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Studies of the Effect of 1-Dodecanol on the Micellization of Sodium Dodecyl Sulfate by Gel Filtration

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The tail analysis of gel filtration was applied to an aqueous sodium dodecyl sulfate (SDS) solution containing solubilized 1-dodecanol. Commercial SDS containing 1-dodecanol as an impurity showed a maximum micellar size at CMC. The addition of 1-dodecanol caused an increase in the micellar size due to solubilization. The amount of 1-dodecanol impurity was estimated from the elution rate of the micelle, R_m, the result being in agreement with that obtained by surface tension measurements.

Concerning the property of aqueous solutions of surfactants employed for solubilizing long-chain alcohols which are sparingly soluble in water, studies have been mainly directed towards the effect of solubilization on the critical micelle concentration (CMC) and the determination of the amount solubilized. Studies on the estimation of the effect of the solubilizate on micellar size are rather few.[1]

The addition of solubilizates is known to lower the CMC and to increase the micellar size as measured by the visual dye method,[2] viscosity,[3] light scattering,[1] and others. However, the application of the gel filtration method affords a more simple and direct means of studying the solubilization by micelles especially near CMC. In the present report, the elution behavior of SDS micelles solubilizing 1-dodecanol was studied and the change of the CMC and the micellar size due to solubilization are discussed.

Experimental

Materials. Sodium dodecyl sulfate was prepared by the same method as described in a preceding paper,[4] and a commercial SDS without purification was also used. A solubilized system was prepared by dissolving known amounts of SDS and 1-dodecanol (DOH) or tritium labelled 1-dodecanol (TDOH) in ethanol, evaporating the ethanol and dissolving the residue in water. The labelled 1-dodecanol was kindly supplied by Dr. K. Tajima of our laboratory.

Procedures. The apparatus used for gel filtration was essentially the same as that reported in Ref. 4. The gel filtration experiments were made using two columns of 1.1 × 30.5 cm and 1.2 × 10 cm gel beds packed with Sephadex G-50 fine (Pharmacia, Uppsala, Sweden). To the gel column previously equilibrated with water, a known amount of the sample solution was added and was eluted with water. The elution curve was obtained by automatically recording the electrical conductance or the refractive index of solution eluted. All of the gel filtration experiments were carried out in an air thermostat at 30 °C. For the purpose of radioactivity measurement, eluates were taken in 1 ml fractions, and 30 μl of the eluate from each fraction was completely evaporated in a planchet at room temperature. The radioactivity of each eluate was determined by a 2π windowless gas flow counter.

As mentioned in a previous paper,[4] from the measurement of the elution volumes, V_f, V_m, V_s, the relative elution rates of the front and micelles were calculated from

$$R_f = V_s/V_f,\ R_m = V_s/V_m,\ R_s = 1$$

respectively, where, the elution rate of single ions was conventionally taken to be unity.

Surface tension measurements of aqueous solutions of SDS were carried out using a du Noüy tensiometer at room temperature (25 °C).

Results and Discussion

In order to study the solubilization by micelles by the tail analysis[5] of gel filtration, SDS solutions with solubilized TDOH were used. Figure 1 shows the elution curves obtained for SDS solutions with and without DOH, where A and B indicate the tails of the DOH and SDS micelles of the solubilized system measured by radioactivity and the electrical conductance, respectively, and C is the tail of SDS micelles measured by the electrical conductance for the system without any solubilizate. The elution curve A indicates the practical insolubility of 1-dodecanol in the intermicellar solution, and the agreement of elution volumes between A and B indicates the perfect incorporation of 1-dodecanol into micelles. Furthermore, a larger elution volume of C compared with A and B indicates the increase in size of the micelles due to solubilization.

Figure 2 shows the fronts of the elution curve of the solubilized system shown in Fig. 1. The shapes of the fronts for A and B are rather different compared with the similarity in the shapes of A and B tails shown in Fig. 1. Front A shows a sharp peak and is situated in advance of the front B which has a usual slope. This is explained as follows. A part of micelles containing the solubilizate decomposes at the front during gel filtration, resulting in the precipitation of solubilized 1-dodecanol, whereby a part of the precipitate is resolubilized and concentrated in the undecomposed

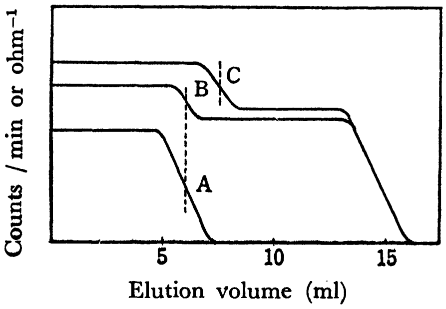

Fig. 1. Elution tail of micellar solution containing solubilized TDOH.
Curve A is from radioactivity measurement, curves B and C are from conductance, respectively (C, 1-dodecanol free).

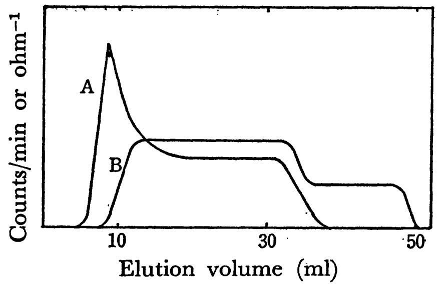

Fig. 2. Front of elution curve for micellar solution of SDS containing solubilized TDOH.
A, radioactivity measurement; B, conductance measurement.

