The Salt-Induced Sphere–Rod Transition of Micelles of 1-Tetradecylpyridinium Bromide in Aqueous NaBr Solutions

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Static light scattering from aqueous NaBr solutions of 1-tetradecylpyridinium bromide (TPB) has been measured over the range of NaBr concentrations from 0 to 0.50 mol dm^{-3} at 25 °C, and the micelle molecular weight has been estimated. For 0—0.20 mol dm^{-3} NaBr, the reduced intensity of scattered light does not show any angular dependence, and the molecular weight of the spherical micelle of TPB slightly increases from 27.6×10^3 to 41.4×10^3 with increasing NaBr concentration. Beyond 0.20 mol dm^{-3} NaBr, the angular dissymmetry of the reduced scattering intensity and a steep increase in the micelle molecular weight from 41.4×10^3 to 177.8×10^3 are observed. Therefore, TPB has been considered to form rodlike micelles. The linear double logarithmic relationship between molecular weight and ionic strength holds for spherical and rodlike micelles, respectively. From the intersection of these two lines, the threshold NaBr concentration for the sphere-rod trainsition of TPB micelle is estimated to be 0.19 mol dm^{-3}, where the micelle has a molecular weight of 41.3×10^3.

Most ionic surfactants with an alkyl chain longer than the decyl one can form rodlike micelles in aqueous salt solutions, when the simple salt having a common counter ion is added up to a concentration exceeding a certain threshold.[1] In general, the longer the alkyl chain a cationic surfactant possesses, the lower its threshold salt concentration for the sphere-rod transition is. For example, the threshold NaBr concentration for tetradecyltrimethylammonium bromide is 0.12 mol dm^{-3},[2] which is lower than that for dodecyltrimethylammonium bromide, 1.80 mol dm^{-3}.[3] Hexadecyl- and tetradecyltrimethylammonium chlorides can form rodlike micelles at NaCl concentrations above 1.18[4] and 2.70 mol dm^{-3},[2] respectively, while micelles of dodecyltrimethylammonium chloride remain spherical up to 4.00 mol dm^{-3} NaCl.[5]

We have previously observed that 1-dodecylpyridinium chloride (DPC)[6] and bromide (DPB)[7] form spherical micelles alone even in a saturated solution of the corresponding sodium halide, whereas 1-dodecylpyridinium iodide (DPI) forms rodlike micelles above 0.007 mol dm^{-3} NaI.[8] In general, the size of spherical micelles formed by an ionic surfactant gradually increases when the concentration of added salt increases up to the threshold salt concentration for the sphere–rod transition or up to the saturation of the salt.[1] On the contrary, the aggregation number of spherical micelles of DPB increases from 46.0 to 70.7 with increasing NaBr concentration from 0 to 0.30 mol dm^{-3}, but it remains constant at NaBr concentrations from 0.30 to 6.00 mol dm^{-3}. From these our observations, we expect that 1-tetradecylpyridinium bromide (TPB) will form rodlike micelles when NaBr is present beyond a threshold concentration.

Trap and Hermans[9] measured static light scattering on aqueous TPB solutions in the presence of KBr from 0 to 0.05 mol dm^{-3} at 30 °C, and found that the micelle molecular weight gradually increased from 28.1×10^3 to 55.6×10^3 with KBr concentration. Venable and Nauman[10] carried out light scattering measurements on aqueous NaBr solutions of TPB at NaBr concentrations of 0 and 0.05 mol dm^{-3} at room temperature, and found that TPB formed spherical micelles with a molecular weight of 22.3×10^3 in water, but in 0.05 mol dm^{-3} NaBr it formed large micelles with a molecular weight of 90.4×10^3, which were not expected to be spherical. Jacobs et al.[11] determined the aggregation number of TPB micelles in 0.5 mol kg^{-1} NaBr to be 136, which corresponded to the molecular weight of 48.5×10^3, by static light scattering. However, the above results differ from each other, so that it has not been clarified whether TPB can form rodlike micelles or not in the presence of NaBr or KBr.

In the present work, static light scattering is measured on aqueous NaBr solutions of TPB at 25 °C; the NaBr concentration ranges from 0 to 0.50 mol dm^{-3}.

