Studies of the Effect of Ethanol and Sodium Chloride on the Micellization of Sodium Dodecyl Sulfate by Gel Filtration

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(Received November 26, 1975)

The effects of the addition of ethanol and sodium chloride to aqueous solutions of sodium dodecyl sulfate (SDS) were studied by the gel-filtration method. With an increase in the concentration of ethanol, the CMC decreased and then increased after passing a minimum, while the micellar weight increased and then decreased, showing a corresponding maximum. Above about 40 vol% ethanol, no micelle formation was observed. The micellar weight and aggregation number in the presence of ethanol were measured in the SDS concentration range of a constant elution rate of micelles. A decrease in the CMC and an increase in the micellar weight of SDS were observed with an increase in the concentration of NaCl from 0 to 10 mmol/l. The gel-filtration study enabled us to make a direct experimental confirmation of the effects of ethanol and NaCl on the micelle formation of SDS.

A number of studies have been made on the effects of additives on the CMC and micellar size of SDS.[1] However, relatively few have been reported concerning the effect of mixed solvents. According to Ward,[2] the CMC of aqueous SDS decreased with the addition of ethanol up to 10 vol% and then increased, while above 40 vol% no micellization occurred. Herrmann and Benjamin[3] and Becher[4] found a decrease in the micellar weight in water with an increase in the ethanol concentration for nonionic detergents. As for the effect of ethanol on the micellar size of SDS, only a few reports are available.[4]

Contrary to the effect of alcohol, the addition of NaCl to an aqueous SDS solution is known to decrease the CMC and to increase the micellar size.[1,5] In the present report, the effects of ethanol and NaCl on the micellar size and on the CMC of SDS in the aqueous solution have been studied by the gel-filtration method, which gives us direct experimental information.

Experimental

Materials. Sodium dodecyl sulfate prepared from 1-dodecanol and chlorosulfuric acid was purified by the extraction of the 1-dodecanol with diethyl ether and by subsequent recrystallization from ethanol.[6] Distilled water was degassed by boiling prior to use. Poly(vinyl alcohol)s (PVA), products of the Nippon Gosei Kogyo Co., Itd., and Blue Dextran 2000 obtained from pharmacia, Uppsala, Sweden, were used as the standard substances of the molecular weight. The purest grade ethanol was used after dehydration and distillation. The sodium chloride was purified by recrystallization from an aqueous solution by the addition of ethanol.

Apparatus and Procedure. The apparatus used for gel-filtration was essentially the same as that reported in the preceding papers.[6,7] The gels used were Sephadex G-50 and CPG-10 of Electro-Nucleonics, Inc. The gels were equilibrated with the mixed solvent of a known ethanol-water composition to be studied, and 30 ml of a SDS solution of the same ethanol-water composition was charged on top of the gel column. The elution was performed by using a mixed solvent of the same composition. An elution curve was obtained by recording the electrical conductance of the effluent as a function of the elution volume. The elution curve for a solution with a concentration larger than CMC

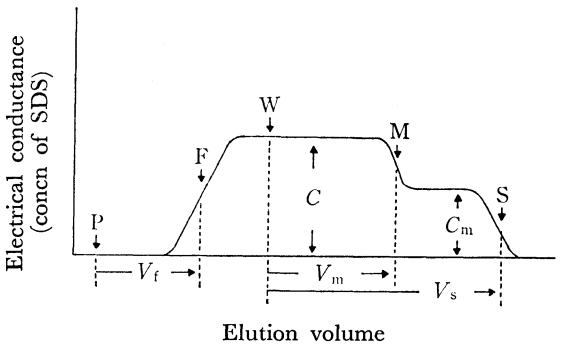

Fig. 1. Elution curve for SDS in ethanol-water solvent system.

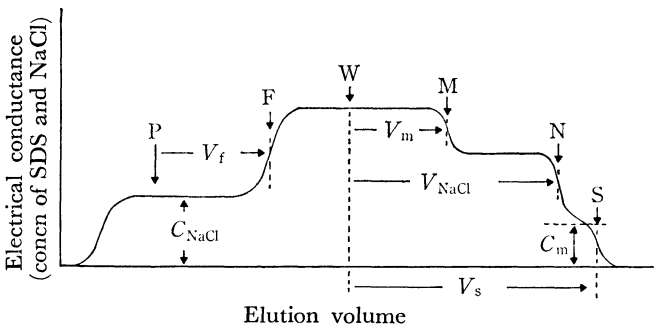

Fig. 2. Elution curve for SDS in aqueous sodium chloride solution, P, F, W, M, S, being the same as in Fig. 1. N; tail of NaCl.

is shown schematically in Fig. 1. In this figure, the ordinate is the conductance proportional to the concentration of SDS, while the abscissa is the volume eluted. P and W are the points of the sample and the water charges respectively, and F, M, and S, the front of the solution and the tails of micelles and single ions respectively. From this curve, the elution volumes of the SDS solution front, V_f; micelles, V_m, and single ions, V_s, were obtained; they are shown in Fig. 1. The lower plateau of Fig. 1 corresponds to the CMC of SDS (C_m), and the higher one, to the total concentration of SDS (C).

