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The Second CMC of the Aqueous Solution of Sodium Dodecyl Sulfate. I. Conductivity

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The conductivity studies of the aqueous solution of sodium dodecyl sulfate (SDS) over the concentration range of 0—0.12 M revealed that there exists a so-called 2nd critical micelle concentration (CMC) at about 65 mM in addition to the 1st CMC at 8.3 mM. The 2nd CMC was greatly influenced by additives; sodium chloride lowered the 2nd CMC, whereas organic substances, such as dodecyl alcohol and *n*-hexane, raised it. Moreover, the specific conductivity-concentration curve of the pure SDS solution broke upward at the 2nd CMC, and its slope increased in the presence of sodium chloride, while it bent toward the concentration axis in the presence of a certain amount of dodecyl alcohol or *n*-hexane. These facts may afford a clue for explaining the micelle structure above the 2nd CMC.

It has been known that, in surfactant solutions, in addition to an initial critical micelle concentration (1st CMC), there occurs a change in the properties of surfactant solutions at a concentration above the 1st CMC, which is usually called the 2nd CMC.

Several works have been done on the 2nd CMC. Tyuzyo *et al.*[1-3] have found a method of estimating the 2nd CMC from the viscosity data. Ekwall and his co-workers[4-9] measured the density, viscosity, and vapor pressure of an aqueous sodium caprylate solution over a wide concentration range above the 1st CMC and discussed the change in the micelle structure. Rovins *et al.*[10] have investigated the 2nd CMC by measuring the viscosity and light-scattering of aqueous solutions of 2-dodecylaminoethanol salts. In our

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laboratory we measured the conductivity and viscosity of the Aerosol-OT solution,[11] the conductivity, sound velocity, and viscosity of sodium dodecyl sulfate (SDS) solution,[12] and the fluorescence spectrum of acridine orange which was added to an SDS solution;[13] the presence of the 2nd CMC was ascertained in these systems. Thus, it has been revealed by various methods that the 2nd CMC exists in surfactant solutions. However, how the shape and size of the micelle vary at the 2nd CMC is still little known.

It is well known that the impurity of an electrolyte or non-electrolyte which is present in a surfactant solution lowers the 1st CMC and increases the micelle size. It can be expected, therefore, that the 2nd CMC may also be greatly influenced by such impurities.

In our studies, SDS was chosen as the surfactant because it is the most typical anionic surfactant and because the properties of its aqueous solution have been extensively studied by many workers and by various methods. In order to obtain some information about the micelle structure, the effect of additives on the properties of the aqueous solution of SDS was investigated. On the other hand, since there is no direct means to determine simultaneously both the size and shape of the micelle, it is difficult to discuss the micelle structure by only one method. In this studies, therefore, the micelle structure of the aqueous solution of SDS was investigated mainly in the concentration region above the 1st CMC, through systematic studies including measurements of the conductivity, light-scattering, density, viscosity, and depolarization of fluorescence. In the present paper, which is the first of a series of our studies, the results of the conductivity measurements will be reported.

Experimental

Materials. SDS was synthesized according to the method of Dreger.[14] Dodecyl alcohol (DA) was obtained from the Wako Pure Chemical Co., and its purity was determined by means of gas chromatography as 99.7%. The sulfonation of the DA was carried out by adding the DA, drop by drop, to an acetic acid solution of chlorosulfonic acid. The SDS thus obtained was recrystallized several times from the conductivity water and butyl alcohol respectively, and was then purified by a liquid/liquid extraction technique in which a 10% solution of SDS in 50% aqueous alcohol was extracted with 60/80 petroleum ether for 48 hr.[15] Reagent-grade benzene and hexane were purified by fractional distillation. Ultra-pure sodium chloride was obtained from the E. Merck Co. and was used without further purification.

