Formation of Spherical and Rod-like Micelles of Cetyltrimethylammonium Bromide in Aqueous NaBr Solutions

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Static light scattering from aqueous NaBr solutions of cetyltrimethylammonium bromide (CTAB) has been measured at 35°C with 488-nm laser light, and the molecular weight, radius of gyration, and the other parameters of its micelles have been evaluated. In water, spherical micelles are formed above a critical micelle concentration, 0.04×10^{-2} g cm⁻³, and each micelle consists of 91 monomers of CTAB. In aqueous solutions having NaBr concentrations higher than 0.06 *M*, rod-like micelles are formed, besides spherical micelles. The molecular weight of rod-like micelles increases rapidly with increasing NaBr concentration. The rod-like micelle formed in 0.5 *M* NaBr has molecular weight as high as 3,470,000, and is considerably flexible. The persistence length of micelle is evaluated to be 44 nm. Electron micrographic observations have been carried out for specimens prepared from CTAB solutions in water and in 0.5 *M* NaBr at 35°C. A specimen prepared from aqueous solution of CTAB and negatively stained with uranyl acetate displays many globular images, which have a uniform diameter around 5–6 nm and can be assigned to spherical micelles. A specimen from 0.5 *M* NaBr solution shows tortuous thread-like images with a uniform diameter of 4.5–6 nm, which can be regarded as flexible rod-like micelles. Thus, the size and shape of spherical and rod-like micelles of CTAB observed by the light-scattering measurement are confirmed by electron microscopy. (a) 1985 Academic Press, Inc.

INTRODUCTION

Surfactants in aqueous solutions generally form spherical micelles above certain critical concentrations, and some surfactants further associate into rod-like micelles with increasing micelle concentration. In the case of ionic surfactants, the rod-like micelles can be formed only above a certain threshold salt concentration, characteristic of the surfactant and the salt species (1-4): the threshold salt concentration for the sphere-rod transition of micelle is determined by the molecular structure of surfactant ions dominating its geometrical adaptability to the micelle structure, so that a surfactant having a longer hydrocarbon part is more readily incorporated into a rod-like micelle rather than into a spherical micelle.

In this work we choose a cationic surfactant having long hydrocarbon part, i.e., cetyltrimethylammonium bromide (CTAB), and investigate the sphere-rod transition of its micelles in aqueous NaBr solutions by means of static light scattering. CTAB is one of the most popular cationic surfactants used for various investigations, but its micelle size and shape have not been well characterized systematically, especially with reference to the ionic strength of solution. Recently, Nicoli *et al.* (5– 8) and Candau *et al.* (9) published results of dynamic light scattering of CTAB micelles in aqueous NaBr or KBr solutions.

There are few electron microscopic observations for micelles. Electron microscopic images of spherical micelles, which were constituted from molecules of surfactants with carbon atoms of 14 to 22, were reported by Bachmann *et al.* (10). We have presented electron micrographs of rod-like micelles of dimethyloleylamine oxide prepared from its aqueous solution and 0.01 M NaCl solution (11). Tortuous thread-like images which were identified as flexible rod-like micelles with a

uniform diameter were observed. In this work we present electron micrographs of spherical and rod-like micelles of CTAB and compare their size and shape with that from light-scattering measurements.

EXPERIMENTAL

Materials. CTAB was purchased from Nakarai Chemical Company, Inc., Kyoto, and recrystallized twice from an ethanol-acetone mixture. The purity of the surfactant was examined by the thermal decomposition gas chromatography and surface tension methods: neither an appreciable peak arising from homologs on its chromatogram nor a minimum at the critical micelle concentration on the surface tension curve of its aqueous solution was observed. Special grade NaBr was ignited for 2 h and stored in a desiccator until use. Water was glass-redistilled from alkaline KMnO₄.

