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CHARACTERISTICS OF RODLIKE MICELLES OF ALKYLTRIMETHYLAMMONIUM HALIDES IN AQUEOUS SODIUM HALIDE SOLUTIONS: THEIR FLEXIBILITY AND ENTANGLEMENT

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Static light scattering has been measured for aqueous NaCl solutions of tetradecyl- and hexadecyltrimethylammonium chlorides (C_{14}TAC and C_{16}TAC) and for aqueous NaBr solutions of their homologous bromide derivatives (C_{14}TAB and C_{16}TAB) at 25 or 35 °C. The threshold salt concentration of sphere-rod transition depends on the alkyl chain length and the counterion species. The persistence length of a long rodlike micelle has been evaluated as 37 - 60 nm for C_{14}TAB, C_{16}TAC and C_{16}TAB. Solution properties of long rodlike micelles in semidilute regime are investigated on the basis of the blob model and the scaling laws. Electron micrographs prove the existence of spherical micelles and semiflexible rodlike micelles.

INTRODUCTION

Molecules of ionic surfactants in aqueous solutions form spherical micelles above the critical micelle concentration and sometimes associate into large micelles which are rodlike. Formation of rodlike micelle is induced by surfactant concentration,[1-3] salt concentration,[3-8] some additives,[9] and temperature.[8,10-12]

Many workers have discussed the flexibility of rodlike micelles, whether they are stiff or flexible,[5,12-18] and almost all of them have suggested the formation of flexible rodlike micelles. If the wormlike chain model[19] is applied to such rodlike micelles, the persistence length represents their flexibility parameter. The persistence length of long rodlike micelles was first reported for micelles of hexadecylpyridinium bromide in aqueous NaBr solution.[20] Those for rodlike micelles of dodecyldimethylammonium halides in aqueous sodium halide solutions[3,21,22] was longer than that of hexadecylpyridinium bromide but shorter than that of dimethyloleylamine oxide in aqueous NaCl solution.[23,24]

The behavior of polymers in semidilute solutions, in which the concentration of polymers is still dilute but polymers are not isolated, is different from that in dilute solutions and can be treated by the scaling law.[25] Such a treatment was applied to semidilute micelle solutions of alkyltrimethylammonium bromides.[2,18]

We have measured static light scattering from aqueous sodium halide solutions of tetradecyl- and hexadecyltrimethylammonium halides and have investigated the formation of rodlike micelles in concentrated salt solutions and their flexibility.[3,26,27] These rodlike micelles entangle together in semidilute solutions. We describe the dependence of the solution properties of alkyltrimethylammonium halide micelles on the alkyl chain length, together with their dependence on the salt concentration and the counterion species. Moreover, we report the visual observation of spherical and rodlike micelles by means of electron microscopy.

LIGHT SCATTERING

Suppose that micelles are composed of many scattering centers arranged in a spherically symmetric fashion but are far apart from one another, and, therefore, the external interference effect of light scattering can be separated from its internal interference effect. Then the reduced intensity of light scattered at a scattering angle, θ, from a micellar solution is generally described by[28,29]

$$R_\theta - R_\theta{}^o = K(c - c_o)MP(\theta)S(\theta), \qquad (1)$$

where R_θ and $R_\theta{}^o$ are the reduced scattering intensities at a surfactant concentration, c (g cm^{-3}), and the critical micelle concentration, c_o (g cm^{-3}), respectively. K is the optical constant and M is the average molecular weight of micelles. P(θ) is the particle scattering factor, and S(θ) is the structure factor which arises from the nonrandom arrangement of micelle particles. They originate from the internal and external interference effects of micelles, respectively.

For dilute micellar solutions, eq. (1) can be expanded in terms of the micelle concentration and yields the equation

$$\frac{K(c - c_o)}{R_\theta - R_\theta{}^o} = \frac{1}{MP(\theta)} + 2B(c - c_o), \qquad (2)$$

where the external interference effect is represented by the second virial coefficient, B.

For small scattering angles,

$$1/P(\theta) = 1 + (1/3)R_G{}^2\mu^2 \qquad (3)$$

regardless of the micelle shape, with the magnitude of scattering vector,

$$\mu = (4\pi\tilde{n}_o/\lambda)\sin(\theta/2), \qquad (4)$$

where R_G is the average radius of gyration of micelles, $\tilde{n}_o$ is the refractive index of solvent and λ is the wavelength of incident light in vacuo.

When there is no angular dependence of light scattering, as exemplified for $C_{16}TAC$ in 0.5 M NaCl in Fig. 1(a), the internal interference effect is negligible and the reciprocal envelope at an arbitrary scattering angle, usually 90°, increases linearly with increasing micelle concentration. According to eq. (2), its intercept at zero micelle concentration and the slope provide the average molecular weight of micelles and the second virial coefficient, respectively.