Experimental

Materials. 1-Tetradecylpyridinium bromide was synthesized from 1-bromotetradecane and pyridine. 1-Bromotetradecane was obtained from Aldrich Chemical Co., Inc. and redistilled in vacuo. Pyridine purchased from Kanto Chemical Co., Inc. was dried over molecular sieve 3A. A mixture of freshly distilled 1-bromotetradecane (130.1 g, 0.469 mol) and dry pyridine (115.2 g, 1.457 mol) was refluxed at 131 °C for 8h. After the mixture was cooled in an ice-water bath, the precipitates obtained were recrystallized three times from acetone (40.9% yield). The TPB sample was insoluble in aqueous solutions of NaBr concentrations higher than 0.5 mol dm^{-3}.

The surface tension of aqueous solution of the TPB sample did not show any minimum around the critical micelle concentration (cmc), 2.65×10^{-3} mol dm^{-3}, as shown in Fig. 1. This

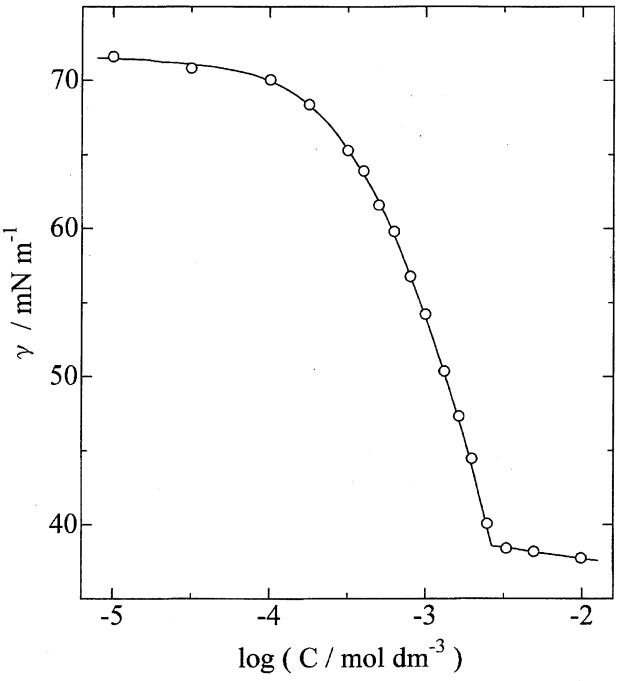

Fig. 1. Relationship between surface tension, γ and logarithm of concentration, C, for aqueous TPB solutions.

value of cmc is in good agreement with the literature value of 2.71×10^{-3} mol kg^{-1}.[12] The molecular area at the cmc was calculated to be 41×10^{-2} nm^2 molecule^{-1} by means of the Gibbs adsorption isotherm.

Apparatus. Light scattering was measured at 488 nm on a Laser Light Scattering Photometer DLS-700 with a 5—7 mW argon ion laser, manufactured by Otsuka Denshi Co., Inc., Osaka, Japan. The incident light was vertically polarized, and all components of the scattered light were collected. The photometer was calibrated with scattering from purified benzene, as previously described.[7] The temperature was regulated to 25±0.2°C, by circulating water of constant temperature from a Julabo F10-VC Thermostat. Solutions and solvents for light scattering measurements were filtered four or five times through a Millipore filter having a 0.10 or 0.22 μm pore size.

The specific refractive index increment was also measured at 488 nm and at 25 °C on a Differential Refractometer RM-102 with a 50 W iodine lamp (Otsuka Denshi Co., Inc.) The method of its calibration was also described previously.[7]

The refractive index of aqueous NaBr solutions at 488 nm and 25 °C was calculated from tabulated values at other temperatures and at other wavelengths[13] with the method described previously.[7]

Results

Excess reduced scattering intensity, $R_{90}-R_{90}^0$, of aqueous NaBr solutions of TPB is shown in Fig. 2 as a function of TPB concentration, c (g cm^{-3}), at lower NaBr concentrations, C_S (mol dm^{-3}). Above the critical micelle concentration, c_0 (g cm^{-3}), it suddenly increases with increasing TPB concentration and the increase is convex upword.