Methods. Light scattering was measured on a Union Giken Automatic Light Scattering Analyzer LS-601, by using an argon ion laser (Nippon Electric Co., GLG3000, 15 mW). Laser beam at 488 nm was vertically polarized and the total scattered light in vertical and horizontal polarizations was collected. Then the reduced intensity of light scattered at a scattering angle θ can be calculated by

$$R_{\theta,U_{\rm v}} = \phi_{90} \frac{I_{\theta}}{I_0} \frac{\sin \theta}{2} , \qquad [1]$$

where I_0 and I_{θ} are the directly measured intensities of incident and scattered light, respectively. Hereafter, we omit the suffix, U_v , for R_{θ} . The calibration constant, ϕ_{90} , for solutions was determined by

$$\phi_{90} = \frac{\tilde{n}_0^2}{\tilde{n}_b^2} \phi_b \qquad [2]$$

using the calibration constant, ϕ_b , for pure benzene and correcting for the difference in refractive index, where \tilde{n}_0 and \tilde{n}_b are the refractive indices of the solvent and benzene, respectively. The calibration constant, ϕ_b , was determined with reference to the reduced in-

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tensity of light scattered from benzene, which was evaluated as 34.11×10^{-6} cm⁻¹ at 488 nm from the data of Pike *et al.* (12). Optical clarification of solvents and solutions was carried out by filtering a solution through a Millipore membrane into a cylindrical cell under pressure and by repeating the filtration seven times. The Millipore filter GSWP having pore size of 0.22 μ m had been previously cleaned by soaking in and then filtering redistilled water. A cylindrical quartz cell with 2 cm in outer diameter was put in a cell housing filled by xylene and kept at $(35 \pm 0.1)^{\circ}$ C by circulating water of constant temperature around it.

Specific refractive index increment was measured on a Union Giken differential refractometer RM-102A at $(35 \pm 0.1)^{\circ}$ C for the light with a wavelength of 488 nm, isolated by a filter from the light of an iodine lamp. The apparatus was calibrated by aqueous solutions of NaCl.

Electron micrographs were taken with a JEM 100C electron microscope operated at 80 kV and at a numerical magnification of 50,000. Solutions of CTAB in water and in 0.5 M NaBr were prepared and incubated at $(35 \pm 1)^{\circ}$ C. An aliquot of each solution was put on a carbon-coated electron microscope grid. After excess solution was sucked up by filter paper, specimens on the grid were negatively stained with 1% uranyl acetate solution.

RESULTS

Light-Scattering Measurement

The reduced scattering intensity of solutions in the 90° direction, R_{90} , is shown as a function of surfactant concentration, c (g cm⁻³), in Fig. 1a. The reduced scattering intensity increases above a certain concentration. This concentration can be identified with the critical micelle concentration, c_0 (g cm⁻³), and its values are given in Table I. The critical micelle concentration is lower, and the reduced scattering intensity is stronger, as the NaBr concentration is higher.

Figure 1b shows the dissymmetry, $z_{60} = R_{60}/R_{120}$. The dissymmetry of solutions in



FIG. 1. The reduced scattering intensity in the 90° direction (upper) and the dissymmetry at 60° (lower) of scattered light as functions of surfactant concentration. NaBr concentration (*M*): \Box , 0; \blacksquare , 0.1; \bigcirc , 0.2; \bullet , 0.3; \triangle , 0.5.

water and in 0.1 *M* NaBr is close to unity. At higher NaBr concentrations, the dissymmetry increases above the critical micelle concentra-

tion and becomes constant at high surfactant concentrations. The constant value is higher as the NaBr concentration is increased. The value, 1.71, found in 0.5 M NaBr is nearly equal to the theoretical value for rigid-rod particles, $\cot(\theta/2) = 3^{1/2}$ (13).

Light scattering from a dilute micellar solution at a scattering angle θ is described by

$$\frac{K(c-c_0)}{R_{\theta}-R_{\theta}^0} = \frac{1}{MP(\theta)} + 2B(c-c_0), \quad [3]$$

where R_{θ}^{0} is the reduced intensity at the critical micelle concentration and is substantially equal to that of the solvent, M is the average molecular weight of micelles, and B is the second virial coefficient. K is the optical constant given by

$$K = \frac{2\pi^2 \tilde{n}_0^2 (\partial \tilde{n} / \partial c)_{C_s}^2}{N_A \lambda^4}, \qquad [4]$$

where $(\partial \tilde{n}/\partial c)_{C_s}$ is the specific refractive index increment of the solution of constant NaBr concentration, $C_s(M)$, for the light of wavelength, λ , and N_A is the Avogadro number. The values of $(\partial \tilde{n}/\partial c)_{C_s}$ are also given in Table I. The particle scattering factor, $P(\theta)$, at small scattering angles is related to the average radius of gyration of micelles, R_G , by

$$\left(\frac{1}{P(\theta)}\right)_{\theta:\text{small}} = 1 + \frac{16\pi^2 \tilde{n}_0^2}{3\lambda^2} R_G^2 \sin^2\left(\frac{\theta}{2}\right) [5]$$

irrespective of particle shape.