If the salt is sufficiently present in micellar solution, the angular dependence of the Zimm plot is manifest and it increases with an increase in micelle concentration. Simultaneously, the reciprocal envelope of light scattering at zero scattering angle levels off and reaches a constant value at high micelle concentrations, as illustrated for $C_{16}TAC$ in 1.5 M NaCl

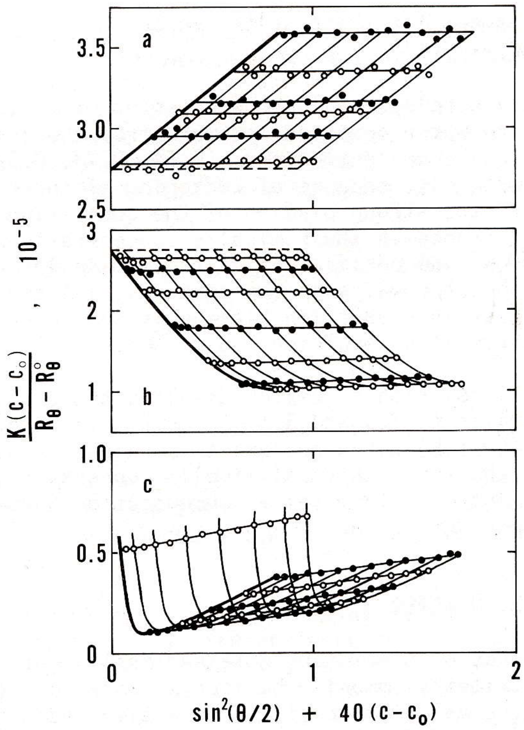

Figure 1. The Zimm plots of light scattering for aqueous NaCl solutions of $C_{16}TAC$ at 25 °C. NaCl concentration (M): a, 0.5; b, 1.5; c, 3.0.

in Fig. 1(b). This feature suggests the formation of micelles with large molecular weight at finite micelle concentrations, while small spherical micelles are formed at the critical micelle concentration.

The molecular weight of spherical micelles can be evaluated from the extrapolation to zero micelle concentration of the Zimm plot at zero scattering angle. On the other hand, the molecular weight and the radius of gyration of rodlike micelles are calculated from the constant value at high micelle concentration of the Zimm plot at zero scattering angle and from its angular dependence at the same micelle concentration. In this case, the second virial coefficient may be neglected, because the electrostatic repulsion is shielded by the high ionic strength. Trap and Herrmans[30] reported that the second virial coefficients of micellar solutions of $C_{14}TAB$ and octadecyltrimethylammonium bromide were approximately zero in 0.05 M NaBr.

At further high salt concentrations, the reciprocal envelope of light scattering in the zero direction increases after its initial decrease with an increase in micelle concentration, and then its angular dependence again becomes lower, as seen in Fig. 1(c) for $C_{16}TAC$ in 3.0 M NaCl. Rodlike micelles overlap and entangle at high micelle concentrations, like polymers in semidilute solutions.[25] The molecular weight and the radius of gyration of rodlike micelles may be calculated for the micelle concentration at the minimum of the reciprocal envelope of light scattering in the zero direction.

The reciprocal envelope of light scattering for aqueous sodium halide solutions of alkyltrimethylammonium halides belongs to one of three types shown in Fig. 1, except for their salt-free solutions and for 3.0 M NaCl solution of $C_{14}TAC$.[3,26,27]

The reciprocal envelope of light scattering of $C_{14}TAC$, $C_{14}TAB$, $C_{16}TAC$ and $C_{16}TAB$ in water deviates downward from the initial straight line at certain micelle concentrations, (0.64, 0.77, 0.32, and 0.35) x 10^{-2} g cm^{-3}, respectively, because of weakening of intermicellar repulsion caused by the strong binding of the counterion on the micelle.[31] The difference in their micelle concentrations is related to that in the second virial coefficient of these micelles which will be described later: when the value of the second virial coefficient is large, even a small increase in counterion binding is sufficiently effective to suppress the electrostatic repulsion.

The 3.0 M NaCl solution of $C_{14}TAC$ displays the profile of two-step micellization, similar to 2.0 and 3.0 M NaBr solutions of dodecyltrimethylammonium bromide ($C_{12}TAB$)[1]: the reciprocal envelope of light scattering is constant above the first critical micelle concentration but decreases gradually with an increase in micelle concentration beyond the second critical micelle concentration.

SPHERICAL MICELLES IN WATER

Numerical values of parameters obtained from light scattering for micelles of alkyltrimethylammonium halides in water are summarized in Table I, together with the value of specific refractive index increment, $(\partial\tilde{n}/\partial c)$. The values[30,32,33] for dodecyltrimethylammonium chloride ($C_{12}TAC$) and $C_{12}TAB$ are also included in Table I. The specific refractive index increment depends on counterion species, and it is 0.158 - 0.160 cm^3 g^{-1} for chloride derivatives and 0.153 - 0.154 cm^3 g^{-1} for bromide derivatives, independent of the wavelength of incident light, 436 and 488 nm.

The second virial coefficient increases with an increase in the alkyl chain length, and it is higher for chloride derivatives than for bromide derivatives. The second virial coefficient is mainly affected by the electrostatic repulsion between micelles and also by the short-range excluded volume effect for micelles, that is, steric repulsion. Micelles of surfactant with long alkyl chain should suffer more strongly from steric repulsion than micelles with short alkyl chain, because the electrostatic repulsion is stronger for micelles of short alkyl chain than micelles of long alkyl chain, as is obvious from the comparison of the degree of ionization. Since Cl^- adsorbs on a micelle less tightly than

Table I. Characteristics of Spherical Micelles of Alkyltrimethylammonium Halides in Water

	T	$(\partial\tilde{n}/\partial c)$	c_o	C_o	M_s	m_s	B	Ref.
	(°C)	$(cm^3 g^{-1})$	$(10^{-2} g cm^{-3})$	$(10^{-3} M)$	(10^4)		$(10^{-3} cm^3 g^{-1})$	
$C_{12}TAC$	25	0.158[a)]	0.51	19.3	1.15	43.6	7.5	32
$C_{12}TAB$	23	0.154[a)]	0.44	14.4	1.54	50.0	7.6[c)]	33
$C_{14}TAC$	25	0.159[b)]	0.24	8.22	1.82	62.3	31.0	3
$C_{14}TAB$	25	0.153[b)]	0.13	3.86	2.38	70.8	18.1	3
$C_{16}TAC$	25	0.160[b)]	0.08	2.50	2.58	80.7	78.2	27
$C_{16}TAB$	35	0.153[b)]	0.04	1.10	3.3	91	46	26

a) at 436 nm. b) at 488 nm. c) Ref. 30.

