Solubilization of a Water-Insoluble Dye in Aqueous Solutions of Dodecyltrimethylammonium Halides, and Its Relation to Micelle Size and Shape

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The solubilization properties of aqueous sodium halide solutions of dodecyltrimethylammonium halides have been measured for a water-insoluble dye, Sudan Red B, and they are related to the micelle size and shape, by referring to the molecular weight data already reported. The solubilization power of micellar solutions of dodecyltrimethylammonium chloride toward Sudan Red B is 2.8×10^{-3} mole of dye per mole of surfactant, independent of the NaCl concentration up to 4.0 *M*, where only spherical micelles are formed. The solubilization power of micellar solutions of dodecyltrimethylammonium bromide slightly increases with increasing NaBr concentration and abruptly increases from 2.9×10^{-3} to 3.9×10^{-3} mole of dye per mole of surfactant, at 1.0–1.5 *M* NaBr, corresponding to the sphere–rod transition. The solubilization power of dodecyltrimethylammonium bromide is higher in rodlike micelles than in spherical micelles. The solubilization capacity of a spherical micelle composed of dodecyltrimethylammonium ions is nearly independent of counterion species, either chloride or bromide ion. The solubilization capacities of both spherical and rodlike micelles increase with their size almost linearly. From the density measurements of aqueous solutions of dodecyltrimethylammonium halides, the partial molar volume of surfactants is derived, and it is found that dodecyltrimethylammonium ions have an equal contribution to the partial molar volume of surfactant. The packing state of dodecyltrimethylammonium ions in micelles is common for both surfactants, and also for spherical and rodlike micelles.

INTRODUCTION

It is known that the solubilization power of an aqueous solution of ionic surfactant is enhanced by the addition of salt (1) and is also dependent on the counterion species (2–4). The addition of salt to an aqueous micellar solution not only increases the micelle size but also sometimes alters the micelle shape from spherical to rodlike (5).

In a previous paper (6) we have shown that the addition of NaCl to aqueous solution of dodecyldimethylammonium chloride increases the solubilization of a water-insoluble-azo-dye, Sudan Red B (Merck Sudan III), in its micelles. The increase in solubilization power is parallel to the increase in size of spherical micelle and occurs abruptly when the micelle shape changes from spherical to rodlike.

In another work (7), it was demonstrated by light scattering that dodecyltrimethylammonium chloride (DTAC) forms only spherical micelles in solution above the critical micelle concentration (CMC), and that the size of its micelles slightly increases as NaCl is added. In contrast, light scattering measurements on aqueous solutions of dodecyltrimethylammonium bromide (DTAB) (8) have shown that the size of its spherical micelles increases slightly by the addition of NaBr up to 4.0 *M*, and that rodlike micelles are also formed at NaBr concentrations above 1.8 *M*.

This noticeable effect of counterion species would cause a difference in the behavior of solubilization between DTAC and DTAB micelles in aqueous sodium halide solutions.

In the present work we measure the solubilization behavior of DTAC and DTAB mi-

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celles in aqueous salt solutions against Sudan Red B (1-[4′-(3″-tolylazo)-3′-tolylazo]-2-naphthol) and discuss the results with reference to micelle size and shape as well as to the effect of counterion species. For DTAC the effects of LiCl as well as of NaCl are examined, and for DTAB the effect of addition of NaBr is investigated, all up to their highest salt concentrations.

EXPERIMENTAL

Materials. DTAC was the same sample as previously purified and used (7). DTAB was purchased from Tokyo Kasei Kogyo Company, Inc., recrystallized twice from an ethanol–acetone mixture, and dried *in vacuo* for 10 h at room temperature.

Two batches of Sudan Red B were kindly provided to us by Dr. K. Tori and Professor E. Ohnishi, respectively. They were labeled as Sudan III by Merck but were found to be Sudan Red B from its color index number 26110. In this experiment they were used without further purification. Sudan Red B in ethanol gave absorption spectra having a band at 502 nm with a shoulder around 520 nm and weak bands around 400 and 425 nm.

