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The Second CMC of the Aqueous Solution of Sodium Dodecyl Sulfate. II. Viscosity and Density

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Our viscosity and density studies of an aqueous solution of sodium dodecyl sulfate have revealed that the 2nd critical micelle concentration (CMC) exists in addition to the 1st CMC and that the 2nd CMC is greatly influenced by such additives as sodium chloride, dodecyl alcohol, and benzene; these results are in good agreement with those obtained from the conductivity measurements described in the previous paper. The reduced viscosity of the micelle ($\eta_{sp.m}/C_m$) *vs.* C_m curve showed a knick at the concentration corresponding to the 2nd CMC as obtained by Tyuzyo and his co-workers. The molar volume of the hydrated micelle was calculated by using the equation: $\eta_{r.m}=1+2.5\phi_m+14.1\phi_m^2$; it has been found to decrease at about the 2nd CMC, similarly to the partial specific volume ($\bar{v}$) of SDS obtained from the density measurement. This may be attributed to a change in the micelle structure at the 2nd CMC, caused by a variation in the type of aggregation and by a decrease in the counter-ion binding by the micelle.

In our previous paper (Part 1), the micelle structure of an aqueous solution of sodium dodecyl sulfate (SDS), mainly in the concentration region above the 1st critical micelle concentration (CMC), has been studied from the point of view of conductivity measurements.[1] It was revealed by the conductivity studies that a so-called 2nd CMC exists at about 65 mM in addition to the 1st CMC at 8.3 mM, and also that the 2nd CMC is greatly influenced by such additives as sodium chloride, dodecyl alcohol, and benzene.

In the present study, density and viscosity measurements were carried out in order to obtain some more information about the micelle structure of the aqueous solution of SDS. This study can be expected to afford a new clue for clarifying the micelle structure above the 2nd CMC.

Experimental

Materials. The SDS, sodium chloride, dodecyl alcohol, and benzene used in this study were the same as those described in our previous paper,[1] and the aqueous solutions of SDS, both in the absence and presence of the additives, were prepared in the same manner as in the above work.

Procedures. A capillary viscometer of the Ubbelohde type was designed and employed to minimize the effect of the surface tension. Since dust has a great influence upon the flow time, particular attention was given to protect the solution from contamination with dust; the entrances of the viscometer were equipped with glass-filters, the viscometer was carefully cleaned and rinsed with dust-free, distilled water and alcohol, and the solution was introduced into the viscometer through a glass-filter. The flow time was determined by repeating the measurements at least four times, using a stop-watch, in a water-thermostat of 25.000± 0.005°C after the temperature equilibrium had been established. The flow time of pure water was 570.00 sec. The density was measured by using pycnometers of the improved Ostwald type,[2] with capacities of 9—10 m*l*.

Results and Discussion

Viscosity, No Additive. The relative viscosity (η_r) of the aqueous solution of SDS is plotted against the concentration of SDS in Fig. 1a. As may be seen from this figure, 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.[1,3,4]

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[1] M. Miura and M. Kodama, This Bulletin, **45**, 428 (1972).

[2] Hennion, *Ind. End. Chem., Anal. Ed.*, **9**, 479 (1937).

[3] T. Yasunaga, H. Oguri, and M. Miura, *J. Colloid Interface Sci.*, **23**, 352 (1967).