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Br^-,[34,35] the electrostatic effect on the second virial coefficient is stronger for chloride derivatives than for bromide derivatives.

The aggregation number, $m = M/M_1$, where M_1 is the molecular weight of a surfactant, ranges from 44 to 91, indicating that the micelles are spherical. Now, we approximate that a micelle in water is a sphere, on the basis of the estimation by Tartar[36] for micelles of alkyltrimethylammonium bromide from C_{10} to C_{14}.

Then the radius of the sphere, r, and the surface area per ionic head group of surfactant molecule or ion, A_1, are associated with the volume, V, and the surface area of a sphere, A:

$$V = (4/3)\pi r^3 = \bar{V} m_s/N_A \qquad (5)$$

and

$$A = 4\pi r^2 = A_1 m_s, \qquad (6)$$

where $\bar{V}$ is the partial molar volume of surfactant in a sphere, m_s is the the aggregation number of a sphere, and N_A is Avogadro's number. Numerical values of the aggregation number, the partial molar volume, the radius and the surface area of spherical micelles in water are plotted in Fig. 2 as a function of alkyl chain length of alkyltrimethylammonium halides.

The aggregation number, the partial molar volume and the radius of a spherical micelle rise linearly with an increase in alkyl chain length, and those are larger for bromide derivatives than for chloride derivatives. The larger aggregation number for longer alkyl chain homolog is caused mainly by the stronger hydrophobic cohesion between surfactants with the longer alkyl chain. A similar increase was reported for bromide derivatives with a wider range of alkyl chain length by Debye[37] and Trap and Herrmans,[30] although the numerical values of Trap and Herrmans were higher than those of Debye and ours. The smaller aggregation number of chloride derivatives than that of bromide derivatives is the result of stronger electrostatic repulsion between surfactants in a micelle with the larger degree of ionization.

According to Güveli et al.[38] and Corkill et al.,[39] the partial molar volume of alkyltrimethylammonium bromide in aqueous solutions was severely increased with the alkyl chain length from C_8 to C_{16}, and that of a micellar surfactant exhibited stronger dependence on alkyl chain length than that of a monomeric surfactant. The volume of the hydrophobic core per CH_2 group is suggested to be larger for micelles of longer alkyl chain. We have observed that the difference between the partial molar volume of bromide derivatives and that of chloride derivatives comes from the difference between the partial molar volumes of Cl^- and Br^- and the partial molar volume of hydrophobic core of micelles is independent of the counterion species.[40] This indicates that the packing of surfactants in the hydrophobic core of a micelle is nearly identical, irrespective of whether the counterion is chloride or bromide.

The surface area per ionic head group on a micelle decreases gradually with an increase in alkyl chain length, and it is larger for chloride derivatives than for bromide derivatives. The smaller the degree of ionization, the weaker the electrostatic repulsion of ions in a micelle, and the surface area per ionic head group decreases. While Tarter[36] described the scarce dependence on alkyl chain length of the surface area per surfactant on a micelle of alkyltrimethylammonium bromide, Zana[41] reported a gradual decrease in surface area of alkyltrimethylammonium bromide with an increase in alkyl chain length from C_8 to C_{16}, although the values given by them are smaller than ours.

These structural characteristics of micelles may be reflected in the

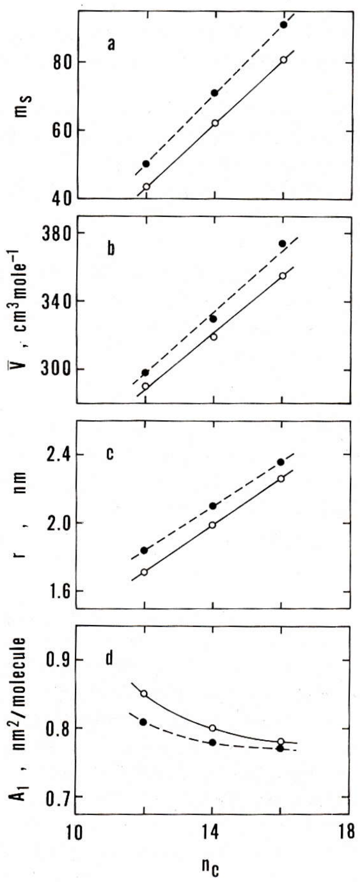

Figure 2. Characteristics of spherical micelles of alkyltrimethylammonium halides in water and their dependence on alkyl chain length. a, micelle aggregation number; b, partial molar valume; c, radius; d, surface area per ionic head group. o, chloride derivatives; •, bromide derivatives.

solubilization of additives in micellar solutions. We have observed the solubilization properties of alkyltrimethylammonium halides toward a water-insoluble dye in connection with the characteristics of a micelle.[40,42]

SALT-INDUCED SPHERE-ROD TRANSITION

Figure 3 shows the double logarithmic plot of the micelle aggregation number vs. the ionic strength for aqueous sodium halide solutions of alkyltrimethylammonium halides, including $C_{12}TAC$[32] and $C_{12}TAB$.[1] The aggregation number of spherical micelles increases slightly with an increase in ionic strength, indicating the formation of ellipsoidal micelles.[36]

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The logarithms of the threshold salt concentration of sphere-rod transition, C_s^*, and the micelle aggregation number, m*, at the threshold salt concentration[42] are plotted against the alkyl chain length of surfactant in Fig. 4. Linear relations hold for both chloride and bromide derivatives. The threshold salt concentrations can also be obtained from the solubilization measurement toward a water-insoluble dye,[42] and their values are on the same line as the light scattering measurement, as seen in Fig. 4.