Figure 3 shows the excess reduced intensity of light scattered in the 90° direction from aqueous NaBr solutions of TPB at higher NaBr concentrations. The reduced intensity also increases with increasing TPB concentration, but its in-

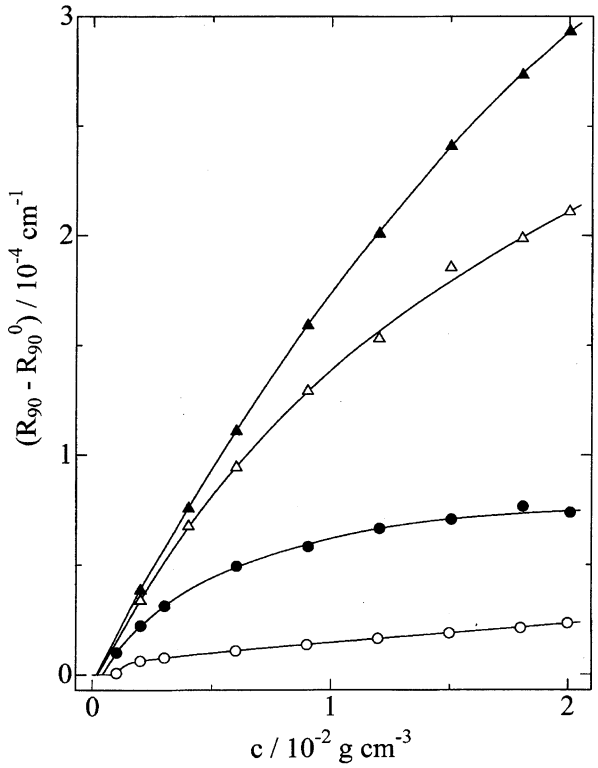

Fig. 2. Excess reduced intensity of scattered light from aqueous NaBr solutions of TPB at lower NaBr concentrations. C_S/mol dm^{-3}: ○, 0; ●, 0.01; △, 0.05; ▲, 0.10.

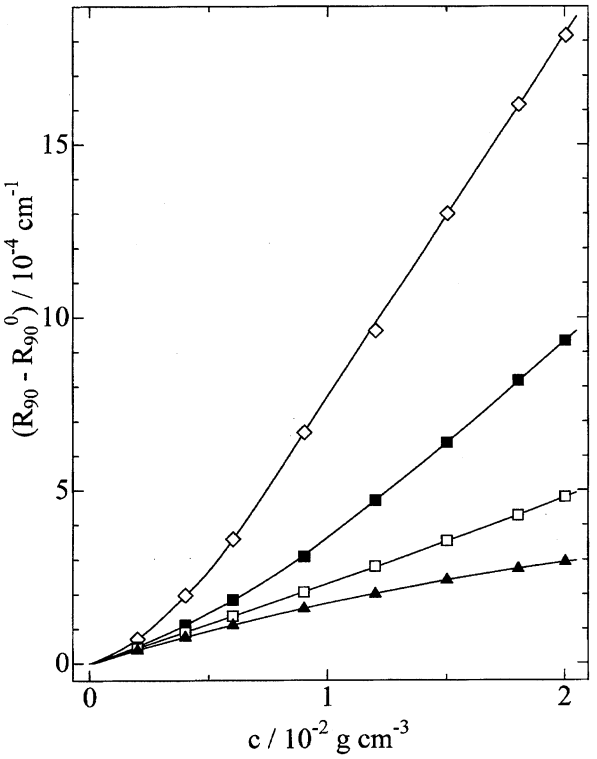

Fig. 3. Excess reduced intensity of scattered light from aqueous NaBr solutions of TPB at higher NaBr concentrations. C_S/mol dm^{-3}: ▲, 0.10; □, 0.20; ■, 0.30; ◇, 0.50.

crease is nearly linear in 0.20 mol dm^{-3} NaBr and convex downward in 0.30 and 0.50 mol dm^{-3} NaBr.

The critical micelle concentration, C_0 (mol dm^{-3}), decreases with increasing NaBr concentrations, as given in Table 1. It follows the Corrin–Harkins equation:

$$\log C_0 = -0.526 \log (C_0 + C_S) - 3.940 \quad (1)$$
$$0 \leq C_S \leq 0.50 \text{ mol dm}^{-3}$$

as shown in Fig. 4. The coefficient of $\log (C_0+C_S)$ for aqueous NaBr solutions of TPB, -0.526 is slightly larger than -0.573 for aqueous NaBr solutions of DPB,[7] which forms spherical micelles alone, and larger than -0.703 for aqueous NaI solutions of DPI,[8] which undergoes the salt-induced sphere-rod transition.

Table 1 also gives values of the specific refractive index increment of solutions and of the refractive index of solvents, i.e., water and aqueous NaBr solutions. The specific refractive index increment is represented by

$$(\partial \tilde{n}/\partial c)C_S = 0.1664 - 0.0139 C_S \quad (2)$$
$$0 \leq C_S \leq 0.50 \text{ mol dm}^{-3}$$

if values at 0 and 0.30 mol dm^{-3} NaBr are omitted.