The Debye plot of light scattering at 90° scattering angle for aqueous solutions of CTAB is shown in Fig. 2a. The Debye plot

Properties of CTAB Micelles in Solution at 35°C												
C _s (M)	$(\partial \vec{n} / \partial c)_{C_4}$ (cm ³ g ⁻¹)				Rod-like							
			Spherical					*				
		$(10^{-2} \text{ g} \text{ cm}^{-3})$	M (10 ⁴)	m	M (10 ⁴)	т	$\begin{array}{c} c^{*} \\ R_{\rm G} \\ (10^{-2} \text{ g} \\ (\text{nm}) \\ cm^{-3}) \end{array}$	C* (M)				
0	0.153	0.040	3.3	91								
0.1	0.155	0.020	5.0	137	14.6	401	5.6 ^a	33	0.91			
0.2	0.155	0.015			66.2	1820	36.2	0.55	0.015			
0.3	0.153	0.010			197	5410	51.0	0.59	0.016			
0.5	0.150	0.005			347	9530	80.2	0.27	0.007			

TABLE I

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FIG. 2. The Debye plots of light scattering at the scattering angle, θ , against the micelle concentration. (a) and (b) $\theta = 90^{\circ}$; (c) $\theta = 0^{\circ}$. The symbols represent the same NaBr concentrations as in Fig. 1.

increases linearly with an increase in micelle concentration, $c - c_0$, but deviates downward at micelle concentrations above 0.3×10^{-2} g cm^{-3} . There is no angular dependence of light scattering for these solutions, indicating that the average radius of gyration of the micelles is smaller than (488/20 =) 24 nm. Hence, the extrapolation of the initial straight line to zero micelle concentration on Fig. 2a leads to the reciprocal of the micelle molecular weight, and its slope gives the value twice as large as that of the second virial coefficient. The micelle molecular weight is equal to 33,000, which means the formation of spherical micelles of aggregation number, 91, in water. The second virial coefficient is obtained as 46×10^{-3} cm³ g^{-1} , indicating the strong electrostatic repulsion between spherical micelles.

The Debye plot at the 90° scattering angle for 0.1 M NaBr solution decreases gradually with an increase in micelle concentration and approaches a constant value, as seen in Fig. 2b. Since the angular dependence is negligible, the value extrapolated to zero micelle concentration gives the reciprocal molecular weight of spherical micelles. On the other hand, the value obtained by extrapolation to high micelle concentrations gives approximately the reciprocal molecular weight of rod-like micelles. Here, the contribution of the second virial coefficient is assumed to be negligible. Incidentally, Trap and Hermans (14) reported that the second virial coefficients of micellar solutions of myristyltrimethylammonium bromide and stearyltrimethylammonium bromide are approximately zero in 0.05 M NaBr.

When the dissymmetry is large, the reciprocal angular envelope of light scattering at each micelle concentration must be extrapolated to zero scattering angle in order to obtain the micelle molecular weight. The Debye plots at zero scattering angle for solutions of CTAB with high NaBr concentrations level off and give constant values at high micelle concentrations, as shown in Fig. 2c. The reciprocal of the constant value is essentially equal to the molecular weight of rod-like micelles in a given NaBr solution. Table I includes the values of micelle molecular weight, M, and micelle aggregation number, m = M/364.5.

It would be pertinent to comment on the general trend of the second virial coefficient of micellar solutions upon addition of a simple salt. While the second virial coefficient is positive and large for charged spherical micelles in water, it is lowered with increasing salt concentration owing to the shielding of electrostatic repulsion, in spite of a little increase in micelle size. At a certain salt concentration, which is equal to the threshold salt concentration of the sphere-rod transition, the second virial coefficient vanishes. Beyond this concentration of salt, rod-like micelles are formed with increasing micelle concentration, besides spherical micelles. The size of rod-like micelles is also determined by the salt concentration. Since the electrostatic effect of rod-like micelles is completely shielded, the second virial coefficient of solutions of rod-like micelles is mainly contributed by the excluded volume effect and other nonelectric interaction. Unless the contour length of rod-like micelle is very long, their excluded volume effect is not large and the second virial coefficient remains still small.