Reagent grade NaCl and NaBr were ignited for 1 h and stored in a desiccator until use. Amino acid analysis grade anhydrous LiCl was obtained from Wako Pure Chemical Industries, Inc. and used without further purification. Ethanol was a spectrograde reagent from Nakarai Chemicals, Inc. Water was redistilled from alkaline $KMnO_4$ in a glass still.

Apparatuses. Measurements of absorption spectra of dye solubilized in micelles in water and 1.0 *M* sodium halides were carried out on a Shimadzu double beam spectrophotometer UV-200S equipped with a recorder U-125MU, and for these measurements water of constant temperature at (25 ± 0.1)°C was circulated through a cell jacket. For all the other solutions a Hitachi 228 double beam spectrophotometer was utilized at room temperature (25 ± 1°C), together with an attachment of Hitachi MB-6390 personal computer Basic Master level 3. Quartz cells with path length of 5 and 10 mm were used.

The density of aqueous solutions of surfactant was measured at (25 ± 0.01)°C in a water bath, by using an Ostwald pycnometer having a volume of 5 cm^3.

Solubilization measurements. After crystalline Sudan Red B was added to an aqueous salt solution of surfactant, the suspension was shaken for 2 days at (25 ± 0.2)°C in a water-bath incubator BT-22, Yamato Scientific Company, Inc. The excess insoluble dye was filtered off with a Millipore filter, FGLP 01300, having a pore size of 0.2 μm. An aliquot of the first filtrate was discarded, minimizing the error from the adsorption of dye on the filter. The remaining filtrate was diluted with an equal volume of ethanol, and the absorption spectra of the mixed solution were measured.

The concentration of Sudan Red B in the mixed solutions was calculated from absorption spectra of reference solutions; reference solutions were prepared by mixing an aqueous salt solution and an ethanol solution of Sudan Red B with an equal volume ratio. Absorption spectra of Sudan Red B in reference solutions had a main band at 506–507 nm and a shoulder around 530 nm. The molar extinction coefficients, ϵ, of the main band obeyed Lambert–Beer's law, and were not perturbed by the presence of surfactant.

As seen in Table I, the molar extinction coefficient was independent of the salt concentration, C_s (*M*), and, on the average, it was 3.18×10^4 liters $mole^{-1}$ cm^{-1}. This indicates that the dye in the mixed solution would not be influenced by the presence of surfactant and salt, and surfactant molecules are present in monomeric form. Then the molar concentration of Sudan Red B solubilized in aqueous salt solution of surfactant, *S*, can be obtained as

$$S = 2A'/\epsilon d \qquad [1]$$

where A' is the optical density of the mixed solution and d is the path length of quartz cell.

The attainment to solubilization equilibrium was examined as follows: an aliquot of

TABLE I

Molar Extinction Coefficient of Sudan Red B in Aqueous Ethanol Solution and Solubilization Parameters of Micellar Solutions of DTAC and DTAB toward Sudan Red B

	C_s (M)	ϵ (10^4 liters mole^{-1}cm^{-1})	S_e (10^{-3} mole dye/ mole surfactant)	m'	Σ (mole dye/mole micelle)
DTAC in NaCl solution	0.00	3.09	2.81	43.6	0.122
	1.00	3.32	2.80	65.4	0.183
	2.01	3.19	2.66	70.3	0.187
	3.01	3.10	2.71	73.3	0.199
	3.98	3.12	2.87	75.8	0.217
DTAC in LiCl solution	3.95	3.13	2.87		
	4.95	3.18	2.95		
	9.93	3.20	—		
	13.2	3.23	—		
DTAB in NaBr solution	0.00	3.09	2.85	53.0	0.151
	0.52	3.22	2.99	71.9	0.215
	1.00	3.41	2.93	76.3	0.223
	1.25	3.15	3.39	77.5	0.263
	1.53	3.14	3.90	78.8	0.307
	2.05	3.13	4.05	92.8	0.376
	2.98	3.20	4.50	120.0	0.540
	4.01	3.13	5.06	186.5	0.943

shaken suspension was taken out at each adequate time interval after the addition of dye and filtered to remove the insoluble dye, and absorption spectra of the filtrate were measured. Optical densities at 506–507 nm are plotted against the time in Fig. 1. The solubilization equilibria were attained after shaking for 12 h. Alternative examination was performed on suspensions shaken for 2 and 3–4 days, respectively. In all cases, values of solubility from both suspensions were in agreement with one another within experimental errors.