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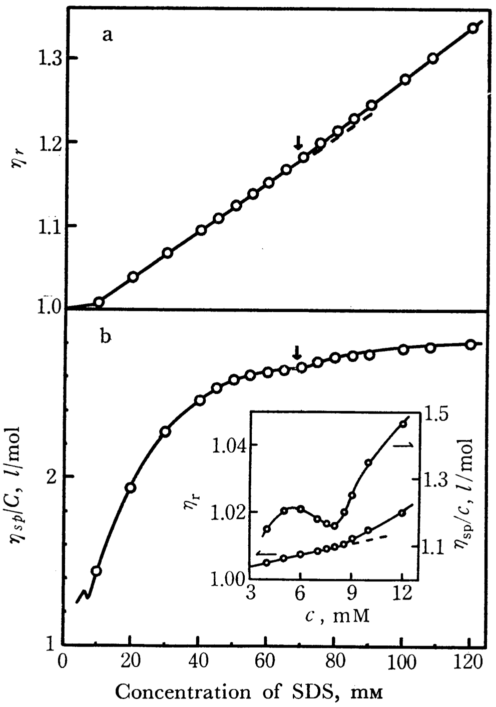

Fig. 1. Relative and reduced viscosities of SDS solution. The arrow in the figure indicates the 2nd CMC. a: Relative viscosity. b: Reduced viscosity. The viscosities in the neighborhood of the 1st CMC are shown under enlargement in Fig. 1b.

The reduced viscosity (η_{sp}/C) is also plotted against the concentration in Fig. 1b ; the results in the neighborhood of the 1st CMC are also shown in an enlarged form in Fig. 1b. As can be seen in Fig.1b, the reduced viscosity shows a minimum at the 1st CMC, as was found by Tyuzyo and his co-workers,[5,6] and then increases markedly above the 1st CMC. Tyuzyo and his co-workers did the following operations, presuming that above the 1st CMC the concentration of the detergent monomer in a solution which is in equilibrium with the micelle is almost constant:—

$$C_m = C - C_{cmc(\mathrm{I})}, \tag{1}$$

$$C_m{}^\circ = C_{cmc(\mathrm{II})} - C_{cmc(\mathrm{I})}, \tag{2}$$

$$\eta_{sp\cdot m}/C_m = (\eta_{r\cdot m} - 1)/C_m = (\eta_r/\eta_{r\cdot cmc(\mathrm{I})} - 1)/C_m, \tag{3}$$

$$[\eta_1]_m = \lim_{C_m\to 0}(\eta_{sp\cdot m}/C_m), \tag{4}$$

$$[\eta_2]_m = \lim_{C_m\to C_m{}^\circ}(\eta_{sp\cdot m}/C_m), \tag{5}$$

where C is the total concentration of SDS; C_m is the concentration of a micellar substance; $C_{cmc(\mathrm{I})}$ and $C_{cmc(\mathrm{II})}$ are the 1st and 2nd CMC's as obtained from viscosity measurements respectively; $\eta_{r.cmc(\mathrm{I})}$ is the relative viscosity of the solution against water at the 1st CMC; $\eta_{r.m}$ and $\eta_{sp.m}/C_m$ are the relative and reduced viscosities of the micellar substance respectively, and $[\eta_1]_m$ and $[\eta_2]_m$ are the intrinsic viscosities of the micellar substance at the 1st and 2nd CMC's respectively.

The reduced viscosity of micellar SDS, as obtained from Eq. (3), is plotted against the concentration of micellar SDS in Fig. 2, where a knick corresponding to the 2nd CMC appears as in the experiments done by Tyuzyo and his co-workers.[5,6] The values of $[\eta_1]_m$ and $[\eta_2]_m$ obtained from Fig. 2 by means of Eqs. (4) and (5) are, respectively, 2.0 and 2.8; those values agree fairly well with the reference values.[6]

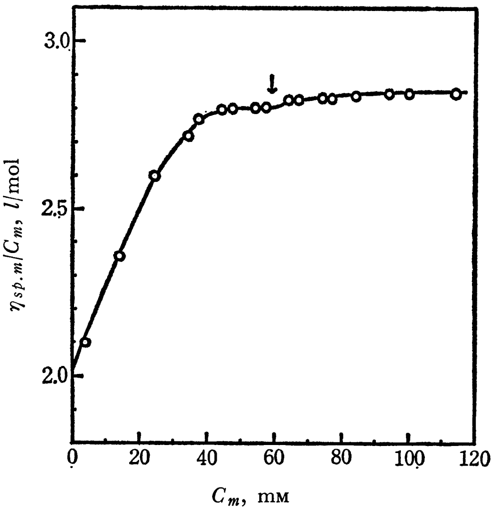

Fig. 2. Reduced viscosity of SDS micelle.