Values of the radius of gyration of rod-like micelles can be obtained from the slope at small scattering angles of the reciprocal angular envelope. The reciprocal angular envelope for 0.2 and 0.3 M NaBr solutions of CTAB increases linearly with an increase of $\sin^2(\theta/2)$, and its slope gives the value of the radius of gyration. The reciprocal angular envelope for 0.5 M NaBr solution has a linear region at small scattering angles, while it deviates downward from this line at high angles. as seen in Fig. 3. The constant values of the radius of gyration obtained at high micelle concentrations are given in Table I for each NaBr solution. These values can be assigned to the rod-like micelles.

Electron Microscopic Observation

Figure 4 shows an electron micrograph of specimen prepared from aqueous solution of CTAB at the surfactant concentration of 0.10 $\times 10^{-2}$ g cm⁻³. There are many globular images with a diameter around 5–6 nm. The images look like polyhedra with rough surfaces.



FIG. 3. Angular dependence of the reciprocal angular envelope for 0.5 M NaBr solution of CTAB. Micelle concentration $(10^{-2} \text{ g cm}^{-3})$: from top to bottom; 0.020, 0.045, 0.071, 0.171.

However, their size is fairly homogeneous. They may be identified with spherical micelles. While most micelles are located randomly from one another, there is a domain where spherical micelles form a regular array. In this domain, almost 50 micelles are arranged in a hexagonal lattice, keeping the intermicellar distance of 5.3 nm.

Electron micrographs of specimens prepared from 0.5 M NaBr solutions with the CTAB concentrations of (0.05 and 0.50) $\times 10^{-2}$ g cm⁻³ are shown in Fig. 5. Here, thread-like images are dispersed over a wide region of photographs. These images have a uniform diameter of about 4.5-6 nm in cross section for the specimen from the dilute solution, while images from the concentrated solution seem to have larger diameters. Thread-like images are long and tortuous. They may be identified with rod-like micelles. The micelles are not well separated from one another. The micelles dispersed in solution are deposited on the surface of microscopic grid, where they superpose one another. Accordingly, it is not possible to follow the locus of a single rod-like micelle and to measure its contour length.

It is also likely that the micelles in solution, especially rod-like micelles, would be subject to strong perturbation during the treatment of staining and drying.

DISCUSSION

(1) The Debye Plot of Light Scattering

The Debye plot at 90° scattering angle gives a measure of micelle molecular weight and the intermicellar interaction, if the angular dependence is negligible. The initial positive slope of the Debye plot for CTAB micelles in water indicates the strong interaction between spherical micelles, as suggested by the value of the second virial coefficient of 46×10^{-3} cm³ g⁻¹. A similar value of the second virial coefficient was reported by Trap and Hermans (14): $\sim 30 \times 10^{-3}$ cm³ g⁻¹ at 50°C.

The Debye plot on CTAB micelles in water displays a breakpoint at micelle concentrations



Fig. 4. Electron micrographs of specimen prepared from aqueous solution of CTAB at concentration of 0.10×10^{-2} g cm⁻³.



FIG. 5. Electron micrographs of specimen prepared from 0.5 M NaBr solution of CTAB. Surfactant concentration (10^{-2} g cm⁻³): (a) 0.05; (b) 0.50.

of 0.3×10^{-2} g cm⁻³, giving a deviation from the initial slope. Ekwall *et al.* (15) reported the same feature for aqueous solution of CTAB, although the corresponding breakpoint occurred at 0.4×10^{-2} g cm⁻³. They interpreted this phenomena as a change in counterion binding; i.e., above this concentration Br⁻ is bound to the micelle more appreciably. This may cause the lowering of the intermicellar interaction above this point and, hence, of the second virial coefficient.

Reiss-Husson and Luzzati (16) observed the concentration-dependent sphere-rod transition of micelles for various ionic surfactants in water by means of the small-angle X-ray scattering, and they reported that the transition takes place at a surfactant concentration, 5.1 $\times 10^{-2}$ g cm⁻³, for CTAB in water. Their value is more than 10 times higher than the values of breakpoint of light scattering, and the sphere-rod transition they observed cannot be identified with the cause of the breakpoint of the Debye plot.

The Debye plot for aqueous NaBr solutions of CTAB decreases with an increase in micelle

concentration, indicating that the sphere-rod equilibrium shifts from sphere to rod (1-4). The decrease is gradual for 0.1 *M* NaBr solution but sharp for 0.5 *M* NaBr solution. This difference depends on whether the molecular weight of rod-like micelles is low or very high. In 0.1 *M* NaBr the rod-like micelle has a size only three times larger than the spherical micelle. However, if the rod-like micelle is sufficiently large, the increase in the average molecular weight is sharp even at low micelle concentrations, so that the extrapolation to the critical micelle concentration is made difficult to obtain the molecular weight of spherical micelle.

