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Solubilization of a water-insoluble dye in aqueous NaBr solutions of alkylpyridinium bromides and its relation to micellar size and shape

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Abstract In order to investigate the effect of added salt on micelle size, shape, and structure the solubilization of Orange OT in aqueous NaBr solutions of decylpyridinium bromide (DePB), dodecylpyridinium bromide (DPB), tetradecylpyridinium bromide (TPB), and hexadecylpyridinium bromide (CPB) has been examined. The solubilization powers of DePB and DPB micelles increase with increasing NaBr concentration up to 2.86 and 3.07 mol dm^{-3}, respectively, but above these concentrations remain unaltered. This suggests that spherical micelles of DePB and DPB can have a maximum and constant size at NaBr concentrations higher than these threshold concentrations. On the other hand, the solubilization powers of TPB and CPB micelles increase in the whole range of NaBr concentration studied. The dependencies of the solubilization powers of their micelles on the counterion concentration change at 0.10 and 0.03 mol dm^{-3} NaBr, respectively, as suggests that TPB and CPB micelles undergo the sphere–rod transition at those concentrations. Orange OT is a more suitable probe for detecting the presence of the maximum- and constant-size spherical micelle than Sudan Red B.

Keywords Solubilization · Alkylpyridinium bromide · Orange OT · Micelle size and shape · Added-salt effect

Introduction

Solubilization of a water-insoluble dye in aqueous solutions of surfactant has been used as a sensitive measure of micelle formation of surfactant. It is also useful as a method for determining relative changes in aggregation number when a surfactant solution is perturbed [1] and as an indication of a micelle structure [2, 3, 4, 5]. Ikeda and coworkers investigated solubilization of a water-insoluble dye, Sudan Red B (1-[4′-(3″-tolylazo)-3′-tolylazo]-2-naphthol), in aqueous micellar solutions of dodecyldimethylammonium chloride [2] and alkyltrimethylammonium halides [3, 4] in the presence of added sodium halide. The solubilization power (molar ratio of solubilizate to micellized surfactant) of these surfactants varies not only with surfactant species but also depends on the micelle shape, either spherical or rodlike. Rodlike micelles have 2–3 times higher solubilization power than spherical micelles.

In previous papers we have shown from light scattering measurements that dodecylpyridinium bromide (DPB) does not form rodlike micelles even when NaBr is present to saturation in solution [6], whereas tetradecylpyridinium bromide (TPB) micelles undergo the sphere–rod transition at 0.19 mol dm^{-3} NaBr [7]. DPB can form common spherical micelles in the presence of NaBr up to 0.30 mol dm^{-3}, but at higher NaBr concentrations it forms only compact spherical micelles having a constant aggregation number of 70.7. On the other hand, TPB can form common spherical micelles in the presence of NaBr up to 0.19 mol dm^{-3}, but at higher NaBr concentrations it can form rodlike micelles, whose aggregation number increases from 116 at 0.20 mol dm^{-3} NaBr to 499 at 0.50 mol dm^{-3} NaBr.

Ikeda and Maruyama [5] measured the solubilization power of DPB micelles toward Sudan Red B in aqueous NaBr solutions. They found that it is constant in the range from 0 to 3.12 mol dm^{-3} NaBr but at higher NaBr concentrations it increases with increasing NaBr concentration as if rodlike micelles are formed.

Porte et al. [8] have shown that hexadecylpyridinium bromide (CPB) micelles undergo the salt-induced sphere–rod transition from quasielastic light scattering, magnetic birefringence, and NMR measurements. Although they have not stated clearly the threshold NaBr concentration for the sphere–rod transition, it is thought to be about 0.05 mol dm^{-3} NaBr from their plot of the Cotton–Mouton constant versus NaBr concentration. According to the results of light scattering measurements of Jacobs and coworkers [9, 10], the aggregation numbers of decylpyridinium bromide (DePB) micelles in 0.5 mol kg^{-1} NaBr and HBr solutions are 49 and 51, respectively. Although there is no study of the added-salt effect on the shape and size of DePB micelles, the results of Jacobs and coworkers and our result on DPB micelles suggest that DePB forms spherical micelles at NaBr concentrations up to its saturation, 6 mol dm^{-3}.