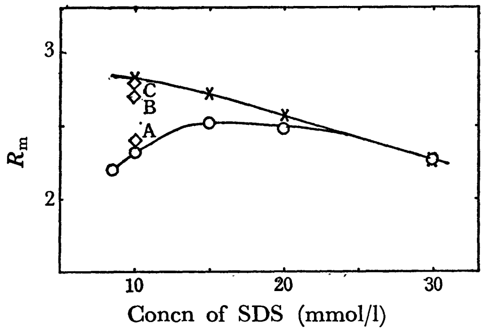

Fig. 3. Dependence of the R_m obtained by tail analysis on concentration of SDS.
○, pure SDS; ×, commercial SDS; ◇, SDS containing (A) 1.1×10^{-2}, (B) 1.5×10^{-2}, (C) 2.2×10^{-2} mol DOH/mol SDS.

micelles, while the rest of the precipitates being larger in size than the micelles advance faster than the micelles. Thus, 1-dodecanol is gradually concentrated in the micelles and forms a sharp peak in front of the micelles. The peak was also confirmed by detecting the front using a differential refractometer which has been described in detail.[6)]

Table 1. Micellar size of SDS

Concn of SDS (mmol/l)	Pure SDS (Å)	Commercial SDS (Å)
8.5	17.6	—
10.0	19.9	27.3
15.0	22.7	25.3
20.0	21.0	23.0
8.12	21.5	(from D. Stigter and K. J. Mysels)[9)]

For the study of the change of the micellar size due to the solubilization, the R_m obtained with commercial SDS containing 1-dodecanol as impurities was plotted against the concentration shown by crosses in Fig. 3. As is seen, the commercial SDS shows remarkably larger R_m values than does a pure sample (open circles); R_m is largest at CMC and decreases with an increase in SDS concentration. At sufficiently high concentrations, both the pure and commercial products gave the same value of R_m. The marked increase of R_m for commercial SDS can be explained as follows. Although the total amount of 1-dodecanol contained as impurities in aqueous SDS solutions near CMC is not very large, the amount of 1-dodecanol solubilized per micelle may become fairly large since the number of micelles formed just above CMC is very few. This causes the formation of large micelles for impure SDS just above CMC. At higher concentrations, the number of micelles increases more rapidly than the amount of 1-dodecanol increases, and the effect of 1-dodecanol solubilization on micellar size becomes practically insignificant at sufficiently large concentrations of SDS. Thus, the micelle radius of commercial SDS, which contains 1-dodecanol as an impurity, is considerably larger than that of pure SDS near CMC. At higher concentrations of SDS, this difference tends to disappear. The hydrodynamic radii of the micelle calculated by the Laurent-Killander equation are shown for pure and impure (containing 1-dodecanol) SDS in Table 1. The increase in micellar size with the increase in the solubilized amount of DOH at a constant SDS concentration of 10 mmol/l was measured by the increase of R_m shown by squares in Fig. 3.

From a comparison of these R_m values with those

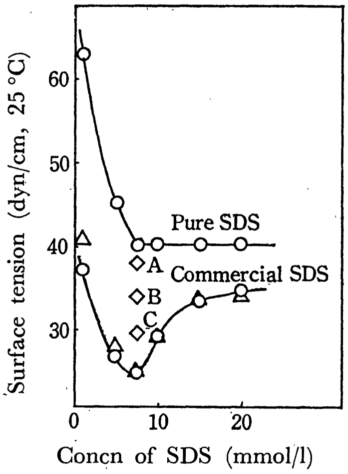

Fig. 4. Dependence of the surface tension on concentration of SDS containing solubilized DOH.
◇ A, ◇ B, ◇ C, △, SDS containing 0.07×10^{-2}, 0.26×10^{-2}, 1.03×10^{-2}, and 2.75×10^{-2} mol DOH per mol SDS, respectively.

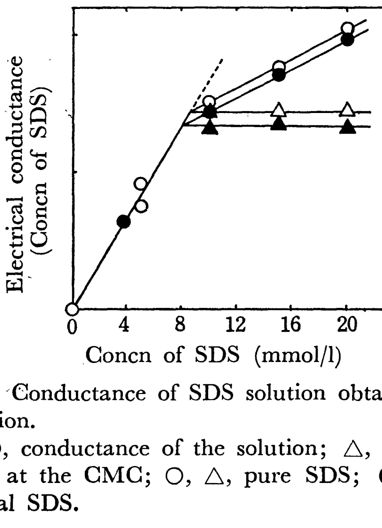

Fig. 5. Conductance of SDS solution obtained by gel filtration.
○, ●, conductance of the solution; △, ▲, conductance at the CMC; ○, △, pure SDS; ●, ▲, commercial SDS.

for commercial SDS used in the present experiment, the impurity (tentatively assumed to be 1-dodecanol) in the commercial SDS is estimated to be about 2.2×10^{-2} mol of DOH per mol of SDS. A similar amount was obtained from the surface tension measurement. Thus, the surface tensions of solutions containing the same amounts of SDS (near CMC) but varying amounts of 1-dodecanol were plotted against the concentrations of 1-dodecanol. Figure 4 shows the results together with the surface tension for commercial SDS. From this figure, about 2.75×10^{-2} mol of DOH/mol of SDS was obtained for the commercial SDS.

It was further confirmed from the plots of the plateau of the elution *vs.* concentration curve shown in Fig. 5[4] that the CMC of impure SDS, 7.8 mmol/l, was lower than that of pure SDS, 8.5 mmol/l, obtained from a similar plot which is in accordance with the general view on the effect of such a solubilizate.[7,8]

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