The threshold salt concentration depends on the alkyl chain length and the counterion species, reflecting the difference in counterion binding. A micelle of surfactant with longer alkyl chain binds counterions more strongly than that with shorter alkyl chain,[41] and the binding of Br^- on a micelle is tighter than that of Cl^-.[34,35] Hence, molecules of a surfactant having longer alkyl chain or bromide ion associate together into rodlike micelles at a lower threshold salt concentration.

The m* values range from 80 to 128, depending on the surfactant species from C_{12} to C_{16}. The linear relation of log m* vs. alkyl chain length is independent of the counterion species, whether chloride or bromide. If the degree of ionization of a micelle is diminished at the threshold salt concentration, the hydrophobic cohesion of surfactant might determine the aggregation number of a micelle. As the partial molar volume of the hydrophobic core would be determined by the alkyl chain length, independent of counterion species,[40] the m* value may not vary with the counterion species. However, this argument is not general, because the micelles of dodecyldimethylammonium chloride and bromide undergo the sphere-rod transition at different aggregation numbers.[1,15]

FLEXIBILITY OF RODLIKE MICELLES

Since Elworthy and Macfarlane[13] first suggested the flexibility of rodlike micelles, the rigidity of rodlike micelles has been discussed by several workers,[5,11,12,14-17,20] and various evidences for their flexibility have been proposed for both ionic and nonionic surfactants in salt solutions. Various workers[12,20-24] have described the flexibility by the persistence length, a, which characterizes the wormlike chain of Kratky and Porod.[19]

If a rodlike micelle behaves as a wormlike chain with circular cross-section of constant diameter, its contour length is represented by

$$L_c \approx M/M_L, \tag{7}$$

where M_L is the molecular weight per length of the micelle. Its mean-square radius of gyration and mean-square end-to-end distance are given by[19,43]

$$\frac{\langle R_G^2\rangle_o}{a^2} = \frac{L_c}{3a} - 1 + \frac{2a}{L_c}\left[1 - \frac{a}{L_c}\left(1 - e^{-L_c/a}\right)\right] \tag{8}$$

and

$$\frac{\langle r^2\rangle_o}{2a^2} = \frac{L_c}{a} - 1 + e^{-L_c/a}, \tag{9}$$

respectively, where the suffix, o, means that the chains are unperturbed or not subject to the excluded volume effect.

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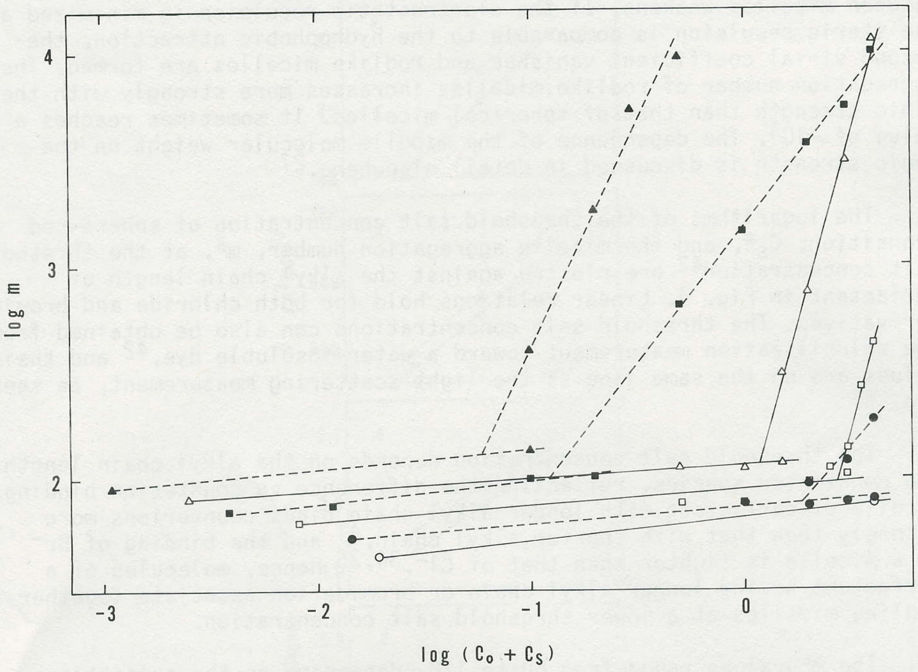

Figure 3. The double logarithmic plot of m vs. ($C_o + C_s$) for micelles of alkyltrimethylammonium halides in corresponding aqueous sodium halide solutions. o, $C_{12}TAC$ at 25 °C; ●, $C_{12}TAB$ at 25 °C; □, $C_{14}TAC$ at 25 °C; ■, $C_{14}TAB$ at 25 °C; △, $C_{16}TAC$ at 25 °C; ▲, $C_{16}TAB$ at 35 °C.