In the present work we examine the solubilization of Orange OT [1-(*o*-tolylazo)-2-naphthol] in aqueous NaBr solutions of DePB, DPB, TPB, and CPB to investigate the effects of added salt on the size and shape of their micelles and to confirm that Orange OT can be used as a probe for determining changes in the micelle shape and size when salt is added.

Experimental

Materials

DePB was synthesized from 1-bromodecane and pyridine. 1-Bromodecane was purchased from Nacalai Tesque and was distilled in vacuo. Pyridine, obtained from Nacalai Tesque, was dried over a molecular sieves 3A. A mixture of distilled 1-bromodecane (1.147 mol) and dry pyridine (3.176 mol) was heated at 125 °C for 9 h. After excess pyridine had been removed from the mixture using a rotary evaporator, the precipitate obtained was recrystallized five times from a mixture of acetone and diethyl ether (24% yield). The critical micelle concentration measured by a surface tension method was 51.3×10^{-3} mol dm^{-3} at 25 °C, in good agreement with 51.6×10^{-3} mol dm^{-3} reported by Shirahama and Tashiro [11].

DPB was prepared by repeated recrystallization of precipitates formed by cooling a saturated aqueous solution of 1-dodecylpyridinium chloride and NaBr. The recrystallization was performed by saturated aqueous NaBr solution and then by acetone. 1-Dodecylpyridinium chloride was purchased from Tokyo Kasei Kogyo Co. The surface tension of an aqueous solution of the DPB sample did not show any minimum around the critical micelle concentration, which was found to be 12.0×10^{-3} mol dm^{-3}. This value is in good agreement with 12.1×10^{-3} mol dm^{-3} reported by Venable and Nauman [12].

TPB was the same sample as previously synthesized and used [7]. CPB was obtained from Nacalai Tesque, recrystallized three times from a mixture of acetone and diethyl ether and dried in vacuo.

Orange OT was purchased from Tokyo Kasei Kogyo Co., recrystallized three times from ethanol, and dried in vacuo.

Reagent grade NaBr was ignited for 2 h before use. Water was redistilled from alkaline $KMnO_4$. Ethanol was of reagent grade from Nacalai Tesque.

Apparatus

Measurements of absorption spectra were carried out using a Shimadzu UV-200S double-beam spectrophotometer. Quartz cells of 10-mm path length were used. Water of constant temperature of 25 ± 0.1 °C was circulated through a cell jacket.

Solubilization measurements

Solid Orange OT was added to an aqueous NaBr solution of surfactant in a test tube with a plastic screw cap. The suspension was shaken in a water bath incubator at 25 ± 0.2 °C for 4 days. The solubilization equilibrium was attained within 3 days at most. The suspension containing CPB was shaken at 35 ± 0.2 °C, because CPB was precipitated by adding a very small amount of NaBr at 25 °C. The excess solid dye was filtered off with a Millipore filter, GSWP01300, of 0.22-μm pore size. The filtrate was diluted with ethanol, the weight of which was 1.5 times the weight of the filtrate, to destroy micelles and to dissolve Orange OT solubilized by micelles in the mixed solution, and an absorption spectrum was measured.

The concentration of Orange OT in the mixed solution was calculated from a calibration curve obtained from absorption spectra of reference solutions. The reference solutions were prepared from an aqueous NaBr solution and an ethanol solution of Orange OT with 2:3 (w/w) ratio. The absorption spectra of Orange OT in the water–ethanol mixture had a main band at 496 nm, the absorbance of which was used to determine the amount of solubilized dye. The molal extinction coefficient at 496 nm decreased from 1.74×10^{4} to 1.58×10^{4} kg mol^{-1} cm^{-1} with increasing NaBr concentration.

Results

The solubility of Orange OT, C_D,, in aqueous NaBr solutions of DePB is shown in Fig. 1 as a function of DePB concentration, C. At a given NaBr concentration, C_S, the solubility is zero below the critical micelle concentration, C_0, but increases linearly with increasing DePB concentration above it. As the NaBr concentration increases, the rate of increase in solubility slightly increases and the critical micelle concentration decreases, as shown in Table 1. C_0 in water is slightly lower than that measured by surface tension.

As in the case of DePB, the solubilities of Orange OT in aqueous NaBr solutions of DPB, TPB, and CPB also remain zero below the critical micelle concentration but increase linearly with surfactant concentration above it. The increase in NaBr concentration raises the rate of increase in the solubility and diminishes the critical micelle concentration, as shown in Tables 2, 3, and 4.

