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The Second CMC of the Aqueous Solution of Sodium Dodecyl Sulfate. III. Light-scattering

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In our previous papers, the micelle structure of the aqueous solution of sodium dodecyl sulfate (SDS) has been investigated, mainly in the concentration region above the 1st critical micelle concentration (CMC), through the measurements of the conductivity,[1] the viscosity, and the density.[2] In the present study, the light-scattering measurements were carried out in order to obtain further information about the micelle structure of the aqueous solution of SDS.

Experimental

Dust-free water was obtained by the distillation method.[3] The SDS solutions were prepared in the same way as has previously been described[1] and then repeatedly filtered through a Graba-type filtering apparatus (membrane ultrafilter, No. 8) under a pressure of 5—10 cmHg until the solutions became completely clear. The light scattering was measured with a Brice-type light-scattering photometer (Shimadzu Seisakusho) using a semioctagonal cell. The reduced scattering intensities (R_θ) at θ=45, 90, and 135° were calculated by the following equation:

$$R_\theta = \phi_\theta \cdot G_\theta / G_0 \qquad (1)$$

where G_θ and G_0 are the intensities of the scattered light at θ° and 0° respectively, and where ϕ_θ is the apparatus constant, which was determined by using the Rayleigh ratio (R_{90}) of benzene.[4] The refractive index increments (dn/dC) were measured with a Debye-type differential refractometer (Shimadzu Seisakusho). All the measurements were made at 25°C and at the wavelengths of 436 and 546 mμ.

Results and Discussion

Figure 1 shows a plot of R_{90} against the concentration of SDS in the neighborhood of the 1st CMC. R_{90}

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

2) M. Kodama and M. Miura, *ibid.*, **45**, 2265 (1972).

3) M. Nakagaki and H. Inagaki, "Hikari Sanran Zikken Hou," Nankodo, Tokyo (1965), p. 108.

4) C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 1616 (1950).

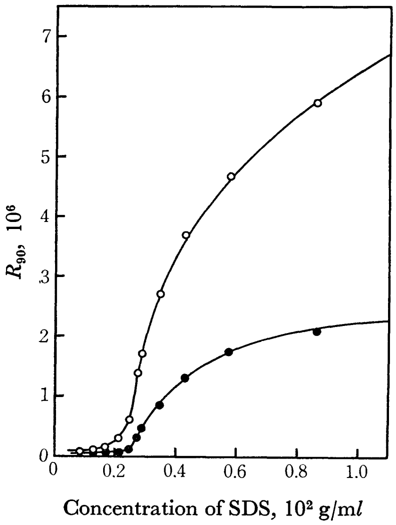

Fig. 1. Light-scattering of SDS solution in the neighborhood of the 1st CMC.
—○—: R_{90} at 436 mμ, —●—: R_{90} at 546 mμ.

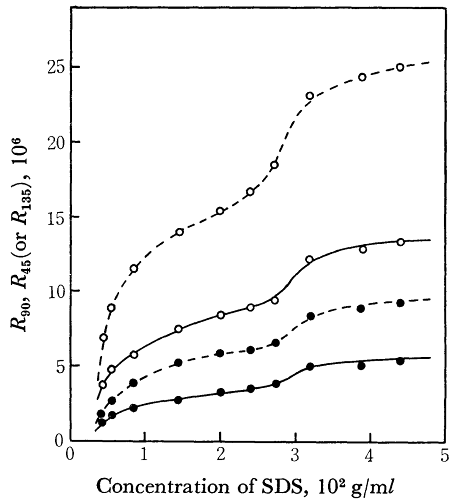

Fig. 3. Light-scattering of SDS solution in the neighborhood of the 2nd CMC.
—○—: R_{90} at 436 mμ, —●—: R_{90} at 546 mμ, --○--: R_{45}(or R_{135}) at 436 mμ, --●--: R_{45} (or R_{135}) at 546 mμ.

remains small until the 1st CMC is reached, and then it increases with the concentration of the SDS solution. As is well-known, the Debye Eq. (2) is used to calculate the micellar molecular weight; the reciprocal of the micellar molecular weight is obtained by plotting $K(C-C_0)/(R_{90}-R_{90,0})$ against $(C-C_0)$:

$$K(C-C_0)/(R_{90}-R_{90,0}) = 1/M + 2B(C-C_0), \qquad (2)$$

where $R_{90,0}$ is the Rayleigh ratio at the 1st CMC, M is the micellar molecular weight, B is a constant, C is the concentration of the solution (g/ml), C_0 is the 1st CMC, $K=2\pi^2 n_0^2(\partial n/\partial C)^2/N_A\lambda^4$, n and n_0 are the refractive indices of solution and solvent respectively, N_A is the Avogadro number, and λ is the wavelength of the light.