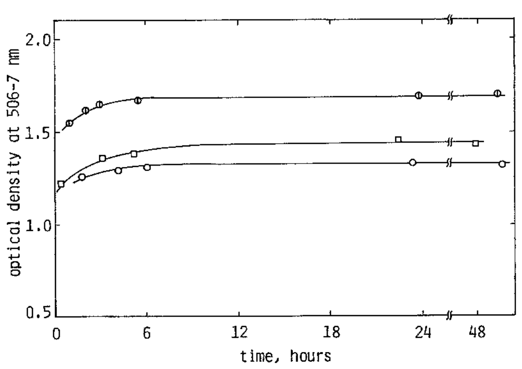

FIG. 1. The rate of solubilization of Sudan Red B in surfactant micelles in water. Surfactant concentration (10^{-2} g cm^{-3}): ○, 1.034 for DTAC; ◑, 1.167 for DTAC; □, 1.059 for DTAB.

The extraction of Sudan Red B by chloroform from aqueous salt solutions of surfactant which was previously performed (6) was not adopted in the present work, because water and chloroform layers did not separate perfectly but formed emulsion, especially, in the case of absence of salt.

RESULTS

The molar concentration of Sudan Red B solubilized in aqueous NaCl solutions of DTAC, S (M), is plotted against the surfactant concentration, C (M), in Fig. 2. The solubility of Sudan Red B in aqueous solutions of DTAC increases above the surfactant concentrations equal to the CMC, C_0 (M). The CMC value of DTAC is 0.018$_8$ M in water, 0.001$_7$ M in 1.0 M NaCl, and lower than 0.001 M for so-

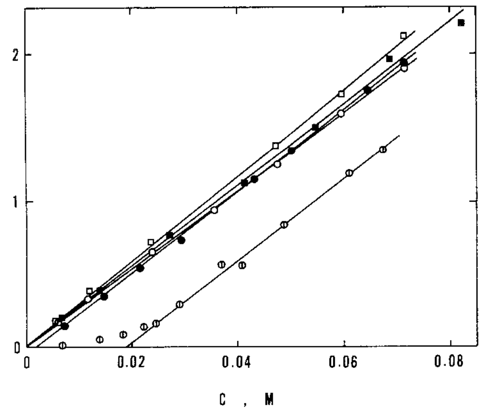

FIG. 2. Solubility of Sudan Red B in aqueous solutions of DTAC as a function of surfactant concentration. NaCl concentration (*M*): ⦶, 0; ●, 1.00; ○, 2.01; ■, 3.01; □, 3.98.

lutions of higher NaCl concentrations. These values are consistent with those measured by the light scattering method (7).

The molar concentration of dye solubilized in aqueous NaBr solutions of DTAB is shown in Fig. 3 as a function of surfactant concentration. The CMC value of DTAB in water is obtained to be 0.014_7 *M*, and the CMC values of DTAB in aqueous NaBr solutions are lower than 0.002 *M*, coinciding with those from light scattering (8).

The increase in solubility above the CMC is linear with an increase in surfactant concentration, as seen in Figs. 2 and 3. The slope of the straight line at a given salt concentration represents the moles of solubilized dye per mole of micellar surfactant and is called the solubilization power, S_e; that is,

$$S_e = S/(C - C_0) \qquad [2]$$

since the dye is insoluble in surfactant solutions below the CMC. The slight and nonlinear solubility of dye in DTAC micelles in water near the CMC may be attributed to contaminant homologs with longer hydrocarbon chains (7). If the micelle size and shape are not varied by the micelle concentration, and if the intermicellar interaction does not perturb the solubilization, the solubilization power of surfactant should be independent of the micelle concentration; that is, the solubilized amount of dye per mole of micellar surfactant is constant at a given salt concentration.