Figure 1 indicates that the solubility of Orange OT increases linearly with increasing micelle concentration, $C-C_0$, at a given NaBr concentration. The slope of the straight line,

$$S_e = \frac{C_D}{C - C_0}, \quad (1)$$

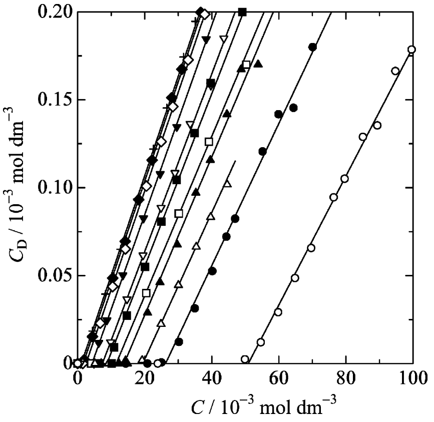

Fig. 1 Solubility of Orange OT in aqueous NaBr solutions of decylpyridinium bromide (DePB) at 25 °C. C_S/mol dm^{-3}: 0 (*open circles*); 0.10 (*closed circles*); 0.20 (*open up triangles*); 0.35 (*closed up triangles*); 0.49 (*open squares*); 0.73 (*closed squares*); 0.97 (*open down triangles*); 1.90 (*closed down triangles*); 2.77 (*open diamonds*); 3.60 (*closed diamonds*); 4.39 (*crosses*)

Table 1 Critical micelle concentrations, C_0, and solubilization powers toward Orange OT, S_e, of decylpyridinium bromide in aqueous NaBr solutions at 25 °C

C_S/mol dm^{-3}	C_0/10^{-3} mol dm^{-3}	S_e/10^{-3}
0	50.8	3.67
0.10	26.2	4.02
0.20	19.4	4.18
0.35	13.8	4.49
0.49	11.6	4.63
0.73	8.7	4.94
0.97	7.4	5.03
1.90	4.3	5.36
2.77	2.5	5.61
3.60	1.7	5.64
4.39	1.1	5.61

represents the number of moles of solubilized dye per mole of micellar surfactant and is called the solubilization power [13]. Its values obtained by the least-squares method for DePB, DPB, TPB, and CPB are given in Tables 1, 2, 3, and 4.

The logarithm of the solubilization power of DePB and DPB in micellar form is plotted in Fig. 2 against the logarithm of the counterion concentration, $\log(C_0 + C_S)$. As the counterion concentration or the NaBr concentration increases, the solubilization power of DPB increases initially, but it becomes constant above 3.07 mol dm^{-3} NaBr. It is expressed by

$$\log S_e = 6.21 \times 10^{-2} \log(C_0 + C_S) - 1.972, \quad 0 \le C_S/\text{mol dm}^{-3} \le 3.07, \tag{2a}$$

$$\log S_e = -1.942, \qquad 3.07 \le C_S/\text{mol dm}^{-3} \le 5.49. \tag{2b}$$

Table 2 C_0, S_e, aggregation numbers, m, and solubilization capacities, Σ, of dodecylpyridinium bromide in aqueous NaBr solutions at 25 °C

C_S/mol dm^{-3}	C_0/10^{-3} mol dm^{-3}	S_e/10^{-3}	m^a	Σ
0	11.7	8.09	46.0	0.372
0.005	9.78	8.39	47.4	0.398
0.010	8.41	8.40	48.8	0.410
0.050	4.09	8.88	56.3	0.500
0.100	2.72	9.22	61.2	0.565
0.297	1.49	9.86	70.5	0.696
0.492	0.98	10.0	70.7	0.707
0.972	0.71	10.6	70.7	0.749
1.896	0.44	11.1	70.7	0.785
2.774	0.27	11.5	70.7	0.813
3.596	0.25	11.3	70.7	0.799
4.391	0.27	11.5	70.7	0.813
5.486	0.18	11.5	70.7	0.813

[a] The aggregation numbers are estimated from Eq. (9) in Ref. [6]

Table 3 C_0, S_e, m, and Σ of tetradecylpyridinium bromide in aqueous NaBr solutions at 25 °C