The Guth and Simha equation,[7] which is a form of the Einstein equation extended for use with more concentrated solutions, was used in the present case:

$$\eta_r = 1 + 2.5\phi + 14.1\phi^2. \tag{6}$$

In this equation, ϕ is the volume fraction occupied by particles. It may be necessary to discount the detergent monomer, which play no role as a micellar substance, in the application of Eq. (6) to a micelle system. Therefore, on the assumption that the monomer concentration remains constant above the 1st CMC, the following equation can be obtained for the concentrated solutions containing the spherical micelles:

$$\eta_{r\cdot m} = 1 + 2.5\phi_m + 14.1\phi_m{}^2, \tag{7}$$

where ϕ_m is the volume fraction of hydrated micelles. The value of ϕ_m was calculated by the use of Eq.(7). The molar volume of the hydrated micelle (V_m) was obtained from this relation: $V_m = \phi_m/C_m$. The values of ϕ_m and V_m obtained in this manner are plotted against C_m in Figs. 3a and 3b respectively. It may be seen from these figures that ϕ_m increases linearly with C_m up to the 2nd CMC at about C=55 mM, while, in the range above the 2nd CMC, the curve bends toward the C_m axis, and that this phenomenon is reflected in the V_m *vs.* C_m curve—that is, V_m takes a nearly constant value up to the 2nd CMC and then decreases gradually. The values of V_m in the (I) and (II) parts in Fig. 3b are 0.91 l/mol and 0.80 l/mol respectively. These results may support the view that, in the concentration range between the 1st CMC and the 2nd CMC, the SDS micelle is spherical with a nearly constant volume ($V_{m(\mathrm{I})}$), while above the 2nd CMC it is deformed from the spherical shape to an asymmetric one, accompanied by a decrease in the

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5) N. Sata and K. Tyuzyo, This Bulletin, **26**, 177 (1953).

6) H. Okuyama and K. Tyuzyo, *ibid.*, **27**, 259 (1954).

7) E. Guth and R. Simha, *Kolloid-Z.*, **74**, 266 (1936).

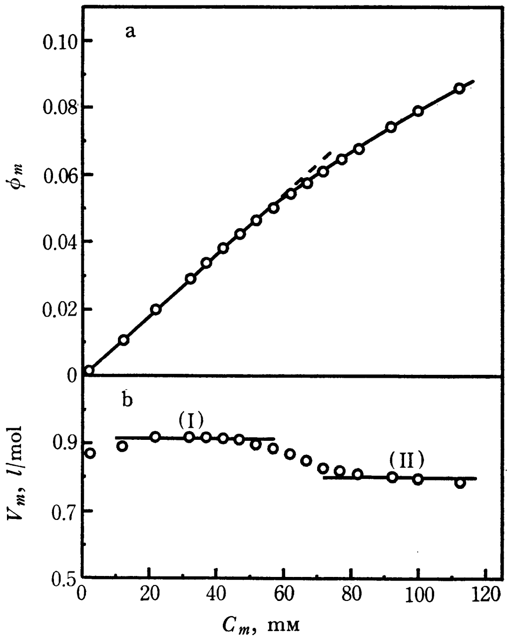

Fig. 3. a: Volume fraction of SDS micelle. b: Molar volume of the hydrated micelle of SDS.