Figure 5 shows Debye plots for micellar solutions of TPB

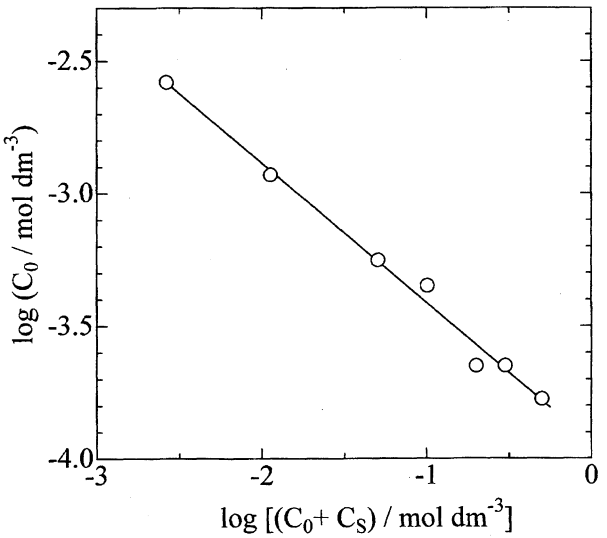

Fig. 4. The Corrin–Harkins plot for TPB micelles in aqueous NaBr solutions.

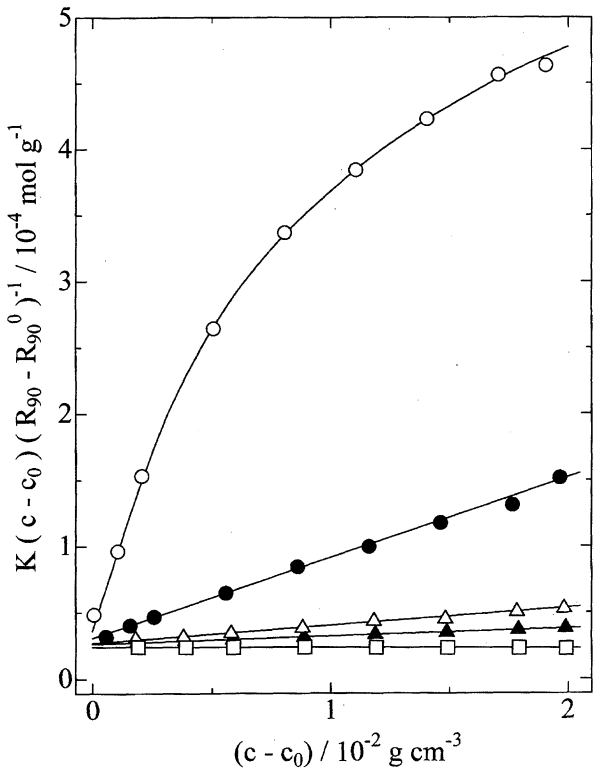

Fig. 5. Debye plots for aqueous NaBr solutions of TPB at lower NaBr concentrations. C_S/mol dm^{-3}: ○, 0; ●, 0.01; △, 0.05; ▲, 0.10; □, 0.20.

at lower NaBr concentrations. They give straight lines with positive slopes except at 0 mol dm^{-3} NaBr. At 0 mol dm^{-3} NaBr, the reduced intensity increases with increasing TPB concentration, but the rate of its increase gradually decreases. Such behavior was observed on light scattering from aqueous solutions of DPB,[7] DPI,[8] and various alkyltrimethylammoniom halides.[2,4,14,15] It has been attributed to changes in the degree of counter ion binding.[15,16]

At NaBr concentrations from 0.01 to 0.20 mol dm^{-3}, the linear relation

$$\frac{K(c-c_0)}{R_{90}-R_{90}^0} = \frac{1}{M} + 2B(c-c_0) \quad (3)$$

holds for Debye plots, where M is the micelle molecular weight and B is the second virial coefficient. The optical constant, K, for the vertically polarized incident light is given

Table 1. Critical Micelle Concentration, Specific Refractive Index Increment, and Optical Constant of Aqueous NaBr Solution of TPB and Refractive Index of Solvent