(2) Salt-induced Sphere–Rod Transition of CTAB Micelles

In Fig. 6 the logarithm of micelle molecular weight of CTAB measured by light scattering, M, is plotted against the logarithm of ionic strength ($C_0 + C_s$), where C_0 is the critical micelle concentration in molar units. The relationship can be represented by two straight



FIG. 6. The double logarithmic plot of M vs ($C_0 + C_s$) for CTAB micelles. \bigcirc , In water and NaBr solutions at 35°C (present work); \boxplus , water, 30°C (Ref. (19)); \square , water, 25°C (Ref. (15)); \square , water, 20°C (Ref. (23)); \square , KBr, 34°C (Ref. (18)); \square , KBr, 30°C (Ref. (14)); \blacksquare , KBr, 30°C (Ref. (9)).

lines, each corresponding to the spherical and rod-like micelles. They are given by

 $\log M = 0.09 \, \log(C_0 + C_s) + 4.78$ $C_s < 0.10 \, M \quad [6a]$ $\log M = 2.07 \, \log(C_0 + C_s) + 7.22$ $C_s \ge 0.06 \, M. \quad [6b]$

The slope of 0.09 is identical with that for spherical micelles of dodecyltrimethylammonium bromide (3), but the slope of 2.07 is twice as large as that for its rod-like micelles. The threshold NaBr concentration for the sphere-rod transition of CTAB is 0.06 M, corresponding to the molecular weight, 48,000, and aggregation number, 132.

Micelle molecular weight of CTAB in aqueous KBr solutions was also determined by some workers by means of the light scattering (14, 15, 17–19) and the fluorescence probing method (9, 20, 21). The values of micelle molecular weight in KBr solutions differ from those in the NaBr solutions, as seen in Fig. 6. The double logarithmic plot of M vs $(C_0 + C_s)$ for KBr solutions also gives two portions of straight line:

$$\log M = 0.35 \log(C_0 + C_s) + 5.54$$

$$C_s \le 0.10 M \quad [7a]$$

$$\log M = 2.83 \log(C_0 + C_s) + 8.03$$

 $C_{\rm s} \ge 0.10 \ M.$ [7b]

Then, the threshold KBr concentration for the sphere-rod transition is 0.10 M, corresponding to the molecular weight, 157,000, which gives a too large spherical micelle. The values of molecular weight obtained by Trap and Hermans (14) for CTAB micelles in KBr solutions might be too high. The effect of co-ion species on micelle molecular weight has already been observed for micelles of sodium dodecyl sulfate (2) and later discussed by Doughty (22).

Dynamic light scattering on micellar solutions can derive the diffusion coefficient of micelles, and the results on micellar solutions of CTAB (7, 8) showed that the concentration

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dependence of diffusion coefficient changed from positive to negative, as the NaBr concentration was increased. The concentrationindependent diffusion coefficient of CTAB micelle was observed at 0.08 M NaBr at 40°C and between 0.04 and 0.075 M NaBr at 25°C. These values could be identified with the threshold salt concentrations for the sphererod transition of CTAB micelles in NaBr solutions and are comparable with those from static light scattering as shown above.

(3) Size and Shape of Micelles

Images on an electron micrograph for specimen prepared from an aqueous solution of CTAB can be regarded as spherical micelles. They are globular, as seen in Fig. 4, and have a considerably uniform size, as was also observed on electron micrographs for spherical micelles of some other surfactants (10). Spherical micelles of CTAB were observed to have a radius of 2.5–3 nm. This value is comparable to the radius assignable to a spherical micelle of CTAB, 2.6 nm, and is consistent with the hydrodynamic radius of the spherical micelle. The latter was evaluated to be 2.9 nm at 40°C from the diffusion coefficient of CTAB at infinite dilution (6, 7).

As seen in Fig. 4, there is a domain where micelles are arranged in hexagonal lattice and separated from one another by an equal distance. One may reject the possibility of formation of microcrystal in aqueous solution, because the Krafft point of CTAB in water is fairly lower than 35°C, at which the present experiment has been performed. It is assumed that a domain where spherical micelles form an array could temporarily be formed in water or during the preparation. Strong intermicellar interaction might be a motive force for such a regular array, which is supported by the observed large value of the second virial coefficient.