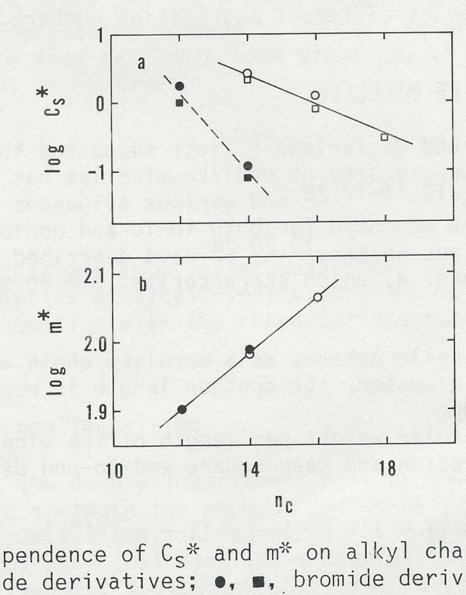

Figure 4. The dependence of C_s* and m* on alkyl chain length. o, □, chloride derivatives; ●, ■, bromide derivatives. o, ●, light scattering method, □, ■, solubilization method.

Table II. Cha
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	C_s	$c-c_o$[a]
	(M)	(10^{-2}gm
$C_{12}TAB$	2.0	
in NaBr	3.0	
(25 °C)	4.0	
$C_{14}TAC$	3.0	~2.0
in NaCl	3.5	~2.0
(25 °C)	4.0	1.0
	0.5	1.5
$C_{14}TAB$	1.0	0.8
in NaBr	2.0	0.3
(25 °C)	3.0	0.2
	4.0	0.2
	1.5	2.0
$C_{16}TAC$	2.0	0.7
in NaCl	3.0	0.2
(25 °C)	4.0	0.2
	0.1	0.4
$C_{16}TAB$	0.2	0.4
in NaBr	0.3	0.2
(35 °C)	0.5	0.1

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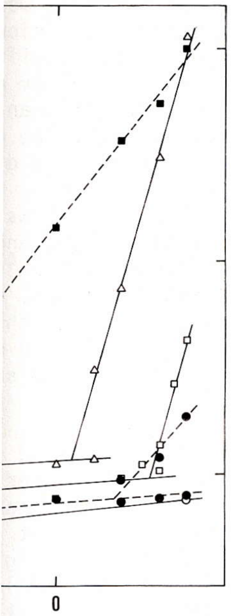

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Table II. Characteristics of Rodlike Micelles of Alkyltrimethyl-Ammonium Halides in Aqueous Sodium Halide Solutions

	C_s (M)	$c-c_o$[a)] (10^{-2}gcm^{-3})	M (10^4)	m	R_G (nm)	L_c (nm)	a (nm)	$L_c/2a$	$<r^2>_o^{1/2}$ (nm)	$(c-c_o)^*$ (10^{-2}gcm^{-3})	$(C-C_o)^*$ (M)
C_{12}TAB	2.0		2.86	93		6.47					
in NaBr	3.0		3.70	120		8.37					
(25 °C)	4.0		5.75	186		13.01					
C_{14}TAC	3.0	~2.02	~4.00	~137		8.75					
in NaCl	3.5	~2.00	7.69	264		16.8					
(25 °C)	4.0	1.01	12.6	432		27.6					
	0.5	1.59	21.9	650	15.2	38.6				2.48	0.074
C_{14}TAB	1.0	0.81	48.5	1440	28.1	85.6				0.87	0.026
in NaBr	2.0	0.30	124	3690	46.4	219	55.5	2.0	135	0.49	0.015
(25 °C)	3.0	0.20	185	5510	63.6	327	60.3	2.7	179	0.29	0.0085
	4.0	0.20	333	9910	77.8	588	37.0	8.0	202	0.28	0.0083
	1.5	2.01	9.88	309	13.5	17.0				1.59	0.050
C_{16}TAC	2.0	0.79	23.7	739	21.5	40.8				0.95	0.030
in NaCl	3.0	0.21	98.9	3090	52.4	170				0.27	0.0085
(25 °C)	4.0	0.20	366	11400	88.8	630	46.4	6.8	233	0.21	0.0065
	0.1	0.49	14.6	401		20.8					
C_{16}TAB	0.2	0.49	66.2	1820	36.2	94.2				0.55	0.015
in NaBr	0.3	0.29	197	5410	51.0	280	41.6	3.4	141	0.59	0.016
(35 °C)	0.5	0.17	347	9530	80.2	494	52.6	4.7	215	0.27	0.007

a) The molecular weight and radius of gyration of rodlike micelles were obtained at given micelle concentrations.

Numerical values of the molecular weight and the aggregation number of rodlike micelles of alkyltrimethylammonium halides in aqueous sodium halide solutions are given in Table II. When the micelle molecular weight is larger than 10^5 or the aggregation number exceeds 300, the angular dependence is measurable in the light scattering experiment and the radius of gyration of rodlike micelles can be determined according to eq. (3). Their numerical values are included in Table II.

The values of M_L for each surfactant may be evaluated from the observed values of m_s and $\overline{V}$ of a spherical micelle in water under the assumption that each surfactant ion occupies the identical area on surface of a micelle, independent of the shape of micelles, and that a rodlike micelle has a radius equal to that of a spherical micelle and consists of a stack of disk-like layers.[3]

Numerical values of contour length, persistence length and end-to-end distance are listed in Table II, together with that of the number of Kuhn's statistical segments, $L_c/2a$, another measure of flexibility. For this calculation we have made an approximation, $<R_G^2>_o \approx R_G^2$. Norisue and Fujita[44] concluded that polymers consisting of 50 or less Kuhn's statistical segments were not perturbed by the excluded volume effect, justifing our approximation.

The number of Kuhn's segments and the end-to-end distance vary with the contour length: the number of Kuhn's segment ranges over 2.0 - 8.0 and the end-to-end distance is 1/3 to 2/3 of the contour length. On the other hand, the persistence length may be regarded as independent of alkyl chain length of surfactant, salt species and the contour length of rodlike micelles within error in the present analysis, and is 37 - 60 nm.