C_S / mol dm^{-3}	$\tilde{n}_0$	c_0 / 10^{-3} g cm^{-3}	C_0 / 10^{-3} mol dm^{-3}	$(\partial \tilde{n}/\partial c)C_S$ / cm^3 g^{-1}	K / 10^{-7} mol cm^2 g^{-2}
0	1.3367	0.94	2.64	0.1655	5.72
0.01	1.3368	0.42	1.18	0.1661	5.71
0.05	1.3374	0.20	0.56	0.1657	5.68
0.10	1.3382	0.16	0.45	0.1652	5.64
0.20	1.3396	0.08	0.22	0.1638	5.55
0.30	1.3410	0.08	0.22	0.1633	5.47
0.50	1.3436	0.06	0.17	0.1594	5.31

by

$$K = \frac{4\pi^2 \tilde{n}_0^2 (\partial \tilde{n}/\partial c)_{C_S}^2}{N_A \lambda^4} \quad (4)$$

where N_A is Avogadro's number, λ the wavelength of the incident light, and $\tilde{n}_0$ the refractive index of the solvent. In 0 mol dm^{-3} NaBr, although the Debye plot is not linear, its adequate extrapolation to the infinite dilution of micelle is possible. We have assumed that the Debye equation Eq. 3 would hold in the limit of zero micelle concentration.

Table 2 gives values of micelle molecular weight and second virial coefficient, together with those of micelle aggregation number, $m=M/356.4$. The micelle molecular weight and aggregation number indicate that the TPB micelle is spherical at NaBr concentrations from 0 to 0.20 mol dm^{-3}.

The molecular weight and aggregation number of the micelle in 0 mol dm^{-3} NaBr are 27.6×10^3 and 77, respectively. These values are almost in agreement with those reported by Trap and Hermans[9] and by Venable and Nauman,[10] in spite of different experimental temperatures.

For the micelle in 0.05 mol dm^{-3} NaBr, our micellar weight and aggregation number are 37.0×10^3 and 104. Trap and Hermans[9] reported 55.6×10^3 and 156 for the micelle in 0.05 mol dm^{-3} KBr at 30 °C. Venable and Nauman[10] reported 90.4×10^3 for the micellar weight in 0.05 mol dm^{-3} NaBr at room temperature (21—31 °C). Our values are quite small but reproducible. The size of TPB micelle may be especially sensitive to the temperature and the kind of coion, i.e. Na^+ or K^+, in the presence of NaBr or KBr. For example, the rise in temperature from 25 to 30 °C causes the micellar weight of sodium dodecyl sulfate to decrease by 41000 in 0.60 mol dm^{-3} NaCl,[17] although such conditions as salt concentration and micellar shape are different from ours.

At NaBr concentrations from 0 to 0.10 mol dm^{-3}, the second virial coefficient is positive and decreases with increasing NaBr concentration. This indicates that electric repulsion operates between spherical micelles in aqueous NaBr solutions up to 0.10 mol dm^{-3}. The increase in NaBr concentration causes the increase in electric shielding of the micelle charge to reduce the second virial coefficient. The negative second virial coefficient in 0.20 mol dm^{-3} NaBr indicates that intermicellar attraction is operative between spherical micelles. However the attraction is not sufficiently strong to promote their aggregation into larger micelles such as rodlike micelles.

Table 2. Molecular Weight, Aggregation Number, and Second Virial Coefficient of Spherical Micelles of TPB in Aqueous NaBr Solutions

C_S/mol dm^{-3}	$M/10^3$	m	$B/10^{-3}$ mol cm^3 g^{-1}
0	27.6	77	28.0
0.01	32.4	91	3.00
0.05	37.0	104	0.67
0.10	37.9	106	0.29
0.20	41.4	116	−0.03
0.30	43.2	121	−0.47

At higher NaBr concentrations, light scattering from micellar solutions of TPB shows angular dissymmetry. Figure 6 illustrates the angular dependence of light scattering from micellar solutions of TPB in 0.50 mol dm^{-3} NaBr.

When angular dependence of light scattering is observed, the excess reduced intensity follows Zimm's equation, expressed as

$$\frac{K(c-c_0)}{R_\theta - R_\theta^0} = \frac{1}{M}\left(1 + \frac{16\pi^2 \tilde{n}_0^2 R_G^2}{3\lambda^2}\sin^2\frac{\theta}{2} + \cdots\right) + 2B(c-c_0), \quad (5)$$

where θ is the scattering angle and R_G is the radius of gyration of micelles. Therefore the excess reduced intensity extrapolated to zero scattering angle must follow Eq. 3 with $R_0 - R_0^0$ instead of $R_{90} - R_{90}^0$.