Figure 4 plots the solubilization power of surfactant micelles against Sudan Red B as a function of salt concentration, and their numerical values are summarized in Table I. It is seen that the solubilization power of DTAC micelles is 2.8×10^{-3} mole of dye per mole of surfactant, independent of NaCl concentration. On the other hand, the solubilization power of DTAB micelles slightly increases with increasing NaBr concentration. At NaBr concentrations between 1.0 and 1.5 *M*, the solubilization power of DTAB micelles abruptly changes, and above 1.5 *M* it moderately increases with increasing NaBr concentration.

The solubility of dye in aqueous LiCl solutions of DTAC was also measured at high LiCl concentrations. As seen in Fig. 5 as well as in Fig. 4, even in the presence of LiCl, the solubilization power of DTAC micelles is scarcely influenced, as long as the LiCl con-

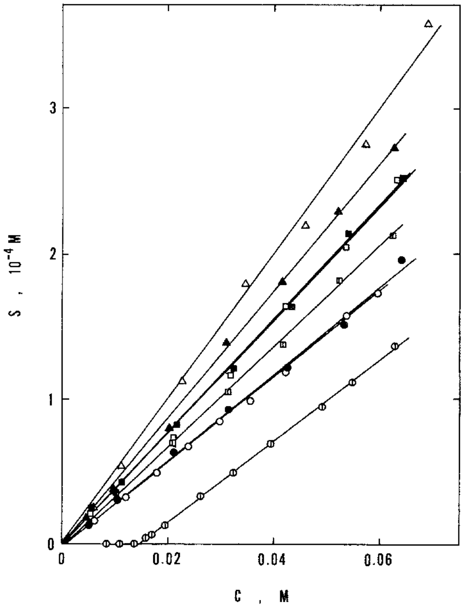

FIG. 3. Solubility of Sudan Red B in aqueous solutions of DTAB as a function of surfactant concentration. NaBr concentration (*M*): ⦶, 0; ●, 0.52; ○, 1.00; ◫, 1.25; ■, 1.53; □, 2.05; ▲, 2.98; △, 4.01.

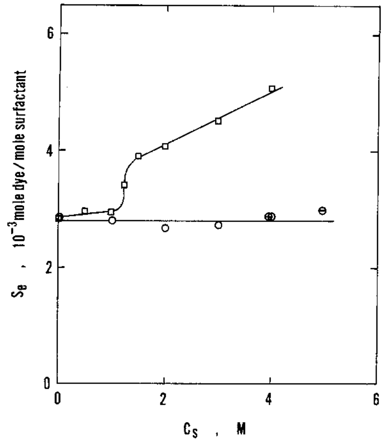

FIG. 4. Solubilization power of micellar surfactants toward Sudan Red B as a function of salt concentration. ○, DTAC in NaCl solution; ⊖, DTAC in LiCl solution; □, DTAB in NaBr solution.

centration is lower than 10 *M*. Table I also includes these data. However, the dependence of the solubility of dye on the surfactant concentration is not linear in 10 and 13 *M* LiCl but is rather sigmoidal against surfactant concentration. Especially, 13 *M* LiCl solutions of DTAC were so viscous that it took twice as long to attain the solubilization equilibrium. The state of DTAC micelles such as their size and mutual interaction could be quite different in such concentrated LiCl solutions.

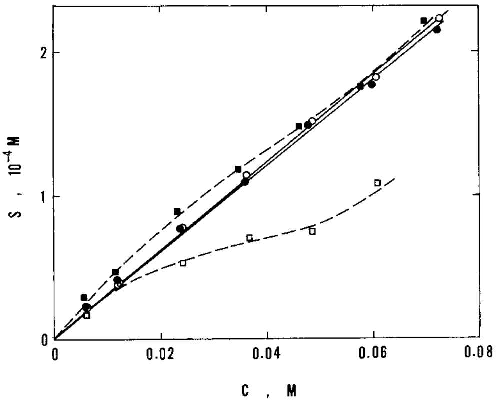

FIG. 5. Solubility of Sudan Red B in aqueous solutions of DTAC as a function of surfactant concentration. LiCl concentration (*M*): ●, 3.95; ○, 4.95; ■, 9.93; □, 13.2.