C_S/mol dm^{-3}	C_0/10^{-3} mol dm^{-3}	S_e/10^{-3}	m^a	Σ
0	2.82	12.6	79.2	0.996
0.010	1.10	14.1	89.5	1.26
0.040	0.52	15.4	101	1.55
0.050	0.42	15.9	103	1.63
0.100	0.30	16.9	109	1.84
0.199	0.24	19.1	120	2.29
0.297	0.23	21.1	227	4.77
0.346	0.23	21.2	288	6.12
0.395	0.23	21.9	356	7.79
0.492	0.17	23.4	503	11.8

[a] The aggregation numbers are estimated from Eqs. (6) and (7) in Ref. [7]

Table 4 C_0 and S_e of hexadecylpyridinium bromide in aqueous NaBr solutions at 35 °C

C_S/mol dm^{-3}	C_0/10^{-4} mol dm^{-3}	S_e/10^{-3}
0	8.15	24.1
0.003	3.00	25.5
0.005	2.29	25.8
0.007	1.97	26.4
0.010	1.57	27.0
0.020	1.00	27.9
0.040	0.80	29.9
0.050	0.94	32.0
0.060	0.77	33.2
0.080	0.77	35.2
0.100	0.87	37.3
0.120	0.76	39.4
0.150	0.62	41.0

This phenomenon is consistent with our previous result from light scattering measurements that the size of the DPB micelle does not depend on NaBr concentration above 0.3 mol dm^{-3} NaBr [6], although the threshold

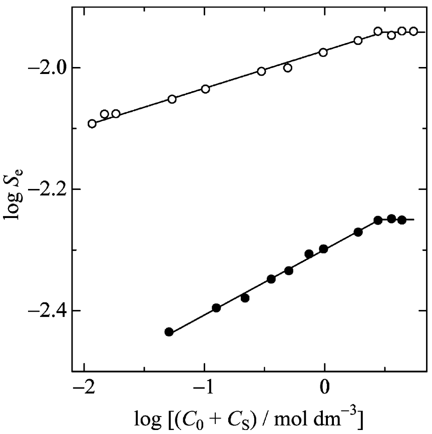

Fig. 2 Double-logarithmic plot of solubilization power of micellar surfactants toward Orange OT against the counterion concentration at 25 °C: DePB (*closed circles*); dodecylpyridinium bromide (DPB) (*open circles*)

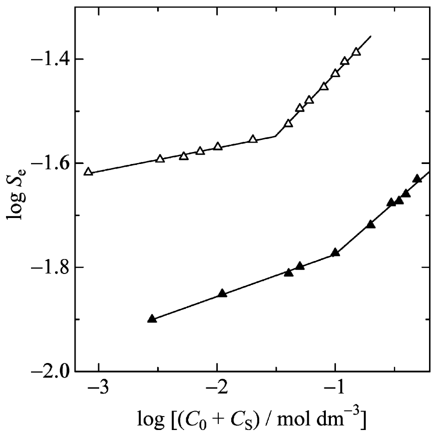

Fig. 3 Double-logarithmic plot of solubilization power of micellar surfactants toward Orange OT against the counterion concentration: tetradecylpyridinium bromide (TPB) at 25 °C (*closed triangles*); hexadecylpyridinium bromide (CPB) at 35 °C (*open triangles*)

NaBr concentrations for limiting the solubilization power and the micelle size are different. This difference in threshold NaBr concentration would arise from the presence of solubilized dye. As in the case of DPB, the solubilization power of DePB increases initially with increasing NaBr concentration but is constant above 2.86 mol dm^{-3} NaBr, as expressed by

$$\log S_e = 1.08 \times 10^{-1} \log(C_0 + C_S) - 2.299,$$
$$0 \leq C_S/\text{mol dm}^{-3} \leq 2.86, \tag{3a}$$

$$\log S_e = -2.250, \qquad 2.86 \leq C_S/\text{mol dm}^{-3} \leq 4.39. \tag{3b}$$