Procedures. The conductivity measurements were carried out by using the apparatus previously described.[16,17] Unplatinized electrodes were employed in order to minimize the adsorption.[18] The concentration of the solution was changed successively by diluting it with conductivity water. The conductivity was measured in a water-thermostat of 25.000±0.005°C after the temperature equilibrium had been established.

In the case of the presence of organic additives, the solutions for conductivity measurements were prepared as follows. Thirty milliliters of a 0.15 M SDS solution were taken in a glass ampoule, and a known amount of DA was added to it. The amount of DA added was below the saturation point.[19] The ampoule was sealed after having been cooled by liquid nitrogen and shaken in a thermostat of 25°C for 48 hr in order to attain an equilibrium of solubilization. A series of ampoules was prepared, each of which contained DA; the molar ratios of DA to SDS were 1/200, 1/100, 1/50, 1/10, and 1/5. The same procedure was also used in the preparation of SDS solutions containing various amounts of solubilized benzene or hexane.[20,21]

Results

No Additives. In general, the 1st CMC of a surfactant solution is determined graphically as the break point in the plot of the specific conductivity *vs.* the concentration. The results of the conductivity measurement of an aqueous solution of SDS in the absence of additives are shown in Fig. 1, where the specific conductivity (κ) is plotted against the concentration of the SDS solution. It may be seen from this figure that a break point appears at about 65 mM in addition to that at 8.3 mM, the latter corresponds to the 1st CMC, while the former, the so-called 2nd CMC, agrees fairly well with the results obtained by other methods.[11-13] It may also be noted that the specific conductivity-concentration curve breaks upward at the 2nd CMC.

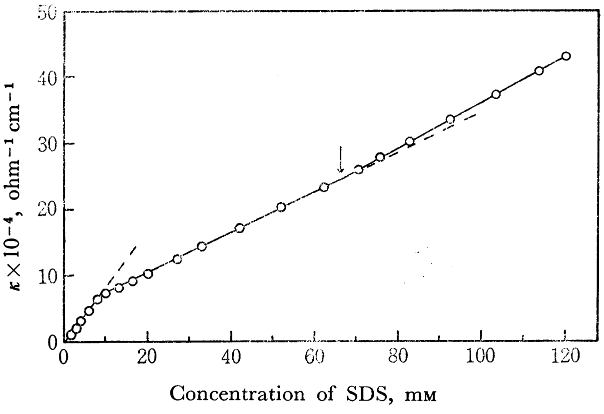

Fig. 1. Specific conductivity of SDS solution. The arrows in Figs. 1 and 2 indicates the 2nd CMC.

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Effect of Sodium Chloride. In general, crude SDS is apt to contain sodium chloride as an impurity, for the latter is formed as a by-product in the process of the synthesis of SDS. Therefore, the effect of sodium chloride on the 2nd CMC of the aqueous solution of SDS was investigated. The specific conductivities of SDS solutions containing various amounts of sodium chloride are plotted against the concentration of SDS in Fig. 2. The 1st CMC of the SDS solution lowers with an increase in the concentration of sodium chloride; this is in agreement with the results obtained by other workers. It is interesting to note that the 2nd CMC lowers and the slope of straight line above the 2nd CMC rises with an increase in the sodium chloride concentration.