Figure 6 shows the density, ρ (g cm^{-3}), of aqueous solutions of surfactants without salt as a function of surfactant concentration, c (g cm^{-3}). The dependence of the density on the surfactant concentration is divided into two linear regions. A crossing point of the two lines is obtained as $0.55_0 \times 10^{-2}$ g cm^{-3} or 0.020_8 *M* for DTAC and $0.45_5 \times 10^{-2}$ g cm^{-3} or 0.014_8 *M* for DTAB, which are consistent with the CMC values obtained from the solubilization and the other measurements (7, 8).

The partial specific volumes, $\bar{v}_1$ and $\bar{v}_m$ (cm^3 g^{-1}), of monomeric and micellar surfactants, respectively, can be evaluated from each straight line by

$$\rho = \rho_0 + (1 - \bar{v}_1\rho_0)c \qquad c \leqslant c_0 \qquad [3]$$

$$\rho = \rho_0' + (1 - \bar{v}_m\rho_0')(c - c_0) \qquad c \geqslant c_0 \qquad [4]$$

where ρ_0 and ρ_0' are densities of solvent and solution at the CMC, respectively, and c_0 is the CMC in the unit of g cm^{-3}. The values of ρ_0' are obtained as 0.9969 g cm^{-3} for DTAC and 0.9975 g cm^{-3} for DTAB.

The values of partial specific and molar volumes are summarized in Table II, where the partial molar volumes, $\bar{V}_1$ and $\bar{V}_m$, are equal to the monomer molecular weight times $\bar{v}_1$ and $\bar{v}_m$, respectively. These values can be compared with the data from the literature (9–11). The partial molar volumes of DTAC and DTAB in water are both larger above the CMC than below the CMC. It is also noted that the partial molar volume of DTAC is smaller than that of DTAB, the differences being 7–8 cm^3 mole^{-1}.

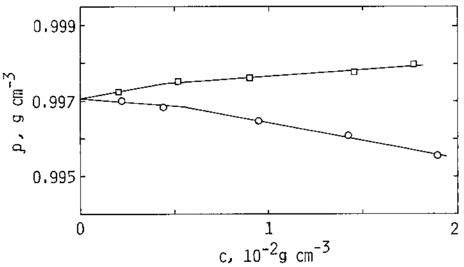

FIG. 6. Density of aqueous solutions of surfactant as a function of surfactant concentration. ○, DTAC; □, DTAB.

TABLE II

Partial Specific Volume and Partial Molar Volume of DTAC and DTAB in Water at 25°C

	DTAC		DTAB		
	Below CMC	Above CMC	Below CMC	Above CMC	Ref.
$\bar{v}$ (cm^3 g^{-1})	1.037	1.100	0.909	0.968	Present work
$\bar{V}$ (cm^3 mole^{-1})	273.7	290.3	280.2	298.4	Present work
		289.0[a]			9
			287.0	295.5	10
			278.1	285.1	11

[a] At 23°C.

DISCUSSION

(A) Solubilization power and micelle shape. As observed by light scattering measurements (7), DTAC forms only spherical micelles, irrespective of the presence of NaCl in concentrations from 0 to 4 *M*. Although the aggregation number of spherical micelle in 4.0 *M* NaCl is nearly twice as large as that in water, the solubilization power of DTAC micelles is constant, independent of the NaCl concentration.