On the other hand, the solubilization power of TPB and CPB does not become constant but increases through the whole range of NaBr concentration measured, as shown in Fig. 3. For TPB the double-logarithmic plot of the solubilization power and the counterion concentration consists of two linear portions, whose slopes change at 0.10 mol dm^{-3} NaBr. These two linear portions are expressed by

$$\log S_e = 8.09 \times 10^{-2} \log(C_0 + C_S) - 1.694,$$
$$0 \leq C_S/\text{mol dm}^{-3} \leq 0.10, \tag{4a}$$

$$\log S_e = 1.99 \times 10^{-1} \log(C_0 + C_S) - 1.576,$$
$$0.10 \leq C_S/\text{mol dm}^{-3} \leq 0.49. \tag{4b}$$

The NaBr concentration dividing two portions is close to the threshold NaBr concentration for inducing the sphere–rod transition of the TPB micelle, 0.19 mol dm^{-3} [7]. In the case of CPB the double-logarithmic plot also consists of two linear portions, which intersect at 0.03 mol dm^{-3} NaBr, as given by

$$\log S_e = 4.50 \times 10^{-2} \log(C_0 + C_S) - 1.481,$$
$$0 \leq C_S/\text{mol dm}^{-3} \leq 0.03, \tag{5a}$$

$$\log S_e = 2.38 \times 10^{-1} \log(C_0 + C_S) - 1.189,$$
$$0.03 \leq C_S/\text{mol dm}^{-3} \leq 0.15. \tag{5b}$$

In each case, the Corrin–Harkins plot, i.e., $\log C_0$ versus $\log(C_0 + C_S)$ plot, also consists of two portions and the NaBr concentration dividing them is almost the same as that in Figs. 2 or 3, as shown in Fig. 4. Such nonlinearity of the Corrin–Harkins plot has been explained in terms of micelle growth and/or a salting-out contribution [14, 15]. The slopes of the linear portion at lower NaBr concentrations, the values of which with the opposite sign are the degree of counterion binding to the micelle [16], have the same value of –0.65 for all the surfactants studied regardless of different alkyl chain length and different temperature. This value is about 0.1 smaller than the values from light scattering measurements [6, 7] but is about 0.15 larger than those estimated from the degrees of counterion binding obtained with the ion-selective-electrode method [17] for DPB and TPB.

The solubilization powers of DPB and TPB toward Orange OT are of the order of 10^{-2} and are not very high. Then we may assume that the states of their micelles would not be influenced very much by the solubilized dye, which would not change their aggregation numbers. The aggregation numbers, *m*, of DPB and TPB micelles without any solubilized dye were previously determined by light scattering [6, 7]. Tables 2 and 3 also include the aggregation numbers calculated from Eq. (9) in Ref. [6] for DPB micelles and from Eqs. (6) and (7) in Ref. [7] for TPB micelles. Then the

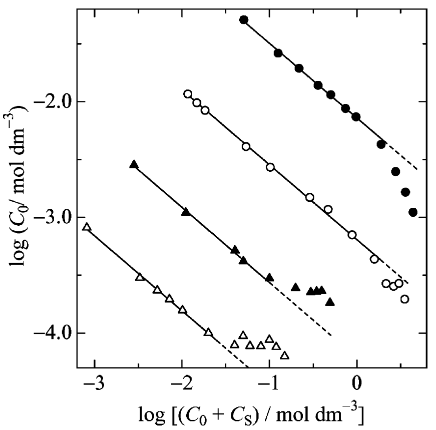

Fig. 4 Corrin–Harkins plot: DePB (*closed circles*); DPB (*open circles*); TPB (*closed triangles*) at 25 °C; CPB (*open triangles*) at 35 °C

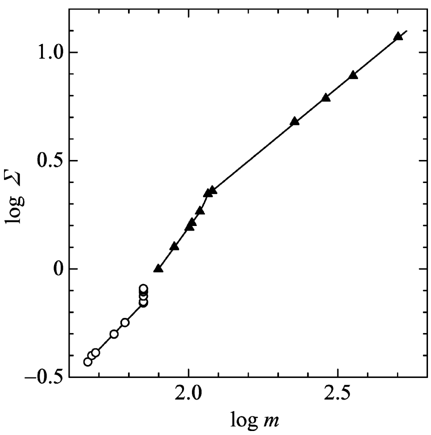

Fig. 5 Double-logarithmic plot of solubilization capacity of surfactant micelles toward Orange OT against micellar aggregation number at 25 °C: DPB (*open circles*); TPB (*closed triangles*)

solubilization capacity of a micelle, i.e., the average number of dye molecules solubilized in a micelle, is given by

$$\Sigma = mS_e. \qquad (6)$$

The solubilization capacities of DPB and TPB micelles are plotted against the micelle aggregation number on a the double-logarithmic scale in Fig. 5, and their values are also given in Tables 2 and 3.