These results indicate that the long rodlike micelles of alkyltrimethylammonium halides are semiflexible, if the micelle molecular weight is larger than 10^6 or the contour length is longer than 200 nm. On the other hand, the short rodlike micelles behave like stiff rather than flexible, because their contour length is not much longer than the length of Kuhn's segments, 2a, as seen in Table II.

The flexibility of ionic rodlike micelles would be caused by the electrostatic repulsion between charges on a micelle: the weaker the electrostatic repulsion between charges, the larger the flexibility of rodlike micelles. The surface charge is determined by the counterion binding. The counterion binding would not depend on the salt concentration, if the salt concentration is high. Then the flexibility must be independent of the contour length of the long rodlike micelles, while the contour length varies with the salt concentration.

The counterion binding on micelles of the longer alkyl chain and of the bromide derivative is stronger than that of the shorter alkyl chain and of the chloride derivative.[34,35,41] Therefore, the flexibility of rodlike micelles of $C_{16}TAB$ may be superior to those of $C_{16}TAC$ and $C_{14}TAB$. However, the thickness of rodlike micelles yields the opposite effect on the flexibility: rodlike micelles of $C_{14}TAB$ are thinner and more flexible than those of $C_{16}TAC$ and $C_{16}TAB$. Consequently, the flexibility of long rodlike micelles of $C_{14}TAB$, $C_{16}TAC$, and $C_{16}TAB$ is alike.

The flexibility of long rodlike micelles has been quantitatively discussed by various workers,[3,12,20-24] and the persistence length was estimated in terms of the wormlike chain model, although the method estimating the contour length of rodlike micelles was different from one another. Porte et al.[5,11,12,20] found, from dynamic light scattering and magnetic birefringence, that rodlike micelles of cetylpyridinium bromide in aqueous NaBr solutions behave as wormlike chains, and estimated its persistence length as short as 20 nm.

Three groups of workers[3,21,22] utilized the same light scattering data to estimate the persistence length of rodlike micelles of dodecyldimethylammonium chloride ($C_{12}DAC$) and obtained different persistence lengths, 82,[21] 45[22] and 35[3] nm. Two groups evaluated the persistence length for rodlike micelles of dodecyldimethylammonium bromide ($C_{12}DAB$) as 45[22] and 31[3] nm.

We have found that the persistence length of rodlike micelles of dimethyloleylamine oxide is longer under the condition of lower or zero degrees of ionization[23,24]: it is as long as 100 - 200 nm, depending on the added NaCl and HCl concentrations, if the micelle molecular weight is larger than 6 x 10^6 or the contour length is longer than 500 nm. The reason for lower flexibility of rodlike micelles of dimethyloleylamine oxide is that they have a larger diameter of cross-section (~ 60 nm)[45] and stronger hydration. The effect of hydration of nonionic head group on the rigidity of a rodlike micelle was already pointed out for hexaoxyethylene hexadecyl ether.[13]

Table III. Chara
and C

C_s (M)	$c-c_o$ (10^{-2} g cm^{-3})
1.0	1.21
	1.60
	2.01
2.0	0.792
	1.20
	1.60
	2.00
3.0	0.299
	0.413
	0.599
	1.01
	1.40
4.0	0.297
	0.400
	0.609
	0.797
	0.997
2.0	1.22
	1.58
	1.97
3.0	0.398
	0.592
	0.803
	1.18
	1.60
	1.98
4.0	0.317
	0.409
	0.613
	0.787

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Table III. Characteristics of Entangled Rodlike Micelles of $C_{14}TAB$ and $C_{16}TAC$ in Aqueous Sodium Halide Solutions at 25 °C

C_s (M)	$c-c_o$ (10^{-2} g cm^{-3})	$\frac{(c-c_o)}{(c-c_o)^*}$	M_ξ (10^4)	m_ξ	ξ_G (nm)	$L_{c,\xi}$ (nm)	a_ξ (nm)	$L_{c,\xi}/2a_\xi$	ξ_r (nm)
(a) $C_{14}TAB$									
1.0	1.21	1.39	42.9	2170	26.6	75.7			
	1.60	1.85	36.4	1080	24.5	64.2			
	2.01	2.32	30.7	913	22.6	54.2			
2.0	0.792	1.62	89.7	2670	41.2	158	143	0.55	133
	1.20	2.43	62.0	1840	32.9	109			
	1.60	3.25	46.5	1380	28.2	82.0			
	2.00	4.06	36.4	1080	24.5	64.2			
3.0	0.299	1.05	179	5310	60.9	316	56.6	2.8	171
	0.413	1.44	157	4670	56.5	277	60.6	2.3	162
	0.599	2.10	131	3890	53.6	231	89.1	2.2	162
	1.01	3.52	80.3	2390	40.2	142	819	0.86	138
	1.40	4.90	60.4	1800	37.2	107			
4.0	0.297	1.06	269	7990	68.5	474	37.0	6.4	180
	0.400	1.43	243	7220	65.0	429	37.9	5.7	172
	0.609	2.17	174	5170	54.4	307	42.0	3.7	149
	0.797	2.84	132	3910	46.5	233	47.1	2.5	132
	0.997	3.55	103	3050	39.8	182	53.0	1.7	117
(b) $C_{16}TAC$									
2.0	1.22	1.29	23.4	732	22.0	40.4			
	1.58	1.67	23.0	719	22.1	39.7			
	1.97	2.09	20.5	639	21.0	35.2			
3.0	0.398	1.46	94.7	2960	52.1	163			
	0.592	2.18	75.3	2350	47.7	130			
	0.803	2.95	64.5	2020	43.8	111			
	1.18	4.33	46.8	1460	37.7	80.5			
	1.60	5.88	34.2	1070	32.5	58.9			
	1.98	7.29	26.8	836	28.7	46.1			
4.0	0.317	1.53	302	9420	79.9	519	48.0	5.4	213
	0.409	1.98	248	7740	72.5	426.	51.9	4.1	197
	0.613	2.96	173	5400	62.4	298	72.8	2.0	181
	0.787	3.80	133	4160	53.1	229	88.4	1.3	161