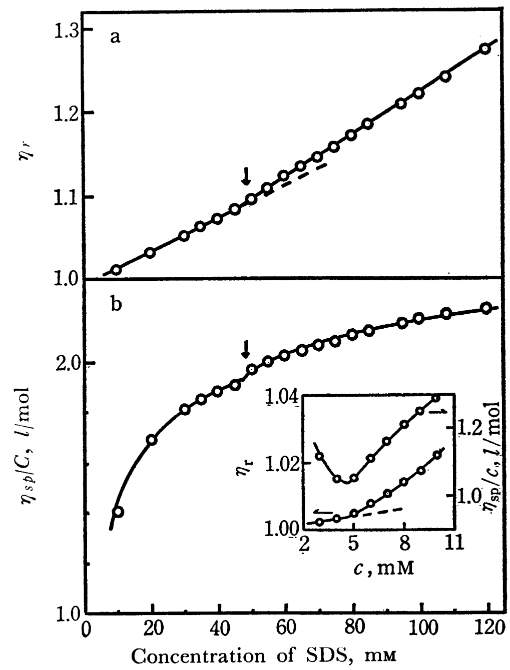

Fig. 4. Relative and reduced viscosities of SDS solution in the presence of 0.01 M NaCl. a: Relative viscosity. b: Reduced viscosity. The viscosities in the neighborhood of the 1st CMC are shown under enlargement in Fig. 4b.

molar volume ($V_{m(\mathrm{II})}$[8–12])

Effect of Sodium Chloride. The results of the viscosity measurements of the SDS solution containing 0.01 M sodium chloride are shown in Fig. 4, while those in the neighborhood of the 1st CMC are shown in the same figure in an enlarged form. The 2nd CMC as well as the 1st CMC is lowered and at the same time the slope of the curve above the 2nd CMC is raised, compared with the results shown in Fig. 1a; this is in agreement with the results obtained by the conductivity measurements. The reduced viscosity of micellar SDS containing 0.01 M sodium chloride is shown in Fig. 5. It may also be seen from this figure that the knick at the concentration corresponding to the 2nd CMC is more remarkable than that in the absence of sodium chloride. The values of $[\eta_1]_m$ and $[\eta_2]_m$ are, respectively, 1.4 and 2.0; each of those values is lower than the value in the absence of an additive. In the presence of sodium chloride, the decrease in the $[\eta_1]_m$ or $[\eta_2]_m$ value may be due to the electroviscus effect predicted for charged systems.[13–16]

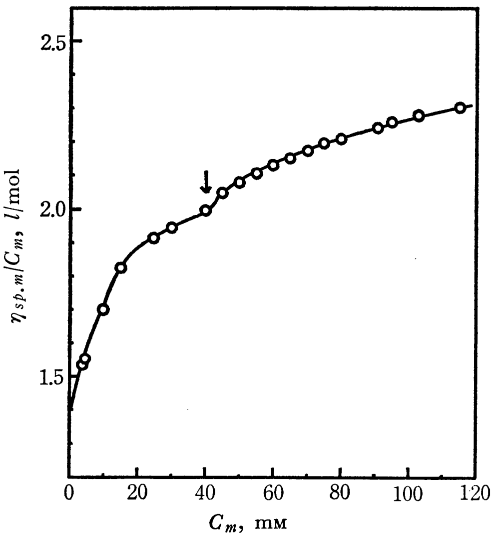

Fig. 5. Reduced viscosity of SDS micelle in the presence of 0.01 M NaCl.

Effect of Dodecyl Alcohol (DA). The results of the viscosity measurements of the SDS solution containing DA in a 1/10 molar ratio of DA to SDS are shown in Fig. 6, where the relative and reduced viscosities are plotted against the concentration of the SDS solution. It may be seen from this figure that no change appears at the concentration corresponding to the 2nd CMC. In this case, there may be no 2nd CMC. It can be concluded from the viscosity measurements, much as in the case of the conductivity measurements, that the presence of a proper amount of DA stabilizes the micelle in the region of low concentrations.

Effect of Benzene. The viscosity measurements of the SDS solution containing benzene in a molar

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

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

10) F. Iwadare and T. Suzawa, *Nippon Kagaku Zasshi*, **90**, 50 (1969).