The logarithm of the solubilization capacity of a spherical micelle of DPB increases linearly against the logarithm of its aggregation number until DPB begins to form the spherical micelle having the maximum and constant aggregation number of 70.7. Although DPB forms the spherical micelle having the maximum and constant size above 0.3 mol dm^{-3} NaBr when any dye is not solubilized [6], Fig. 2 shows that its solubilization power toward Orange OT increases with NaBr concentration up to 3.07 mol dm^{-3}. Therefore the solubilization capacity of the constant-size spherical micelle of DPB is expressed by a vertical line in Fig. 5 in the same way as its solubilization capacity toward Sudan Red B [5].

The double-logarithmic plot of the solubilization capacity and the aggregation number of the TPB micelles consist of two linear portions, which are assigned to spherical and rodlike micelles, respectively. It has been reported that the solubilization capacity of alkyltrimethylammonium halide micelles suddenly rises at a sphere–rod transition [3, 4], but in this case no such sudden increase in solubilization capacity was observed.

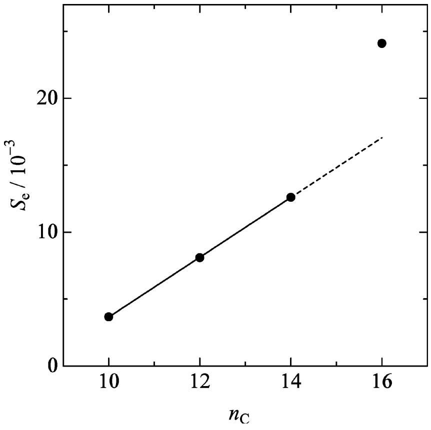

Fig. 6 The solubilization power of surfactant micelles toward Orange OT in water as a function of the number of carbon atoms in an alkyl chain. At 25 °C, DePB, DPB, and TPB. At 35 °C, CPB

Discussion

DPB and TPB form spherical micelles in water [6, 7]. DePB also forms a spherical micelle in water, as judged from the result of Jacobs et al. [9] that its aggregation number is 49 even in 0.5 mol kg^{-1} NaBr. The solubilization power of these spherical micelles increases linearly with the number of carbon atoms in the alkyl chain, n_C, as shown in Fig. 6. The solubilization power increases by 4.46×10^{-3} for each two CH_2 groups and follows the relation

$$S_e = 2.23 \times 10^{-3} n_C - 18.67 \times 10^{-3} \qquad (7)$$

for spherical micelles of alkylpyridinium bromides except CPB in water. Since a micelle of surfactant with a longer alkyl chain has a larger hydrophobic core as long as the micelle shape is spherical, the solubilization power increases with increasing alkyl chain length.

The same relationship between the solubilization power toward Sudan Red B and the number of carbon atoms in the alkyl chain has been reported for spherical micelles of alkyltrimethylammonium halides in water [4]. Comparing the coefficients of Eq. (7) with those of Eq. (4) in Ref. [4], the solubilization power of alkylpyridinium micelles toward Orange OT is about twice as large as that of alkyltrimethylammonium micelles toward Sudan Red B. It is attributed not only to the size of the solubilizate but also to the size of the head group because for the DPB micelle in water the solubilization power toward Orange OT is 3.6 times larger than that toward Sudan Red B [5] and decyltrialkylammonium bromide with longer alkyl chains, i.e., a bulkier head group, has a higher solubilization power toward Orange OT [18].

CPB has been reported by Porte et al. [8] to undergo the salt-induced sphere–rod transition. Although they have not given the threshold NaBr concentration for the transition, it is thought to be about 0.05 mol dm^{-3} NaBr from Fig. 2 in Ref. [8]. The result that the solubilization power of the CPB micelle in water is higher than that expected from Eq. (7), as shown in Fig. 6, seems to indicate that the CPB micelle in water would be rodlike. However, solubilization experiments only for CPB were carried out at 35 °C because CPB was precipitated by adding a very small amount of NaBr at 25 °C. For ionic surfactants an increase in temperature generally causes the solubilization power to increase [19, 20]. From this, the result of Porte et al., and the dependence of the solubilization power on the NaBr concentration, which is mentioned later, we concluded that the higher solubilization power of CPB than that expected from Eq. (7) is not attributed to the formation of a rodlike micelle but to an increase in temperature.