DTAB in NaBr solutions associates into spherical micelles above the CMC, but it can also form rodlike micelles as the NaBr concentration is higher than 1.8 *M* (8). The dependence of the solubilization power of DTAB on NaBr concentration reflects the sphere–rod transition of its micelles: the solubilization power of spherical micelles slightly increases with an increase in NaCl concentration, but the abrupt increase in solubilization power occurs at 1.0–1.5 *M* NaBr. This range of NaBr concentrations is slightly lower than that for the sphere–rod transition (1.8 *M*). The difference in the threshold NaBr concentration between the solubilization and the light scattering results might depend on the higher sensitivity of solubilization to short rodlike micelles than light scattering and it could also be caused by the lowering of threshold salt concentration in the presence of solubilizate. The solubilization power increases with an increase in NaBr concentration above 1.5 *M* NaBr, being parallel to the growth of rodlike micelles.

(B) Solubilization capacity and micelle size. If the micelle aggregation number is not influenced by the solubilization, the average number of dye molecules solubilized in a micelle, i.e., the solubilization capacity of a micelle, Σ, is given by

$$\Sigma = m'S_e. \qquad [5]$$

The aggregation number of micelle, m', at a given salt concentration may be taken from the data given in the literature (7, 8) or their interpolation.

The light scattering measurements on aqueous NaBr solutions of DTAB (8) showed that the sphere–rod conversion of its micelles in 2.0 and 3.0 *M* NaBr occurs at the second CMC, which are located at DTAB concentrations of 0.0201 and 0.0088 *M*, respectively. However, the corresponding behavior of the solubilization was not detected in 2.0 and 3.0 *M* NaBr, because of low experimental accuracy of solubilization measurements below the second CMC. Since the solubilization was measured at surfactant concentrations higher than the second CMC, the aggregation number of rodlike micelles was chosen for the calculation of solubilization capacity of a micelle of DTAB.

Values of the solubilization capacity of DTAC and DTAB micelles are listed in Table I, together with values of the aggregation number. The former is plotted against the latter in Fig. 7. The solubilization capacity of a DTAC micelle in NaCl solution increases with increasing micelle size and changes from 0.12

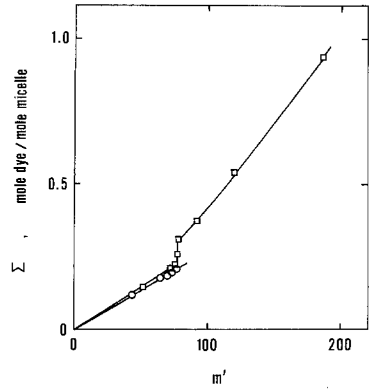

FIG. 7. Solubilization capacity of a micelle toward Sudan Red B as a function of micelle aggregation number. ○, DTAC in NaCl solution; □, DTAB in NaBr solution.

to 0.22. That is, a dye molecule is incorporated in one of eight micelles with $m' = 44$ and one of four micelles with $m' = 76$, respectively.

The solubilization capacity of a DTAB micelle in NaBr solutions also increases with increasing micelle size, but exhibits a sudden rise at $m' = 76$–79. The solubilization capacity of a spherical micelle varies from 0.15 to 0.22 with a change in m' from 53 to 76. Aggregation numbers higher than 79 can be mostly assigned to rodlike micelles. Then their solubilization capacity increases from 0.31 to 0.94 for m' from 79 to 187.

Thus it is likely that the solubilization capacity of a spherical micelle of dodecyltrimethylammonium ion (DTA$^+$) is substantially determined by the micelle aggregation number, independently of counterion species, either chloride or bromide. The present results showing the solubilization capacity of a micelle lower than unity for the dye indicates that the solubilization should be considered to be a kind of complex formation between dye and surfactant, only effective in the micellar form of surfactant.

The double logarithmic plots of solubilization capacity and aggregation number are shown in Fig. 8, which give linear relations. The straight lines are represented by

$$\log \Sigma = 1.0_4 \log m' - 2.62 \qquad 44 \leqslant m' \leqslant 76 \qquad [6]$$

for DTAC micelles in NaCl solutions, and

$$\log \Sigma = 1.0_8 \log m' - 2.68 \qquad 53 \leqslant m' \leqslant 76 \qquad [7]$$

$$\log \Sigma = 1.3_2 \log m' - 2.94 \qquad 79 \leqslant m' \qquad [8]$$

for DTAB micelles in NaBr solutions. The coefficients for both spherical micelles are equal to unity.