Debye plots at higher NaBr concentrations extrapolated to zero scattering angle are shown in Fig. 7. With increasing micellar concentration, they decrease and seem to reach minimum values depending on NaBr concentration as observed for other surfactants.[2—4,8,14,17] This behavior can be thought to represent that spherical micelles formed at cmc aggregate together into large micelles with a size defined by NaBr concentration. These large micelles would be identified as rodlike micelles.

Assuming that the intermicellar interaction is negligible, i.e. the second virial coefficient B equals to zero, one can obtain the molecular weight of rodlike micelle from the minimum value of the Debye plot.[2,4,17] Although the minimum does not appear in Fig. 7, it is expected to be near the highest

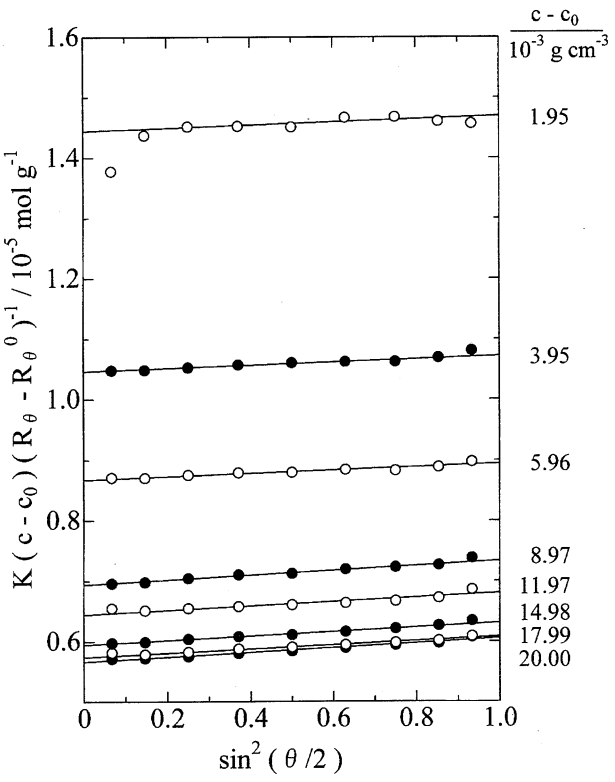

Fig. 6. Angular dependence of reduced intensity of light scattered from aqueous 0.50 mol dm^{-3} NaBr solutions of TPB.

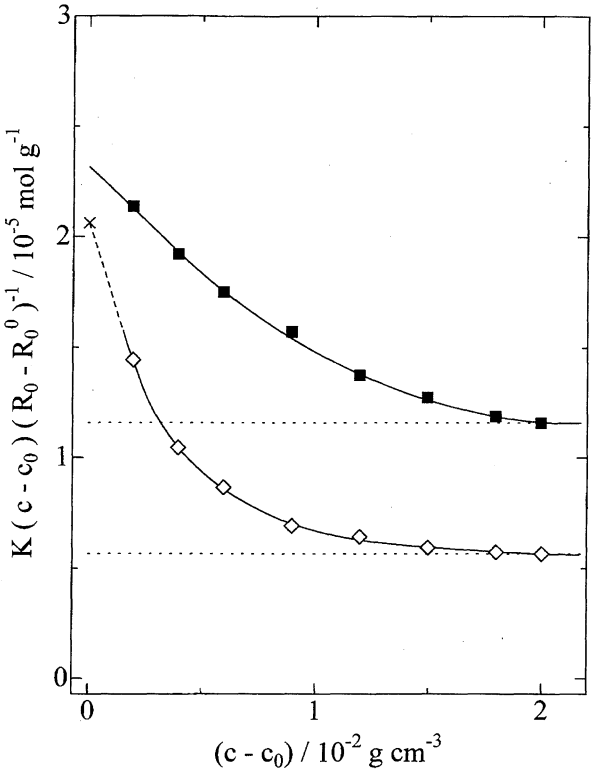

Fig. 7. Debye plots for aqueous NaBr solutions of TPB at higher NaBr concentrations when the scattering angle is 0°. C_S/mol dm^{-3}: ■, 0.30; ◇, 0.50. Dotted lines indicate the values from which the molecular weights of rodlike micelles have been obtained. Broken line represents the extrapolation to the reciprocal molecular weight (×) reported by Jacobs et al.[11]

micellar concentration investigated, and thus we have evaluated the molecular weight of rodlike micelle from the value of Debye plot at the highest concentration, which is denoted by the dotted line in Fig. 7. Molecular weights of rodlike micelles obtained are given in Table 3.