11) P. Ekwall and P. Holmberg, *Acta Chem. Scand.*, **19**, 455, 573 (1965).

12) P. Ekwall, L. Mandell, and P. Solyom, *J. Colloid Interface Sci.*, **35**, 519 (1971).

13) F. Booth, *Proc. Roy. Soc.* (London), **A 203**, 514, 533 (1950).

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15) P. Mukerjee, *J. Colloid Sci.*, **19**, 722 (1964).

16) C. Tanford and J. G. Buzzell, *J. Phys. Chem.*, **60**, 225(1956).

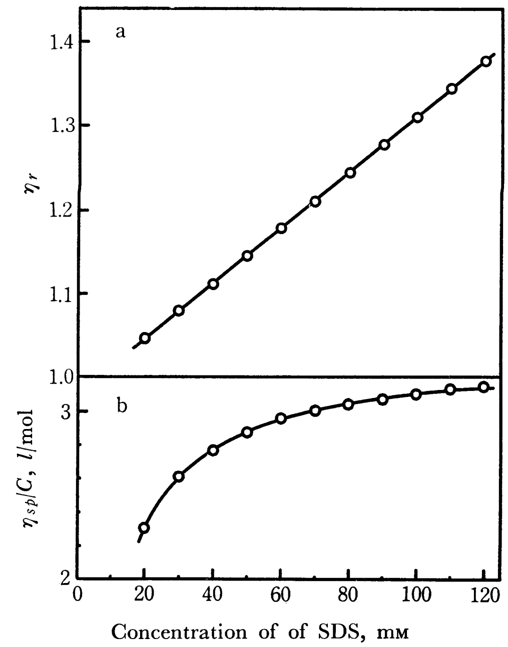

Fig. 6. Relative and reduced viscosities of SDS solution in the presence of DA in a molar ratio of DA to SDS, 1/10. a: Relative viscosity. b: Reduced viscosity.

of 1/4 were also carried out. The results obtained were almost the same as those obtained in the absence of additives, represented in Fig. 1; benzene has no remarkable influence upon the 2nd CMC, a finding in agreement with the results obtained by the conductivity measurements.

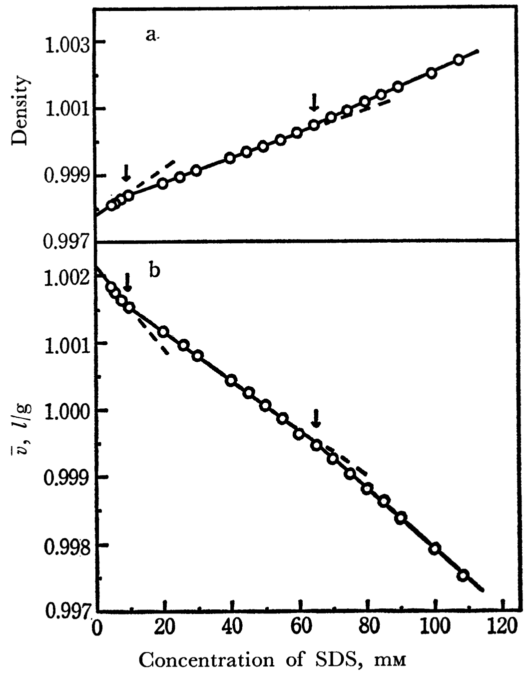

Fig. 7. a: Density of SDS solution. b: Specific volume of SDS solution.