(C) Partial molar volume. From Table II we can see that the partial molar volumes of DTAC and DTAB in water change discontinuously at the CMC, giving their increases, 16.6 and 18.2 cm^3 mole^{-1}, respectively. Since their partial molar volume consists of contributions of DTA$^+$ and counterion, the partial molar volume of DTA$^+$, $\bar{V}_+$, can be derived by subtraction of that of Cl$^-$, 17.8 cm^3 mole^{-1}, or Br$^-$, 24.7 cm^3 mole^{-1} (12), as given in Table III. The values of $\bar{V}_+$ are common for both DTAC and DTAB: 256 cm^3 mole^{-1} in monomeric form and 273 cm^3 mole^{-1} in micellar form. Thus the packing states of spherical micelles of DTA$^+$ in water are almost identical, irrespective of whether the counterion is Cl$^-$ or Br$^-$.

These results can be compared with those for dodecyldimethylammonium chloride (DDAC) and dodecyldimethylammonium bromide (DDAB). The values of partial molar volumes of DDAC and DDAB in water (13, 14) are also listed in Table III. Again, micellization causes the partial molar volume to increase to 8.4 cm^3 mole^{-1} for DDAC and 6.8 cm^3 mole^{-1} for DDAB. When the contributions from Cl$^-$ and Br$^-$ are subtracted, the partial molar volumes of dodecyldimethylammonium ion (DDA$^+$) are nearly common in water, as shown in Table III. The values of $\bar{V}_+$ are 248 ± 2 cm^3 mole^{-1} in monomeric form and 256 cm^3 mole^{-1} in micellar form. Thus the packing states of spherical micelles of DDA$^+$ in water are almost identical, independent of counterion species.

When surfactant ions in water are incorporated in a spherical micelle, the increase of their partial molar volume is twice larger for DTA$^+$ than for DDA$^+$. Thus surfactant ions

TABLE III

Partial Molar Volume and Micelle Parameters of Spherical Micelles of DTA$^+$ and DDA$^+$ in Water

	$\bar{V}$ (cm^3 mole^{-1})		$\bar{V}_+$ (cm^3 mole^{-1})				
Surfactant	Below CMC	Above CMC	Below CMC	Above CMC	m'	V (10^{-20} cm^3)	r (nm)
DTAC	273.7	290.3	255.9	272.5	43.6	2.10	1.7
DTAB	280.2	298.4	255.5	273.7	53.0	2.63	1.8
DDAC	263.9[a]	272.3[a]	246.1	254.5	55.6	2.52	1.8
DDAB	275.2[b]	282.0[b]	250.5	257.3	77.1	3.61	2.0_5

[a] Ref. (13).
[b] Ref. (14).

in a spherical micelle are more loosely packed for DTA$^+$ than for DDA$^+$, reflecting the differences in size of the head group.

Assuming that a micelle formed in water is a sphere with a radius, r, the volume of a spherical micelle, V, can be represented by

$$V = m'\bar{V}/N_A = (4/3)\pi r^3 \qquad [9]$$

where N_A is the Avogadro number. The values of m' can be obtained from light scattering measurements (7, 8, 15, 16). As seen in Table III, the radius of a spherical micelle in water is 1.7–2.1 nm, comparable with the radius estimated from the chain length of a surfactant.

It was reported that the partial molar volume of DTAB in 2.0 *M* NaBr is 298–296 cm^3 mole^{-1} (17). Our result obtained for spherical micelles in water is in agreement with these values. The partial molar volume of DDAC is 274–272 cm^3 mole^{-1} in 1.0–4.0 *M* NaCl (13), where rodlike micelles are formed (8, 15), and it is equal to the value for spherical micelles in water.

We may claim that the partial molar volume of N–CH$_3$-substituted alkylammonium ion in a micelle is defined by the surfactant species and is independent of the counterion species as well as of the micelle size and shape.