In 0.1 M NaBr, spherical micelles formed at the critical micelle concentration further associate together into rod-like micelles with an increase in micelle concentration. The rodlike micelle is merely three times larger than the spherical micelle. Thus, a rigid-rod structure is assumed for the rod-like micelle in 0.1 M NaBr solution. Then, the radius of gyration of a micelle can be calculated from the relations (23)

$$R_{\rm G} = \left(\frac{L^2}{12} + \frac{r^2}{2}\right)^{1/2}$$

$$R_{\rm H} = \frac{L}{2\sigma - 0.19 - 8.24/\sigma + 12/\sigma^2} \quad [8]$$

$$\sigma = \ln(L/r),$$

where L is the length of a rigid rod and r is its radius. The radius of 2.6 nm may be adopted, referring to the minimum hydrodynamic radius for a spherical micelle at high temperature where the swelling would be low (6). The hydrodynamic radius, $R_{\rm H}$, for the rod-like micelle of CTAB in 0.1 M NaBr solution at 35°C is evaluated to be 6.9 nm (5). Then, the value of 5.6 nm can be obtained for $R_{\rm G}$, and 18 nm for L. The overlap threshold concentration of the rod-like micelles in 0.1 M NaBr

$$c^* = M/[(4/3)\pi R_G^3 N_A]$$
 [9]

is calculated as 33×10^{-2} g cm⁻³ or its molar concentration C^* as 0.91 *M*. The behavior of CTAB micelles in 0.1 *M* KBr was recently reported by Candau *et al.* (9). They carried out experiments at more concentrated CTAB concentrations and at a lower temperature, 25° C, and reported that the prolate micelles were entangled together at CTAB concentrations above 0.02 *M*. This concentrations above 0.02 *M*. This concentration is much lower than the overlap threshold concentration given above, but might be perturbed by the dependence of micelle size on temperature and co-ion species.

(4) Flexibility of Rod-like Micelles

It is likely that long rod-like micelles are flexible rather than rigid (1, 24–30). Rod-like micelles of CTAB in solutions with higher NaBr concentrations may also be the case. In order to estimate the flexibility of rod-like micelles of CTAB, we follow an approach, based on the worm-like chain model by Kratky and Porod (31). For this purpose, we need to obtain the contour length, L_c , and persistence length, *a*. We rely on two alternative methods.

Method I assumes that the surface area of micelle per surfactant ion is common for both spherical and rod-like micelles. As the aggregation number of spherical micelles of CTAB in water is 91, and if a spherical micelle is a sphere with the radius. r, of 2.6 nm in water. the area per surfactant molecule on a micelle surface. A. is evaluated as 0.93 nm^2 . Applying this value for the surface area of a molecule in a rod-like micelle, the thickness, d, of 0.97 nm can be estimated for a disk-like layer of rod-like micelles. The structure of rod-like micelles consists of a stack of such disk-like layers. Then, the number of molecules or ions in a layer, $m_{\rm L}$, and the molecular weight per unit chain length, $M_{\rm L}$, are 17 and 6300 nm⁻¹, respectively. Values of parameters are listed in Table II.

The contour length, L_c , of the micelle is given by

$$L_{\rm c} = M/M_{\rm L}.$$
 [10]

For a flexible rod-like micelle, then, the mean-square radius of gyration, $\langle R_G^2 \rangle_0$, and its mean-square end-to-end distance, $\langle r^2 \rangle_0$, are represented by (31, 32)

$$\frac{\langle R_{\rm G}^2 \rangle_0}{a^2} = \frac{L_{\rm c}}{3a} - 1 + \frac{2a}{L_{\rm c}} \left[1 - \frac{a}{L_{\rm c}} \left(1 - e^{-L_{\rm c}/a} \right) \right]$$
[11]

TABLE II

Micelle Parameters for the Calculation of M_L

		Sph	erical	Rod-like				
	m	r (nm)	A (nm²/molecule)	d (nm)	$m_{\rm L}$	<i>M</i> _L (nm ⁻¹)		
СТАВ	91	2.6	0.93	0.97	17	6300		
DDAC	56 ^a	2.1	0.99	0.99	13	3360		
DDAB	77 ^b	2.1	0.72	0.85	16	5400		

^a See Ref. (1).

^b See Ref. (4).