ENTANGLEMENT OF RODLIKE MICELLES

When the concentration of rodlike micelles in aqueous salt solution is high, rodlike micelles contact and entangle one another. The overlap threshold micelle concentration is given by

$$(c - c_o)^* = M/[(4/3)\pi R_G{}^3 N_A] \qquad (10)$$

or

$$(C - C_o)^* = 1000(c - c_o)^*/M_1. \qquad (11)$$

Their numerical values are given in Table II. They decrease steeply with an increase in molecular weight of rodlike micelles. These concentrations are very close to the micelle concentrations at the minimum of the reciprocal envelope of light scattering, as seen in Fig. 1(c).

When rodlike micelles entangle in semidilute solutions above the overlap threshold micelle concentration, they form a network, which can be characterized by blobs, units of the network, and by the correlation length or an average mesh size, ξ, of the network.[25] If M_ξ and ξ_G represent the molecular weight and the radius of gyration of a blob, respectively, the micelle concentration in semidilute solutions corresponds to

$$c - c_o \quad = \quad M_\xi[(4/3)\pi\xi_G{}^3 N_A]. \qquad (12)$$

We postulate that the reduced intensity of light scattered in the $\theta°$ direction from semidilute solutions of micelles can be described by

$$R_\theta - R_\theta{}^o \quad = \quad K(c - c_o)M_\xi[1 - (1/3)\xi_G{}^2\mu^2], \qquad (13)$$

according to the requirement from the blob model. Then the values of M_ξ and ξ_G for rodlike micelles in semidilute solutions are obtainable from experimental light scattering data.

Numerical values of M_ξ and ξ_G for $C_{14}TAB$ and $C_{16}TAC$ are given in Table III. With increasing micelle concentration, the values of M_ξ and ξ_G decrease, indicating that blobs become smaller. Consequently, the reciprocal envelope of light scattering should have a minimum value at the overlap threshold micelle concentration, where a blob is identical with a dispersed micelle.

If M, R_G, L_c, a, and $\langle r^2\rangle_o$ for a blob are represented by M_ξ, ξ_G, $L_{c,\xi}$, a_ξ, and $\xi_r{}^2$, these characteristic parameters of entangled rodlike micelles can be evaluated, according to eqs. (7) -(9). As seen in Table III, the persistence length, a_ξ, of a blob increases with increasing micelle concentration, and simultaneously the contour lengh, $L_{c,\xi}$, the number of Kuhn's segments, $L_{c,\xi}/2a_\xi$, and the end-to-end distance, ξ_r, decrease. These results suggest that the blobs become smaller and behave like stiff in semidilute solutions.

THE SCALING LAW

Rodlike micelles in semidilute solutions can be characterized by the scaling law, as proposed for polymer chains entangled together to form a network.[25] In dilute micellar solution, the radius of gyration of a micelle is related to the number of surfactant molecules or ions in the micelle or micelle aggregation number by

$$R_G \;\cong\; b\,(M/M_1)^\nu \;\sim\; m^\nu, \qquad (14)$$

where b is a length of micelle per unit surfactant molecule. When the micelles contact one another, the overlap threshold micelle concentration is scaled as

$$(c - c_o)^* \sim mR_G{}^{-3} \sim m^{-(3\nu-1)} \sim R_G{}^{-(3\nu-1)/\nu} \qquad (15)$$

from eqs. (10) and (14).

In semidilute solution, since the number of blobs in a micelle is m/m_ξ, the radius of gyration of the micelle may be written as

$$R_G \;\cong\; \xi_G\,(m/m_\xi)^\nu, \qquad (16)$$

instead of eq. (14), and, since the number of surfactants in a blob is M_ξ/M_1, the scaling law for the radius of gyration of a blob is

$$\xi_G \;\cong\; b\,(M_\xi/M_1)^\nu \;\sim\; m_\xi{}^\nu, \qquad (17)$$

similar to eq. (14). It should be noticed that the exponent in eq. (17) may not always be identical with that in eqs. (14) - (16).

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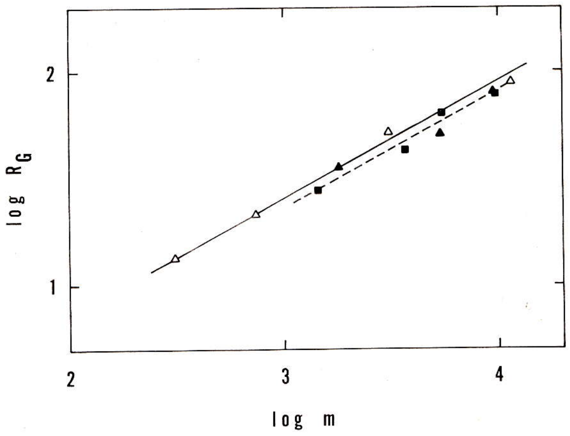

Figure 5. The double logarithmic plot of R_G vs. m for rodlike micelles of alkyltrimethylammonium halides. ■, $C_{14}TAB$ at 25 °C; △, $C_{16}TAC$ at 25 °C; ▲, $C_{16}TAB$ at 35 °C.