(D) Comparison of solubilization properties between DDAC, DTAC, and DTAB. The dependence of the solubilization power of micellar solution on the salt concentration, associated with the sphere–rod transition, has already been reported for aqueous NaCl solutions of DDAC micelles (6). In aqueous solutions of NaCl more concentrated than 1.5 *M*, DDAC forms rodlike micelles having aggregation number larger than 585, and their solubilization power is 4.4 × 10^{-3} mole of dye per mole of surfactant, independent of the NaCl concentration. A surfactant ion in long rodlike micelles can combine with a definite amount of dye molecules, independent of their aggregation number.

On the other hand, the solubilization power of rodlike micelles of DTAB depends on the NaBr concentration. Since rodlike micelles of DTAB are not sufficiently large even at high NaBr concentrations as compared with spherical ones, the amount of solubilized dye per surfactant increases with increasing the aggregation number, as seen in Fig. 4. That is, the aggregation number of rodlike micelles of DTAB is yet 187 in 4.0 *M* NaBr and is much lower than the threshold value of 585 for DDAC in 1.5 *M* NaCl.

The solubilization power of spherical micelles of DDAC formed in water is equal to 2.15 × 10^{-3} mole of dye per mole of surfactant (6) and is smaller than that of DTAC and DTAB. This observation is consistent with the packing of surfactants in a micelle. A dye molecule is more readily incorporated in micelles formed by surfactant ions with a larger head group, because of their looser packing in micelles.

The solubilization power of spherical micelles of DDAC greatly increases with increas-

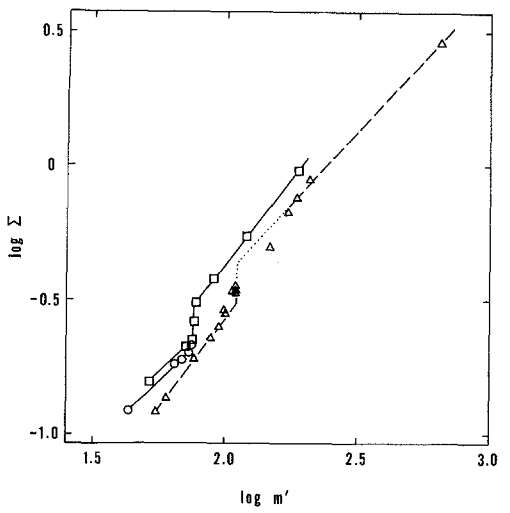

FIG. 8. The double logarithmic plot of solubilization capacity of a micelle toward Sudan Red B against micelle aggregation number. ○, DTAC in NaCl solution; □, DTAB in NaBr solution; △, DDAC in NaCl solution.

ing NaCl concentration. However, the solubilization power of spherical micelles of DTAB increases only slightly with increasing NaBr concentration. In the case of DTAC micelles, the solubilization power remains constant.

In Fig. 8, the solubilization capacity of a DDAC micelle in the presence of NaCl (6) is also plotted against the aggregation number. The straight lines for spherical and rodlike micelles can be represented by

$$\log \Sigma = 1.3_8 \log m' - 3.31 \qquad 56 \leqslant m' \leqslant 104 \qquad [10]$$

$$\log \Sigma = 1.0_3 \log m' - 2.46 \qquad 175 \leqslant m' \qquad [11]$$

indicating that the solubilization capacity of a surfactant micelle toward Sudan Red B should primarily be proportional to the micelle aggregation number or to the micelle volume. This result is consistent with previous ones (3, 6, 18). As seen in Fig. 8, a dye molecule can be incorporated more easily in rodlike micelles than in spherical micelles, and DTA^+ micelles are superior in their solubilization properties to DDA^+ micelles. These differences may be attributed to the array and packing of surfactant ions in a micelle.

The direct effect of different counterion species is not to confer different solubilization properties on surfactant cation but to alter the micelle aggregation number as well as the threshold salt concentration for the sphere–rod transition. Thus the definitely higher solubilization property of DTA^+ is induced for bromide micelles than for chloride micelles in the presence of more than 1.5 *M* NaBr or NaCl, where the former are rodlike while the latter are spherical.

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