The aggregation number of common spherical micelles of DPB increases with NaBr concentration up to 0.30 mol dm^{-3}, but at higher NaBr concentrations the spherical micelle with a maximum and constant aggregation number of 70.7 is formed [6]. The solubilization power of DPB increases at low NaBr concentrations, but even beyond 0.30 mol dm^{-3} NaBr it continues to increase until it stops increasing at 3.07 mol dm^{-3} NaBr, as shown in Fig. 2. Since the solubilization capacity of DPB is smaller than unity over the whole range of NaBr concentration investigated, a micelle of DPB should solubilize less than a molecule of dye and, therefore, the solubilization of dye should cause only a small disturbance on the micelle. However, the maximum- and constant-size micelle is thought to be a closely packed micelle, so it should be more largely influenced by the solubilization of dye than the common spherical micelle. This would be why the threshold NaBr concentration for limiting the solubilization power is 10 times higher than that for limiting the micellar aggregation number.

Ikeda and Maruyama [5] have reported that the solubilization power of DPB toward Sudan Red B is constant at NaBr concentrations up to 3.12 mol dm^{-3} but increases linearly with a further increase in NaBr concentration. On the basis of our previous result that the constant-size spherical micelles are mutually attractive above 3.00 mol dm^{-3} NaBr [6], they concluded that the increase in solubilization power at NaBr concentrations beyond 3.12 mol dm^{-3} was attributable to the formation of rodlike micelles. Although our threshold NaBr concentration for limiting the solubilization power toward Orange OT is in good agreement with their NaBr concentration at which the solubilization power toward Sudan Red B begins to increase, our result suggests that DPB would form the constant-size spherical micelle at NaBr concentrations beyond 3.07 mol dm^{-3}. The cause of this difference between the results for Orange OT and for Sudan Red B remains to be explained, but Orange OT would be a more suitable probe for detecting the formation of the spherical micelle with a maximum and constant size than Sudan Red B.

As in the case of DPB, the solubilization power of DePB increases initially with increasing NaBr concentration but is constant above 2.86 mol dm^{-3} NaBr. Consequently, it would be concluded that DePB forms common spherical micelles, which increase in size with increasing NaBr concentration, at lower salt concentrations and can form a spherical micelle having a maximum and constant aggregation number at higher NaBr concentrations.

On the other hand, for the TPB micelle, which undergoes the salt-induced sphere–rod transition at 0.19 mol dm^{-3} NaBr [7], the solubilization power increases over the whole range of NaBr concentration studied. The double-logarithmic plot, Fig. 3, of the solubilization power and the counterion concentration consists of two linear portions, and the slope above 0.10 mol dm^{-3} NaBr is 2.5 times larger than that below it. It is clear that the latter corresponds to spherical micelles. The former would correspond to rodlike micelles, since the NaBr concentration at which the slope of the double-logarithmic plot changes nearly equals the threshold NaBr concentration for the sphere–rod transition. More than two molecules of dye are solubilized in a micelle above 0.10 mol dm^{-3} NaBr, as revealed by the solubilization capacity given in Table 3, so the solubilization of dye would slightly lower the threshold NaBr concentration. It is known that the solubilization of Sudan Red B slightly diminishes the threshold NaBr concentration for the sphere–rod transition of alkyltrimethylammonium halide micelles [4].

The solubilization power of CPB also increases with increasing NaBr concentration in the same manner as that of TPB. The NaBr concentration dividing two portions of the double-logarithmic plot is 0.03 mol dm^{-3}, at which concentration the CPB is thought to undergo the sphere–rod transition.

Nonlinear Corrin–Harkins plots (Fig. 4) support these conclusions. The Corrin–Harkins plots are linear at low NaBr concentrations where common spherical micelles are formed. On the other hand, the critical micelle concentrations at higher NaBr concentrations deviate from them downward for constant-size spherical micelles of DePB and DPB and upward for rodlike micelles of TPB and CPB. However, this is not necessarily always valid, because both downward and upward deviations have been observed for rodlike micelles of dodecyldimethylammonium chloride and bromide [14].

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