For the study of the effect of NaCl upon the CMC and the micellar size of SDS in aqueous solutions, Sephadex G-50 was used. The gel was equilibrated with an aqueous NaCl solution, and an aqueous solution of NaCl of the same

concentration, but containing SDS in addition, was charged on top of the gel column. The elution was performed by using an aqueous NaCl solution of the same concentration. The elution curve thus obtained is shown schematically in Fig. 2. The notations of P, W, M, S, and F are the same as in Fig. 1, while N is the tail of the NaCl solution. From the front and the three tails of the curve, the elution volumes of SDS front, V_f; the micelles, V_m; the single ions, V_s, and NaCl, V_{NaCl}, were obtained; they are shown in Fig. 2. The concentration of NaCl, C_{NaCl}, and the CMC of SDS, C_m, are estimated from the heights of the plateaus of the curve by using a conversion factor previously determined. The measurements were conducted at 30 °C throughout the experiments.

Results and Discussion

Effect of Ethanol and NaCl on CMC. The conductivity corresponding to the height of each plateau of the elution curve of SDS in the ethanol–water mixture shown in Fig. 1 is plotted against the total concentration of SDS in Fig. 3 for, for instance, the 10 vol% ethanol–water system. Three straight lines passing through a point which corresponds to the CMC of SDS in the mixture were obtained for both Sephadex and CPG-10 gel. The CMC's of the SDS obtained for ethanol–water mixtures are plotted as a function of the ethanol concentration at 30 °C in Fig. 4. Agreement is, as a whole, seen for both Sephadex and CPG gel. Since CPG-10 gel is more stable in a concentrated SDS solution than is Sephadex gel, plotting for a higher concentration has been possible for the former gel. Figure 4 shows that a small amount of ethanol in water lowers, while a larger amount raises, the CMC of SDS. The minimum at about 10 vol% of ethanol was in agreement with that reported by Ward.[2] The CMC above 20 vol% of ethanol was difficult to measure, since the step of the tail, M, corresponding to the micelles becomes obscure.

The elution volumes of front (V_f), micelles (V_m), and single ions (V_s) are plotted against ethanol concentrations up to 100 vol% at a constant SDS concentration (15 mmol/l) in Fig. 5. As may be seen, V_f increases above a 20 vol% ethanol concentration. From 30 up to 100 vol% ethanol, V_f becomes equal to V_s, the tail, M, disappears, and the elution curve observed is a simple one similar to that of the SDS solution below CMC. This means that in the solutions from 30 up to 100 vol% ethanol, the CMC is larger than 15 mmol/l. Presumably, at the SDS concentration a little above 30 mmol/l, as judged from the sharp rise of the curve of Fig. 4, CMC increases so rapidly that the micelle formation is practically prevented and the solute species is mainly of a single molecular type corresponding to V_s. A similar condition may prevail up to a 100% ethanol concentration, as may be seen from the coincidence of V_s and V_m in this region. Thus, the so-called micelles of the inverse type[8] could not be confirmed to form in an ethanol-rich solution or in a pure ethanol solution, at least experimentally by the gel filtration. The present results are rather in accord with those of Ward,[2] who reported a similar decrease in CMC upon the

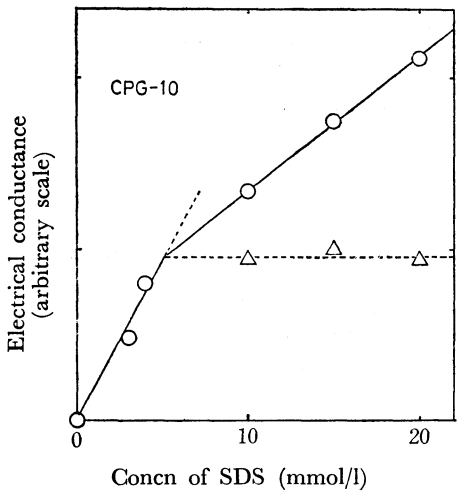

Fig. 3. Conductance of SDS solution obtained by gel-filtration using CPG-10 in the presence of 10 vol% ethanol. ○, conductance of the solution; △, conductance of tail part of solution.