On the other hand, the molecular weight of spherical micelle formed at cmc can be obtained from the intercept of Debye plot extrapolated to the infinite dilution of micelle. For 0.30 mol dm^{-3} NaBr solution, since the Debye plot is almost linear below 6×10^{-3} g cm^{-3} micellar concentration, we can extrapolate it to the infinite dilution and evaluate the molecular weight of the spherical micelle formed at cmc, which is also given in Table 2. In 0.50 mol dm^{-3} NaBr, however, the molecular weight of spherical micelle can not be obtained, because the value of Debye plot increases steeply and nonlinearly with decreasing micellar concentration below 6×10^{-3} g cm^{-3} and in this concentration range we do not have enough data to extrapolate the Debye plot to the infinite dilution.

Table 3. Molecular Weight, Aggregation Number, and Radius of Gyration of Rodlike Micelles of TPB in Aqueous NaBr Solutions

C_S/mol dm^{-3}	$M/10^3$	m	R_G/nm
0.30	87.8	246	<10
0.50	177.8	499	13

For the rodlike micelle in 0.50 mol dm^{-3} NaBr the molecular weight and the aggregation number are 177.8×10^3 and 499, respectively. Our aggregation number is much larger than that of 136 reported for the micelle in 0.5 mol kg^{-1} NaBr by Jacobs et al.[11] This difference in aggregation number will be discussed later.

Although the angular dependence of light scattering is not sufficiently large to evaluate the radius of gyration accurately, the radius of gyration of rodlike micelles is also given in Table 3. It is approximately 13 nm in 0.50 mol dm^{-3} NaBr and is less than 10 nm in 0.30 mol dm^{-3} NaBr. These values are small for a rodlike micelle.

Discussion

Spherical micelles associate together into rodlike micelles when the concentration of an added salt exceeds a threshold. The salt-induced sphere-rod transition of ionic micelles is most clearly revealed by plotting the logarithm of micelle molecular weight against the logarithm of ionic strength or counter ion concentration.[1] The ionic strength is given by concentrations of the surfactant monomer and the added salt, that is C_0+C_S, because the monomer concentration remains almost constant above cmc.

Figure 8 shows the double logarithmic plot for TPB micelles in aqueous NaBr solutions. The plot consists of two straight lines, one each corresponding to the spherical and the rodlike micelles. They are expressed by

$$\log M = 4.68 + 0.09 \log (C_0 + C_S), \quad 0 \leq C_S \leq 0.30 \text{ mol dm}^{-3} \tag{6}$$

and

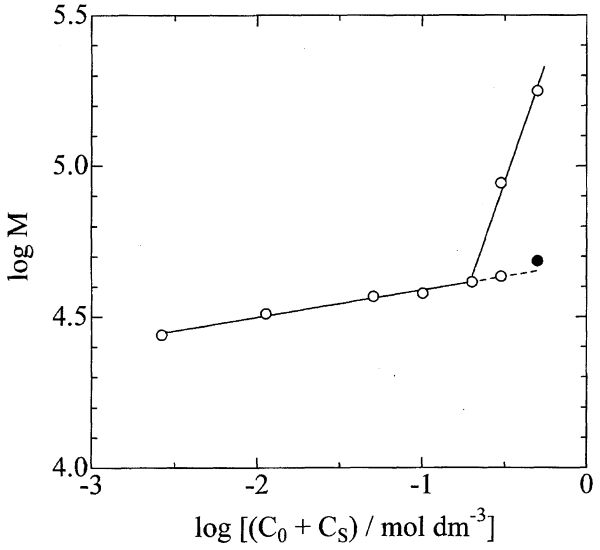

Fig. 8. The double logarithmic plot of molecular weight against ionic strength for spherical and rodlike micelles of TPB in aqueous NaBr solutions. ○, present; ●, Jacobs et al.[11]

$$\log M = 5.74 + 1.58 \log (C_0 + C_S). \quad (7)$$
$$0.19 \leq C_S \leq 0.50 \text{ mol dm}^{-3}$$

The threshold NaBr concentration of the sphere-rod transition of TPB micelle is 0.19 mol dm^{-3}, where its micellar weight is 41.3×10^3, corresponding to the aggregation number of 116.