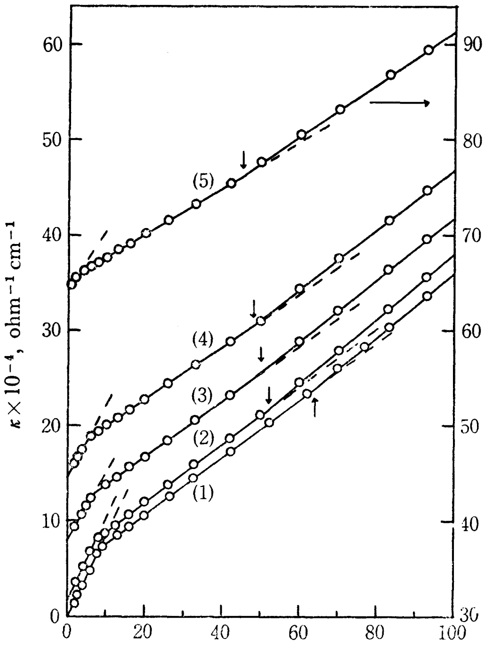

Fig. 2. Specific conductivities of SDS solutions in the presence of NaCl; concentration of NaCl: (1) 0 M, (2) 0.001 M, (3) 0.005 M, (4) 0.01 M, (5) 0.05 M. The plot in the presence of 0.0005 M NaCl was omitted in this figure.

Figure 3 shows the deviation of the specific conductivity ($\Delta\kappa$) from the extrapolation of the linear plot of the specific conductivity *vs.* the concentration below the 2nd CMC in Fig. 2 to a higher concentration. It may be seen from the figure that $\Delta\kappa$ is positive regardless of the sodium chloride concentration and that the angle (α) formed by the two straight lines increases with the sodium chloride concentration.

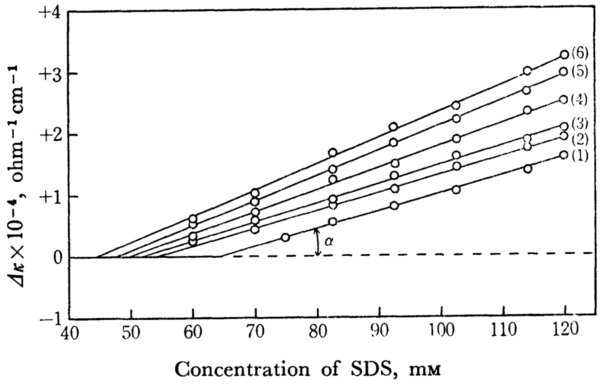

Fig. 3. $\Delta\kappa$ of SDS solutions in the presence of NaCl; concentration of NaCl: (1) 0 M, (2) 0.0005 M, (3) 0.001 M, (4) 0.005 M, (5) 0.01 M, (6) 0.05 M.

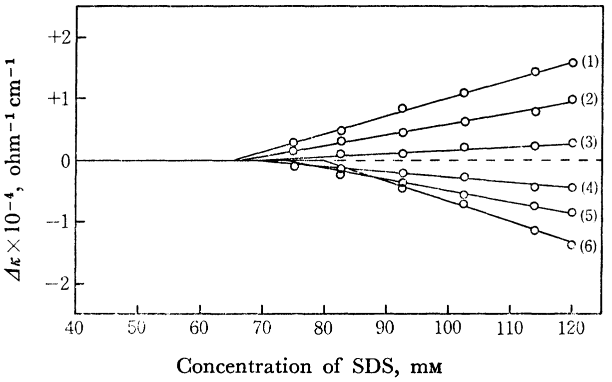

Fig. 4. $\Delta\kappa$ of SDS solutions in the presence of DA; molar ratio of DA to SDS: (1) 0, (2) 1/200, (3) 1/100, (4) 1/50, (5) 1/10, (6) 1/5.

Effect of Dodecyl Alcohol. It is well known that DA, which is the main starting material in the syntheses of SDS, is apt to remain unreacted as a contaminant in crude SDS and has a profound influence upon the properties of the SDS solution. Therefore, the effect of DA on the 2nd CMC of the aqueous solution of SDS was investigated. DA was added to a SDS solution in a molar ratio of DA to SDS, 1/200, 1/100, 1/50, 1/10, or 1/5. The results of the conductivity measurements are presented in Fig. 4, where $\Delta\kappa$ is plotted against the concentration of SDS. The slope of the straight line above the 2nd CMC becomes lower with an increase in the concentration of DA, that is, $\Delta\kappa$ decreases and at last becomes negative when the DA is added in a molar ratio of 1/50 or more to the SDS solution. Moreover, the 2nd CMC increases with the DA concentration. It is of great interest that the results in the presence of DA are quite the opposite of those in the presence of sodium chloride.