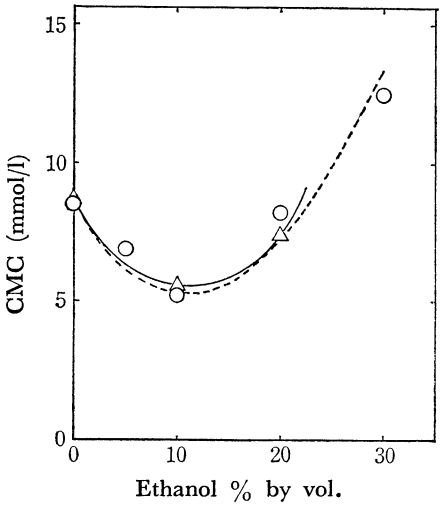

Fig. 4. Critical micelle concentration for SDS in aqueous ethanol. △, ——, Sephadex G-50 fine; ○, ----, CPG-10.

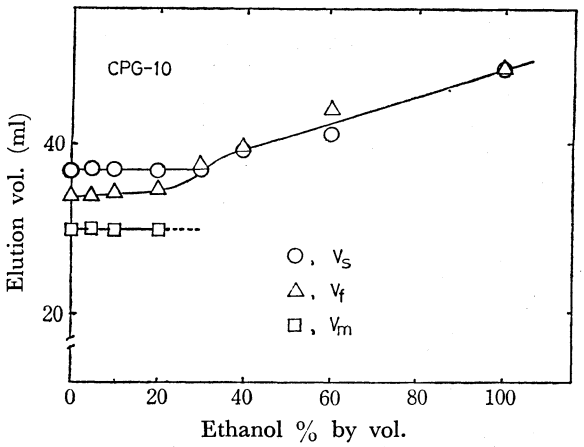

Fig. 5. Elution volume change in aqueous 15 mmol/l SDS solutions as a function of ethanol concentration.

Table 1.

NaCl	CMC
0 mmol/l	8.6 mmol/l
5 mmol/l	6.6 mmol/l
10 mmol/l	5.5 mmol/l
10 mmol/l	5.29 mmol/l[a)]

a) D. Sigter and K. J. Mysels, *J. Phys. Chem.*, **59**, 45 (1955).

ethanol addition and apparently no micellization in a mixed solvent with an ethanol concentration above 40 wt%.

As for the effect of ethanol addition upon CMC, a similar minimum in the concentration *vs.* partial molal volume of ethanol has been reported;[9)] this may suggest water-ethanol interaction affecting the micelle formation and CMC. However, it may be better explained by the fact that the solubilization of ethanol at low ethanol concentrations causes the decrease in the CMC, while the decrease in the amphipathy of the surfactant for a mixed solvent causes an increase in the CMC at high concentrations.

As for the effect of NaCl on CMC, the value of C_m in Fig. 2 is measured as a function of the NaCl concentration, which is shown in Table 1. As may be seen, C_m decreases with an increase in the concentration of NaCl and is in agreement with Stigter's data[13)] for the 10 mmol/l NaCl solution, which is also listed in the table. Further, the applicability of Eq. 8 derived in the previous paper:[6)]

$$\frac{R_m-R_s}{R_s}\cdot\frac{R_f}{R_m-R_f}=\frac{C}{C_m\cdot\alpha}-\frac{1-\alpha}{\alpha} \qquad (8)$$

was tested by plotting the left-hand side of Eq. 8 against the concentration of SDS (C). Here, R_f ($=V_s/V_f$), R_s($=V_s/V_s=1$), and R_m($=V_s/V_m$) ate the relative elution rates of the front, the single ions, and the micelles of SDS respectively; C, the total concentration of SDS; C_m, CMC, and α, the parameter of the rate of micelle decomposition.[6)] The results are shown in Fig. 6. As may be seen, the plots for 0, 5, and 10 mmol/l NaCl show straight lines passing through the point of origin, which confirms Eq. 8 to hold. The decomposition of micelles at the front is found to be instantaneous[6)] ($\alpha=1$) regardless of the NaCl concentration. The points of the intersections of these lines and the horizontal straight line of the ordinate, being unity, determine the C_m values, which are read for 0, 5, and 10 mmol/l NaCl solutions to be 8.6, 6.6, and 5.5 mmol/l respectively. These values are in agreement with the CMC estimated independently from the height of the plateaus of the elution curves, listed in Table 1. The effect of NaCl is also in accord with the general view of the effect of added salt on CMC.[1,10)]

