS and the carbon number of oily materials.
N_c is the number of carbon atoms in the molecules of oily materials.
○=Normal fatty acids; ●=normal higher alcohols.

As is shown in Figs. 2 and 3, the CMC of SDS with oily materials was smaller than that of SDS alone (6.94×10^{-3} mol/l) and decreased with a decrease in the number of carbon atoms in the molecules of the oily materials. As may be seen from Fig. 5, this is considered to be due to the fact that the deep penetration of polar molecules into the palisade layer caused the surface charge density to decrease, leading to a reduction of the free energy of mixing.[8] Figure 6 shows the effect of oily materials added on the CMC of SDS; the following equations can be written:

for normal fatty acids,

$$\mathrm{CMC} = 0.0056\sqrt{N_c} - 0.016$$

for normal higher alcohols,

$$\mathrm{CMC} = 0.0038\sqrt{N_c} - 0.009$$

where N_c is the number of carbon atoms in the molecules of the oily materials.

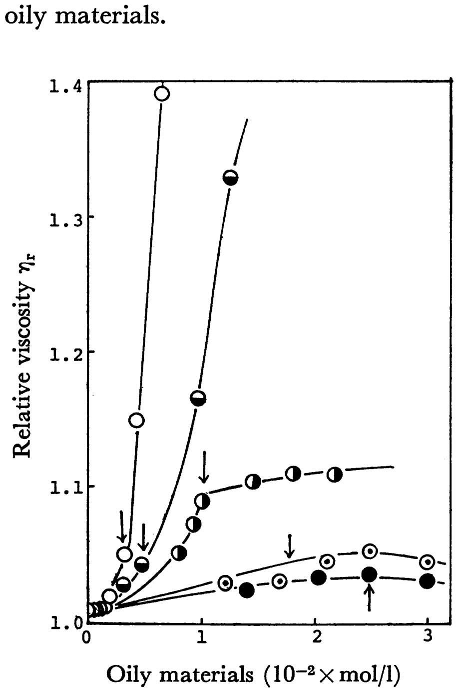

Fig. 7. The relative viscosity of the solutions which were produced by solubilizing oily materials using SDS of given concentration (6.94×10^{-3} mol/l).
●=Octanoic acid; ◑=decanoic acid; ⊙=octyl alcohol; ◒=decyl alcohol; ○=dodecyl alcohol.
Arrows show the limit of solubilization of oily materials in 6.94×10^{-3} mol/l of SDS.

Relative Viscosity and Effective Specific Volume. Figure 7 shows the relative viscosities of the solutions which were produced by solubilizing oily materials using SDS of a given concentration (6.94×10^{-3} mol/l). The arrows in the figure indicate the limits of solubilization in Figs. 2 and 3. For a given concentration of oily materials, the relative viscosity of the solution increased with an increase in the number of carbon atoms in the molecules of oily materials. For the same number of carbon atoms in the molecules of oily materials, the relative viscosity of the normal higher alcohols was larger than for normal fatty acids. Past the limit of solubilization, the relative viscosities of octanoic acid, of decanoic acid, and of octyl alcohol remained approximately constant; on the other hand, that of decyl alcohol and dodecyl alcohol continued to grow. This is considered to be because emulsification occurs and because the effect which polar materials have on relative viscosities under the states of dispersion of emulsion seems to become greater. As may be seen from Fig. 4, there are inflection points in solubilizing power: at a dodecyl alcohol for normal higher alcohols and at a dodecanoic acid for normal fatty acids. According to the study of the rolling-up phenomenon of polar oily materials in SDS solutions,[9] both octanoic acid and octyl alcohol were immediately dissolved or solubilized by SDS solutions, a decanoic acid–SDS solution system occurred simultaneously with solubilization and molecular complex formation at the interface, and a molecular complex was formed at the decyl alcohol and dodecyl alcohol/SDS solution interface. In consideration of the above findings, there must be same changes in the properities of decyl alcohol and decanoic acid. According to Klevens,[7] when the non-polar parts of the solubilizates, polar compounds, become too large to overcome the effects of polar groups in the molecules, the solubilizates exhibit behavior resembling that of hydrocarbons, giving rise to a so-called transition solubilization phenomenon, which represents properties intermediate between polar compounds and hydrocarbons.