Effects of n-*Hexane and Benzene.* Next the effect of non-polar compounds on the properties of the SDS solution were studied. Here, *n*-hexane with a

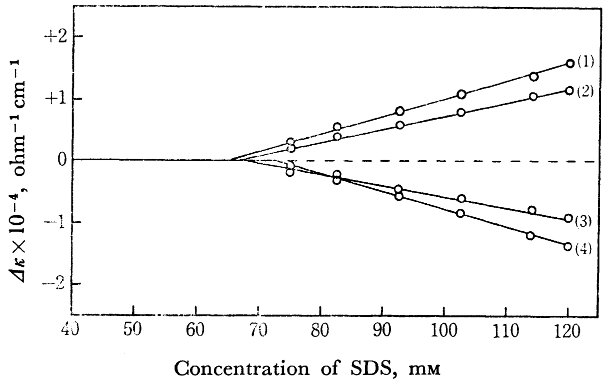

Fig. 5. $\Delta\kappa$ of SDS solutions in the presence of *n*-hexane; molar ratio of *n*-hexane to SDS: (1) 0, (2) 1/100, (3) 1/15 (4) 1/4.

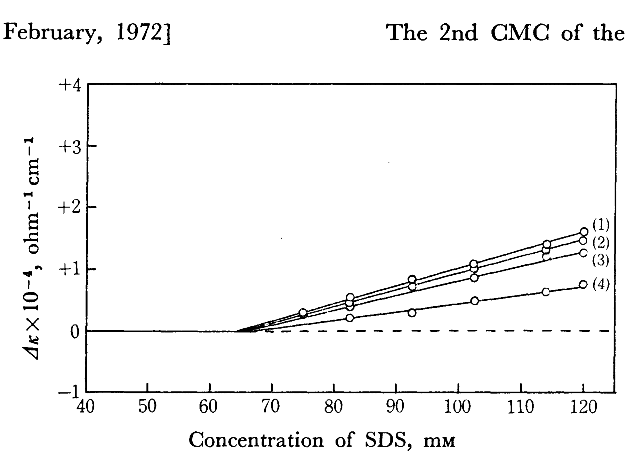

Fig. 6. $\Delta\kappa$ of SDS solutions in the presence of benzene; molar ratio of benzene to SDS: (1) 0, (2) 1/100, (3) 1/10, (4) 1/2.

chain structure and benzene with a ring structure were selected as representatives of nonpolar compounds. The results obtained in the presence of *n*-hexane and those obtained in the presence of benzene are shown in Figs. 5 and 6 respectively. The effect of *n*-hexane is quite similar to that of DA, while benzene does not have such a marked effect.

Effect of Sodium Chloride and DA. Since sodium chloride and DA generally coexist in crude SDS, the effect of these two compounds on the conductivity behavior of the SDS solution was studied; the results are shown in Fig. 7. As may be in Figs. 3 and 4, the results in the presence of sodium chloride are opposed to those in the presence of DA with respect to the 2nd CMC and the slope of the specific conductivity *vs.* the concentration curve above the 2nd CMC. However, when the two compounds coexist, their effects on these two properties compensate each other, as can be seen in Fig. 7.

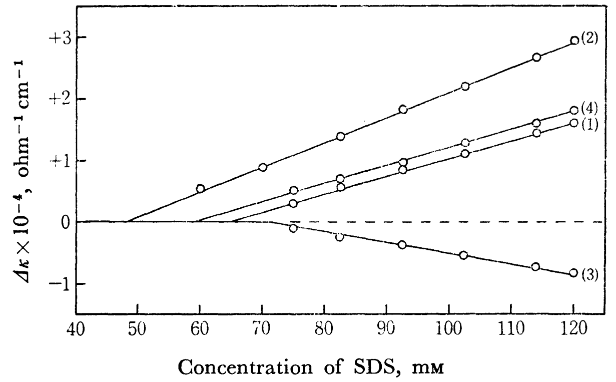

Fig. 7. $\Delta\kappa$ of SDS solutions; (1) no additive, (2) 0.01 M NaCl, (3) DA to SDS 1/10, (4) 0.01 M NaCl and DA in molar ratio of DA to SDS 1/10.