Effect of Ethanol and NaCl on Micellar Size. Since Sephadex gel suffers from a considerable shrinkage upon the addition of a concentrated ethanol solution, it is not suitable for micellar-size determination. Therefore, CPG-10 gel free from such an influence was mainly used in the gel-filtration, especially for the systems with high ethanol concentrations. Figure 7 shows the plots of R_m *vs.* the SDS concentration for each ethanol concentration. In the solutions with concentrations ranging from 0 to 20 vol% ethanol, it is seen that R_m, a measure of the micellar size, is constant independent of the SDS concentration from about 15 to 50 mmol/l SDS for each ethanol concentration, while the size decreases with an increase in the ethanol concentration. Up to 15 mmol/l SDS, R_m slightly increases with the increase of SDS for the system without ethanol.

The measurement of the micellar weight of SDS in an ethanol–water mixture is more complicated than that of SDS in an aqueous solution,[7)] although the basic principles are similar. For the micellar-weight determination of SDS in an aqueous solution, the calibration curve of the elution volume *vs.* the molecular weight of the unhydrated SDS micelle necessary for the calculation (SDS-W in Fig. 8) was obtained from the relation of the elution volume to the molecular

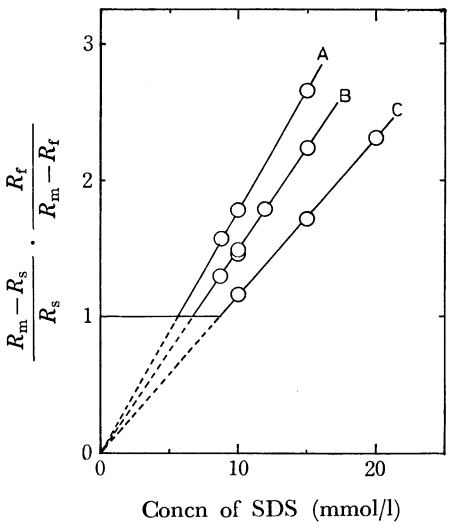

Fig. 6. Relationship between R_f and concentration of SDS in the presence of NaCl using CPG-10 gel. A, NaCl 10 mmol/l; B, NaCl 5 mmol/l; C, NaCl 0 mmol/l.

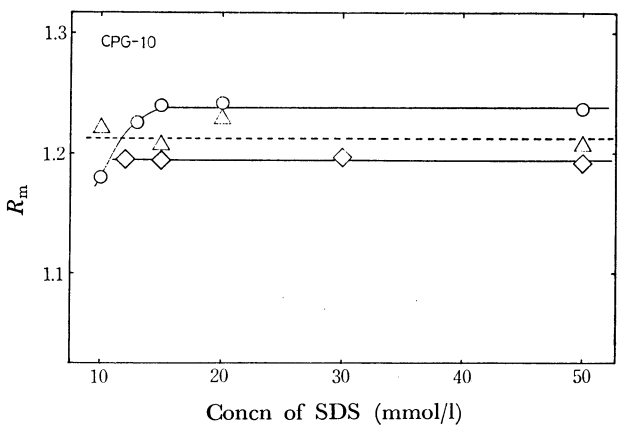

Fig. 7. R_m change of aqueous SDS solution as a function of ethanol concentration. ○, 0 vol% ethanol; △, 10 vol% ethanol; ◇, 20 vol% ethanol.

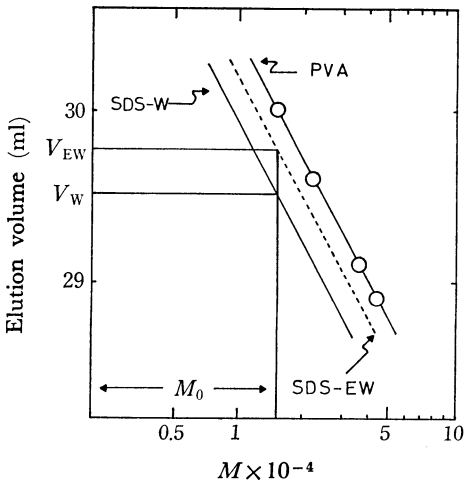

Fig. 8. CPG-10 system calibration curve showing the molecular weights of poly(vinyl alcohol)s relative to V_e as a linear log function.