Based on the relative viscosity, η_r, obtained from Guth and Simha's equation,[10–13] which is a form of Einstein's equation extended to more concentrated solutions:

$$\eta_r = 1 + 2.5\phi + 14.1\phi^2$$

where ϕ is the volume fraction occupied by the spherical particles, the effective specific volume of 1 g of SDS including oily materials, V, is expressed as follows:[6,10]

$$V = \phi/C$$

where C is the concentration of the solution in g/ml. The specific volumes of octanoic acid, octyl alcohol, and decanoic acid changed at the limit of solubilization. From the standpoint of the solubilizing phenomenon, a comparison of polar oily materials based on fixed concentrations is not always appropriate. Therefore, a comparison of the relative viscosity, η_r, with the effective specific volume, V, at the saturation of an solubilized oily material is shown in Table 1. As may be seen from Table 1, as for the relative viscosity there was no apparent regularity, as in Fig. 7. With the effective specific volume, V, the order of increasing specific volume is; octanoic acid<octyl alcohol<decyl alcohol<decanoic acid<dodecyl alcohol; on the other hand, the order of increasing limits of solubilization is; dodecyl alcohol< decyl alcohol<decanoic acid<octyl alcohol<octanoic acid. The oily materials of a greater amount of solubilization in the SDS micelle exhibits a smaller effective specific volume. This result is considered to be due to the difference in the penetration of micelles through the palisade layer resulting from the difference in polar groups.

Table 1. Comparison of the relative viscosity with the effective specific volume at the saturation of oily materials

	N_c	Limits of solubilization (mol/l)	η_r	V (ml/g)
Normal fatty acids	C_8	2.50×10^{-2}	1.040	2.65
	C_{10}	1.00×10^{-2}	1.094	8.58
Normal higher alcohold	C_8	1.83×10^{-2}	1.042	3.40
	C_{10}	0.13×10^{-2}	1.020	3.49
	C_{12}	0.08×10^{-2}	1.050	8.65
SDS alone				1.3

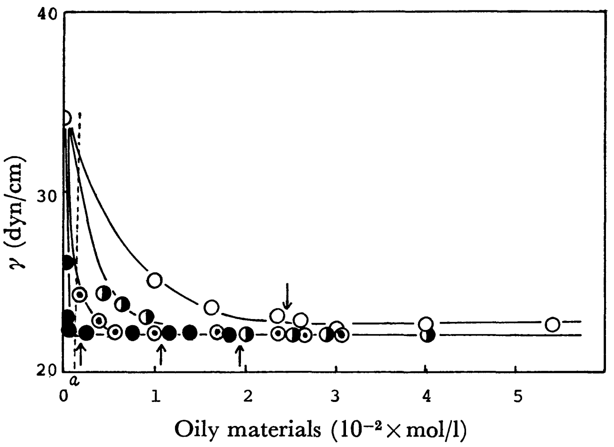

Fig. 8. Surface tension of solutions which is produced by dissolving oily materials in a given concentration of SDS (6.94×10^{-3} mol/l).
○=Octanoic acid; ⊙=decanoic acid; ◐=octyl alcohol; ●=decyl alcohol.
Arrows show the limit of solubilization of oily materials in 6.94×10^{-3} mol/l of SDS.

Surface Tension. Figure 8 shows the surface tensions of solutions which are produced by dissolving oily materials in given concentrations of SDS (6.94×10^{-3} mol/l). The rate of the reduction of the surface tension increased with an increase in the number of carbon atoms in the molecules of oily materials; it was larger for normal higher alcohols than for normal fatty acids with the same number of carbon atoms in the molecule. At the limits of solubilization (arrows in the figure), all the oily materials showed constant values of about 22 dyn/cm, this value remaining fixed even after the formation of a state of emulsion. Nakagawa and his coworkers,[14] with the aid of the electron spin resonance (ESR) spectra and the nuclear magnetic resonance (NMR) spectra, suggested that the lifetime of the benzene molecules in SDS micelles saturated with benzene was 10^{-4} s. It is considered that polar molecules adsorbed onto the air-water interface are en route to transition to polar oily molecules within the micelles or in the solution and are responsible for the reduction of the surface tension.

In connection with the difference in the reduction of the surface tension at a constant concentration of oily material (a in Fig. 8), it is generally true that normal fatty acids and normal higher alcohols with 12 or less carbon atoms form a gaseous membrane when spread over the surface of water at room temperatures. At a constant concentration of oily materials, the more hydrophobic the materials, the more tendency for the materials to reduce the surface tension by adsorbing onto the air-water interface. The fact that the surface tension shows a constant value of about 22 dyn/cm above the saturation of solubilization may be ascribed to the approximately equal contributions of polar materials to the surface tension in the emulsion state, regardless of the kinds of polar oily materials.

The changes in the amount of solubilization and in the relative viscosity, due to the difference between the carbon chain lengths and the kinds of polar groups, result from the difference in the penetration of the palisade layer of the micelles; the difference in the surface tension results from the difference in the state of adsorption of the molecules of oily materials at the air-water interface.

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