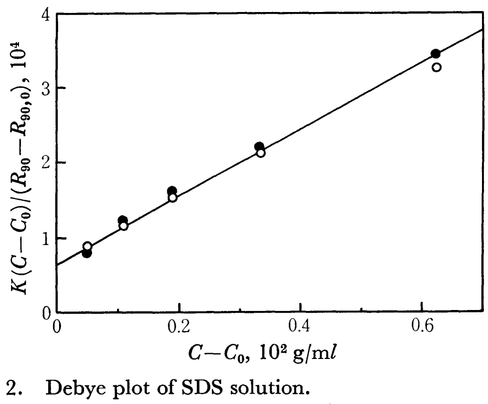

Fig. 2. Debye plot of SDS solution.
—○—: 436 mμ, —●—: 546 mμ.

As can be seen in Fig. 2, the Debye plot for the SDS solutions shows a linear nature at low micellar concentrations. Since the Debye equation is strictly valid only for the uncharged colloidal particles, it is necessary to take into account the effect of the charge of the micelles on the light-scattering properties. Therefore, the aggregation number and also the micellar molecular weight were calculated by using the equation[5] corrected for the effect of the charge of the micelles. The values thus obtained were 60 and 17200 respectively, in fairly good agreement with those obtained by Mysels and Princen.[5]

TABLE 1. THE 1ST AND 2ND CMC'S OF SDS SOLUTION

1st CMC (mmol/l)	2nd CMC (mmol/l)	Method
8.3	70	Light-scattering
8.3	65	Conductivity[1]
8.0—8.5	65—70	Viscosity[2]
8.5	65	Density[2]

The values of R_{90} and R_{45} (or R_{135}) in the high-concentration region of the SDS solution are plotted against the concentration in Fig. 3. It may be noted from this figure that R_{90} shows a marked rise at the concentration corresponding to the 2nd CMC,[1,2] as it does at the 1st CMC in Fig. 1, and that the behavior of R_{45} (or R_{135}) is quite similar to that of R_{90}. The 1st and 2nd CMC's obtained in the present study are listed in Table 1 along with those reported in previous works.[1,2] Ekwall and his co-workers[6] measured the light-scattering of the aqueous solution of cetyl trimethylammonium bromide and found that there is an extremely marked rise in the intensity of the scattered light in the high-concentration region above the 1st CMC. Robins and Thomas[7] also observed similar light-scattering behavior in aqueous solutions of 2-dodecylaminoethanol salts. In our previous paper, the viscosity and density studies of the aqueous solution of SDS revealed that, below the 2nd CMC, only one type of micelle, with an almost constant size and shape, spherical or nearly so, may exist but that at the 2nd CMC there occurs a change in the micelle structure caused by a variation in the type of aggregation of SDS molecules and by a decrease in the counter-ion

5) K. J. Mysels and L. H. Princen, *J. Phys. Chem.*, **63**, 1696 (1959).
6) P. Ekwall, L. Mandell, and P. Solyom, *J. Colloid Interface Sci.*, **35**, 519 (1971).
7) D. C. Robins and I. L. Thomas, *ibid.*, **26**, 415 (1968).

binding by the micelle. Very recently, we found, from our measurements of the fluorescence depolarization of acridine dye solubilized in the SDS micelle, that the micellar volume at the 2nd CMC increases by *ca.* 30% more than that below the 2nd CMC.[8]

It can be concluded, therefore, that the marked rise of R_{45}, R_{90}, and R_{135} at about the 2nd CMC is to be attributed to a certain change in the micelle structure, probably an increase in the size of the micelle. On the other hand, the dissymmetry (Z_{45}), expressed as the ratio of R_{45} to R_{135}, will provide available information regarding the shape of micelle. The values of Z_{45}, however, were in the region of 1.00—1.02 over the whole range of SDS concentrations investigated. Therefore, even in the high-concentration region, the size of the SDS micelle may be too small to cause any appreciable dissymmetry in the scattered light.[9]

8) Y. Kubota, M. Kodama, and M. Miura, to be published.

9) P. Debye and E. W. Anacher, *J. Phys. Colloid Chem.*, **55**, 644 (1951).