weight of hydrated poly(vinyl alcohol) (PVA in Fig. 8). Thereby the difference between the amount of the hydration of poly(vinyl alcohol) and that of SDS was taken into account.[7]

To obtain a similar calibration curve for the micelles in an ethanol–water mixture, we measure the elution volume of the micelles both in water (V_W) and in the ethanol–water mixture (V_{EW}) and find the micellar weight (M_0) corresponding to V_W using the SDS-W relation shown in Fig. 8. Then the straight line passing through the point (M_0, V_{EW}) and parallel to the SDS-W line shown as the broken line (SDS-EW) in the figure may be drawn; it is used as the calibration curve for the determination of the micellar weight of SDS in an ethanol–water mixture. Actually, SDS micelles cannot be used for the measurement of V_W and V_{EW} since they undergo a change in size due to the change in solvent composition, while in the above calculation a micellar weight independent of the solvent composition is assumed.

To avoid this trouble, sodium poly(vinyl sulfate) of nearly the same elution volume as that of SDS micelles was used instead of SDS micelles, assuming that the chemical composition and the amount of hydration are like each other. From the measured elution volume of V_m in the ethanol–water mixture, we calculated the micellar weight and, the aggregation

Table 2.

Additives		Aggregation number of micelle: Standard M. W.	Aggregation number of micelle: Laurent-Killander	Amount of hydration of SDS (g/g)
Ethanol	0 vol%	88	80	0.6
	10 vol%	102	—	0.1
	20 vol%	30	—	0.1
NaCl	5 mmol/l	93	91	0.6
	10 mmol/l	104	91	0.6

Concn of SDS, 15 mmol/l

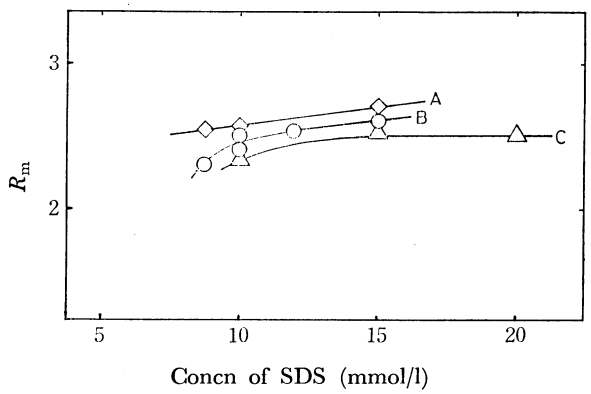

Fig. 9. Dependence of R_m on SDS concentration for different NaCl concentration. A, NaCl 10 mmol/l; B, NaCl 5 mmol/l; C, NaCl 0 mmol/l.

numbers of the SDS micelles. The results are listed in Table 2, together with the amount of hydration of SDS calculated. As may be seen, the aggregation number increases and then decreases with ethanol concentration after showing a maximum. The maximum corresponds to the minimum of CMC mentioned already. It may also be compared with the results of Becher[4] and Herrmann and Benjamin,[3] who showed a decrease in the micellar weight with an increase in the ethanol concentration for nonionic detergents. The amount of hydration is seen to decrease simply with an increase in the concentration of ethanol due to its dehydrating action.

The elution rate of micelles, R_m, in the presence of NaCl is further plotted against the total concentration of SDS (C) in Fig. 9. As may be seen, R_m increased with an increase in the concentration of NaCl.

For the determination of the micellar weight of SDS in an aqueous NaCl solution, a similar method was adopted, but replacing ethanol with NaCl. The elution volume *vs.* the molecular weight of unhydrated SDS micelles in an aqueous NaCl solution was obtained as in the case of Fig. 8. The results thus obtained are listed in Table 2.

The micellar radii of SDS were also calculated according to the Laurent-Killander equation, much as in an earlier report,[7] for both ethanol-water and aqueous NaCl systems; from the results, the aggregation numbers were calculated by taking account of the amount of hydration for the micelles of each system. The results are listed in Table 2. The aggregation numbers of micelles in the aqueous NaCl solution are, on the whole, in agreement with those given in the literature.[13,14] The micellar size was found to increase with an increase in the salt concentration, in agreement with the view that the reduction in the electrical repulsions of the head group of SDS facilitates micellization.[15] The difference in the aggregation numbers of an SDS micelle in water as estimated by the standard molecular weight method and by the Laurent-Killander equation may come from the difference in the methods of estimation, as has been seen in the literature.[13,14]

The author wishes to express his deep gratitude to

Professor Tsunetaka Sasaki of our University for his kind direction and valuable criticism throughout the work.

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