Discussion

As is obvious from Fig. 1, the specific conductivity *vs.* concentration curve of the pure SDS solution breaks upward at the 2nd CMC. When a certain amount of DA is added to the SDS solution, the curve breaks downward, as is seen in Fig. 4. Similar results were obtained for the system of sodium decyl sulfate and decyl alcohol, as is shown in Fig. 8, where the sodium decyl sulfate used was carefully purified. In our previous study,[12] the curve bent toward the concentration axis. This may result from the presence of organic impurities such as DA.

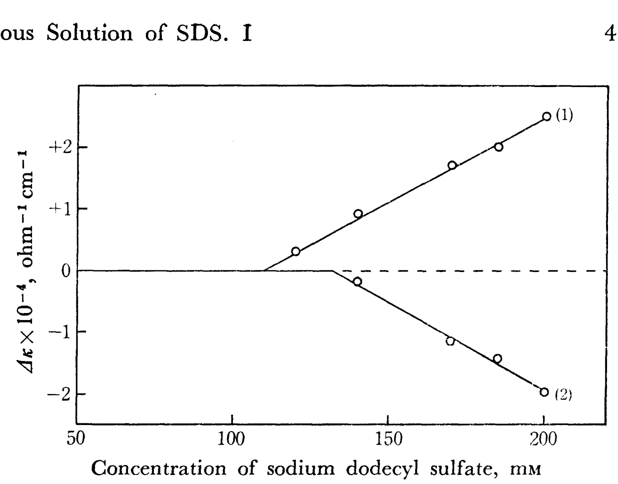

Fig. 8. $\Delta\kappa$ of sodium decyl sulfate solutions; (1) no additive, (2) decyl alcohol in its molar ratio to sodium decyl sulfate 1/10.

In general, the purity of the surfactant can be checked by means of the value of the 1st CMC or by the presence or absence of the minimum in the surface tension *vs.* concentration curve. By the present study, another criterion for the purity of the surfactant was found: the presence of organic contaminants in the surfactant solution can be checked by means of the value of the 2nd CMC and the slope of the specific conductivity *vs.* concentration curve.

In the presence of sodium chloride, the 2nd CMC as well as the 1st CMC lowers, and at the same time $\Delta\kappa$ increases, with an increase in its concentration. On the other hand, in the presence of DA or *n*-hexane, though the 1st CMC loweres, as is well known, the 2nd CMC increases and $\Delta\kappa$ decreases and finally becomes negative with an increase in the concentration of DA or *n*-hexane. It is clear from these results that nonelectrolytes have the same influence on the 1st CMC, but have quite the opposite influence on the 2nd CMC, as compared with electrolytes. These facts may afford a clue for elucidating the micelle structure above the 2nd CMC.

As can be expected from the results shown in Figs. 4 and 5, the specific conductivity *vs.* concentration curve may show no change at the concentration corresponding to 2nd CMC when an appropriate amount of non-electrolyte is present, *e.g.*, an intermediate quantity between 1/100 and 1/50 in molar ratio in the case of DA. The same situation can be deduced when an electrolyte coexists with a non-electrolyte in a certain molar ratio, as can be seen in Fig. 7. In such cases, there may be no 2nd CMC; the presence of a proper amount of the impurities of non-electroytes may stabilize the micelle formed in the region of low concentrations.

Though both *n*-hexane and benzene are nonpolar compounds, the former has a much larger influence upon the 2nd CMC than the latter, as may be seen in Figs. 5 and 6. This may arise from the difference in the mode of solubilization between these two compounds.