Jacbos et al. reported the aggregation number of 136, corresponding to the micelle molecular weight of 48.5×10^3, for TPB micelle in 0.5 mol kg^{-1} NaBr.[11] Their value of molecular weight would pertain to the spherical micelle formed at the cmc, because it was determined by calculating the best straight-line Debye plot from the experimental data at surfactant concentrations below 0.01 mol kg^{-1}, which is nearly equal to 4×10^{-3} g cm^{-3}, with the least-squares method.[18] This is supported by the fact that the value by Jacobs et al. falls on the straight line for spherical micelles, as shown in Fig. 8. On the other hand, we have estimated the molecular weight to be 177.8×10^3 from the value of Debye plot at the TPB concentration of 20×10^{-3} g cm^{-3}, which the minimum of the Debye plot is expected to be close to, so that our value pertains to the rodlike micelle. Consequently, the micelle molecular weight reported by Jacobs et al. would be much smaller than ours. If the number of our data points below 4×10^{-3} g cm^{-3} TPB were sufficient to extrapolate the Debye plot to the infinite dilution, the same molecular weight as theirs would be obtained for a spherical micelle formed at cmc, as shown by a cross and a broken line in Fig. 7.

The slope of the $\log M$ vs. $\log (C_0+C_S)$ plot for spherical micelles of TPB, 0.09, is smaller than that for spherical micelles of DPB, 0.132. Such tendency was observed for alkyltrimethylammonium chlorides, but alkyltrimethylammonium bromides had the opposite tendency, as shown in Table 4. It can not yet be concluded that the molecular weight of spherical micelles of the surfactant with longer alkyl chain depends more weakly on the ionic strength.

Table 5 gives the threshold NaBr concentration, C_S^*, and the slopes of the double logarithmic plot for spherical and rodlike micelles of TPB and other cationic surfactants. The values of each parameter for TPB and for tetradecyltrimethylammonium bromide (TTAB) are nearly equal in spite of the difference in ionic head group. In contrast, their dodecyl derivatives showed quite different behavior: DPB micelle remained spherical over the range of NaBr concentration from 0 to 6.00 mol dm^{-3},[7] while dodecyltrimethylammonium bromide formed rodlike micelles at NaBr concentrations above 1.80 mol dm^{-3}.[3] These results would suggest that the longer the alkyl chain that the ionic surfactants have, the less the difference in ionic head group affects the dependence of size and shape of the micelles on ionic strength.

Table 4. Slope of $\log M$ vs. $\log (C_0+C_S)$ Plot for Spherical Micelles of Various Cationic Surfactants

Alkyl group	Alkylpyridinium bromide	Alkyltrimethylammonium Chloride	Alkyltrimethylammonium Bromide
Dodecy	0.132[7]	0.105[5]	0.085[3]
Tetradecyl	0.09	0.09[2]	0.11[2]
Hexadecyl		0.06[4]	

Table 5. Threshold Salt Concentration for Sphere–Rod Transition, C_S^*, and Slopes of $\log M$ vs. $\log (C_0+C_S)$ Plot for Spherical and Rodlike Micelles of Various Cationic Surfactants

Alkyl group	C_S^* / mol dm^{-3}	Slope: Spherical	Slope: Rodlike
Alkylpyridinium bromide			
Dodecyl	—[a]	0.132	—[a]
Tetradecyl	0.19	0.09	1.58
Alkyltrimethylammonium bromide			
Dodecyl[3]	1.80	0.085	1.11
Tetradecyl[2]	0.12	0.11	1.98

a) No sphere-rod transition.

The great difference between TPB and TTAB is the solubility in aqueous solutions of NaBr concentrations higher than 0.50 mol dm^{-3}. TPB is insoluble above 0.50 mol dm^{-3} NaBr, whereas TTAB was soluble at NaBr concentrations up to 4.0 mol dm^{-3}. Because TPB precipitates before its micelle grows into a rodlike micelle larger than has been observed, the radius of gyration of rodlike micelles formed by TPB is much smaller than that of TTAB, which has the radius of gyration of 77.8 nm in 4.0 mol dm^{-3} NaBr.[2] If TPB was soluble at NaBr concentrations up to 4.0 mol dm^{-3}, the rodlike micelle of TPB would grow into a large one having the same radius of gyration as TTAB had.

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