Density. The partial specific volume of SDS ($\bar{v}$) is calculated on the basis of the following equation (8):[17,18]

$$\bar{v} = v + (1-x)\mathrm{d}v/\mathrm{d}x, \tag{8}$$

where v is the specific volume of the solution and x, the concentration of the solute per gram of the solution. The value of $\mathrm{d}v/\mathrm{d}x$ can be evaluated graphically from the v *vs.* x curve. The density and the specific volume of the aqueous solution of SDS in the absence of an additive are plotted against the concentration in Figs. 7a and 7b respectively. As may be seen from this figure, a break point exists at the 2nd CMC in addition to that at the 1st CMC. The partial specific volume of SDS is shown in Fig. 8; after taking a practically constant value (I) in the concentration range below the 1st CMC, the partial specific volume increases rapidly at about the 1st CMC, remains constant (II) again over a wide concentration range up to the 2nd CMC, then decreases at about the 2nd CMC, and again remains constant (III) above the 2nd CMC. The values of v were estimated from the figure to be 0.871 ml/g and 0.851 ml/g in the (II) and (III) parts respectively. It may be noted that the behavior of the partial specific volume is quite similar to that of the hydrated molar volume obtained from the viscosity measurements shown in Fig. 3b. The partial specific volume and the hydrated molar volume both remain constant in the concentration range between the 1st CMC and the 2nd CMC. This may imply that the micelle structure — that is, the micelle size and shape — does not change in this concentration range.[19] The marked decreases in the partial specific volume and the hydrated volume at the 2nd CMC may be attributed to the change in the micelle structure; the SDS molecules, of which the micelle is composed, occupy a smaller space above the 2nd CMC than below the 2nd CMC as a result of a change in the type of aggregation.

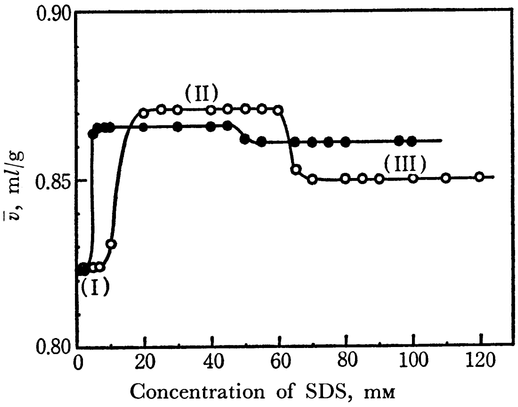

Fig. 8. Partial specific volume of SDS. ○: No additive, ●: 0.01 M NaCl.

Ekwall and his co-workers have observed, from their measurements of the viscosity[12] and density[19] of sodium caprylate solutions, that both the hydrated molar volume and the partial specific volume increased at about the 2nd CMC; they have concluded that these phenomena may be attributed to an increase

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[17] H. Lal, *J. Colloid Sci.*, **8**, 414 (1953).

[18] P. Mukerjee, *J. Phys. Chem.*, **66**, 1733 (1962).

[19] P. Ekwall, H. Eikrem, and L. Mandell, *Acta Chem. Scand.*, **17**, 111 (1963).

in the binding force between the micelle and the counter ion above the 2nd CMC. It is interesting to note that these two kinds of volumes of SDS decrease at the 2nd CMC, contrary to the results obtained by Ekwall and his co-workers. It was revealed from the conductivity measurements of the SDS solutions that the specific conductivity-concentration curve breaks upward at the 2nd CMC.[1) On the assumption that this conductivity behavior may be caused at least partly by an increase in the free counter ion (Na^+) as a result of a decrease in the counter-ion binding by the micelle, the decrease in the hydrated molar volume or the partial specific volume is explicable; the former may be ascribed to the dehydration of the SDS micelle resulting from a decreased counter-ion binding of the micelle, while the latter may be ascribed to a decrease in the volume of the SDS solution due to the interaction between the free counter ion and water, because the partial volume can be regarded as the sum of the volume of the ions themselves and that of the volume change of the solvent associated with the solvent-solute interaction.[18) The partial specific volume of SDS in the presence of 0.01 M sodium chloride is also represented in Fig. 8. The degree of decrease in the partial specific volume above the 2nd CMC is much smaller than that in the absence of sodium chloride. These problems will be discussed in detail later, with more experimental data.