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$$\frac{\langle r^2 \rangle_0}{2a^2} = \frac{L_c}{a} - 1 + e^{-L_c/a},$$
 [12]

where the suffix, 0, means that these quantities stand for the unperturbed chains without the excluded volume effect. Now, from Eqs. [11] and [12], the persistence length and the endto-end distance of micelles can be calculated for each NaBr solution, assuming $\langle R_G^2 \rangle_0 \approx R_G^2$. Their values, together with those of the flexibility parameter (number of Kuhn's segments), $L_c/2a$, are shown in Table III. Flexibility is slightly larger for higher NaBr concentrations, and the end-to-end distance is about $\frac{2}{\pi}$ times of the contour length.

Strong evidence for the flexibility of rodlike micelles of CTAB is manifest in electron micrographs. Thread-like images observed for specimen from 0.5 M NaBr solution at CTAB concentration of 0.05×10^{-2} g cm⁻³, where rod-like micelles are dominant, can be assigned to rod-like micelles. Each micelle is long and tortuous. Although each micelle cannot be observed distinctly from others, its size and shape in solution are considered to be qualitatively well reproduced on the photograph, if its contour length and end-to-end distance are compared with those from light scattering. The CTAB concentration of 0.5×10^{-2} g cm⁻³ in 0.5 M NaBr would be higher than the overlap threshold concentration, as seen from Table I. Then, the crowd of flexible rod-like micelles on the electron micrograph in Fig. 5b may be

interpreted as the mutual penetration of rodlike micelles and their entanglement.

Flexibility of long rod-like micelles has been discussed for some other surfactants (1, 24– 30). Appell *et al.* (27) reported that the persistence length of cetylpyridinium bromide in NaBr solutions is 20 nm, on the basis of a thermodynamical model. Flamberg and Pecora (28) evaluated the persistence length of 82 nm for dodecyldimethylammonium chloride (DDAC). They calculated the contour length by using Tanford's relation (33) of the volume of core to the aggregation number.

In Method II the same procedure is applied for rod-like micelles of CTAB, that is, the core volume of a spherical micelle in water is calculated by Tanford's relation, and the radius of the core is estimated for the spherical micelle. Then, assuming the same radius for the cross section of the rod-like micelles, as well as the same packing, the contour length of a rod-like micelle is evaluated. The results are included in Table III. The persistence length derived by Method II is longer than that by Method I, and it is too long to be treated as a worm-like chain as observed in electron micrographs.

We have also calculated the flexibility of DDAC (1) and DDAB (dodecyldimethylammonium bromide) (4) by Method I, and included their values in Table III. Values of parameters are listed in Table II. The persistence length of DDAC micelles in 4.00 *M* NaCl from

Method	Surfactant	Salt	Т (°С)	C, (M)	M (10 ⁴)	<i>R</i> _G (nm)	<i>L</i> e (nm)	a (nm)	L _c /2a	$\langle r^2 \rangle_0^{1/2}$ (nm)	pH	Ref.
. [CTAB	NaBr	35	0.3 0.5	197 347	51.0 80,2	313 551	34 44	4.6 6.3	138 212		
I {	DDAC DDAB	NaCl NaBr	25 25	4.00 1.50	294 357	88.4 79.7	875 661	30 33	14.8 9.9	223 205		
ľ	DOAO	NaCl	25	0.05 0.01	690 1800	127 210	575 1520	176 107	1.64 7.10	378 549	7 5	(29) (30)
II {	CTAB DDAC	NaBr NaCl	35 25	0.5 4.00	347 294	80.2 88.4	294 460	490 82	0.3 2.8	267 249		(28)

TABLE III Flexibility of Rod-like Micelles

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Method I is close to that estimated (27 nm) from viscosity measurements (13).

Thus, we may have more confidence on Method I than on Method II. Table III also includes the results for dimethyloleylamine oxide (DOAO). The method of calculation, which is called Method I', is based on the value of $M_{\rm I}$ directly derived from the experiments (29, 30). When the data from Methods I and I' are compared with each other, it is clear that almost all of them exhibit the flexibility parameter between 1 and 10, indicating their worm-like nature. Flexibility for DDAC in 4.00 M NaCl is larger than 10. Therefore, rodlike micelles of DDAC behave as random coils. It is likely that the thinner the diameter is, micelles are more randomly coiled. Thus, the rod-like micelles of DDAC and DDAB are more flexibile than those of CTAB and DOAO.

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