There is a requirement that the number of surfactants in a blob should not depend on the micelle aggregation number and only on the micelle concentration.[25] Then

$$M_\xi/M_1 \sim (c - c_o)^x \qquad (18)$$

or, using relation (17),

$$\xi_G \sim (c - c_o)^{x\nu}. \qquad (19)$$

Since $\xi_G \approx R_G$ at $(c - c_o) \approx (c - c_o)^*$, combining eq. (14) with eq. (19) and substituting eq. (15),

$$m^\nu \sim (c - c_o)^{*x\nu} \sim m^{-x\nu(3\nu-1)}. \qquad (20)$$

Hence

$$x = -1/(3\nu-1). \qquad (21)$$

Then, for semidilute solution,

$$\xi_G \sim (c - c_o)^{-\nu/(3\nu-1)} \qquad (22)$$

from eq. (19) or

$$\xi_G/R_G \sim [(c - c_o)/(c - c_o)^*]^{-\nu/(3\nu-1)} \qquad (23)$$

by means of eq. (15). Using eqs. (16) and (23),

$$m_\xi/m \cong (\xi_G/R_G)^{1/\nu} \sim [(c - c_o)/(c - c_o)^*]^{-1/(3\nu-1)}. \qquad (24)$$

From the requirement of mutual independence or no external interference of blobs, the osmotic pressure, Π, for semidilute solution of micelles should be proportional to the number of blobs in the solution. Therefore, by the aid of eqs. (12) and (22),

$$\Pi/kT \sim (c - c_o)/M_\xi \sim \xi_G^{-3} \sim (c - c_o)^{3\nu/(3\nu-1)}. \qquad (25)$$

This relation is in agreement with the demonstration of Daoud et al.[46] Their theory is based on the assumption that the osmotic pressure follows some power of the micelle concentration. The same relation was derived by des Cloiseaux.[47] The derivation is based on the impenetable sphere approximation for the second virial coefficient.

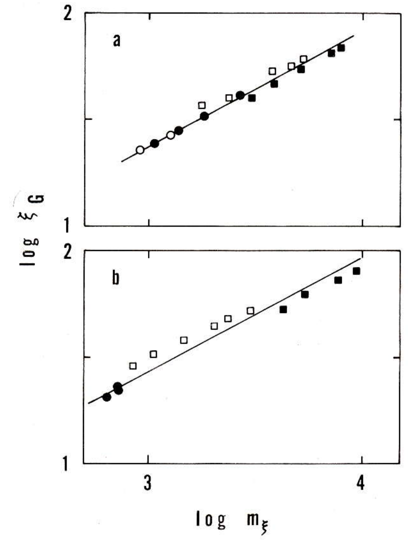

Figure 6. The double logarithmic plot of ξ_G vs. m_ξ for entangled rodlike micelles of $C_{14}TAB$ and $C_{16}TAC$ at 25 °C. a, $C_{14}TAB$; b, $C_{16}TAC$. Salt concentration (M): o, 1; ●, 2; □, 3; ■, 4.

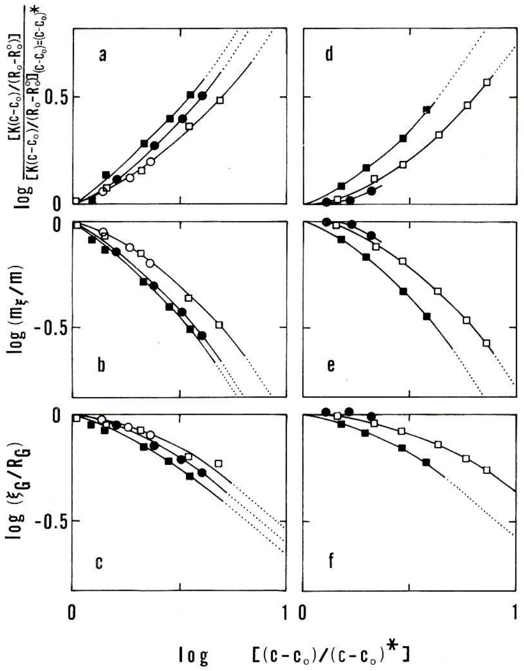

Figure 7. The double logarithmic plot of the reduced values of (a,d) the reciprocal envelope of light scattering in the zero direction, (b,e) the aggregation number and (c,f) the radius of gyration of the blobs in semidilute aqueous sodium halide solutions of $C_{14}TAB$ and $C_{16}TAC$ as a function of the reduced micelle concentration. a, b, c, $C_{14}TAB$; d, e, f, $C_{16}TAC$. Salt concentration (M): o, 1; ●, 2; □, 3; ■, 4.

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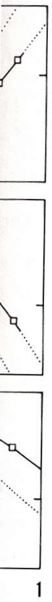

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The light scattering in the zero direction from micellar solutions is related to the osmotic compression by

$$\frac{K(c - c_o)}{R_o - R_o{}^o} = \frac{1}{kT}\left(\frac{\partial\pi}{\partial(c - c_o)}\right)_T. \tag{26}$$

Then, for semidilute solutions,

$$\frac{K(c - c_o)}{R_o - R_o{}^o} \sim (c - c_o)^{1/(3\nu-1)} \tag{27}$$

from eq. (25), or

$$\frac{[K(c-c_o)/(R_o-R_o{}^o)]}{[K(c-c_o)/(R_o-R_o{}^o)]_{(c-c_o)\approx(c-c_o)^*}} \sim \left[\frac{(c-c_o)}{(c-c_o)^*}\right]^{1/(3\nu-1)}. \tag{28}$$

The radius of gyration of rodlike micelles in dilute solutions of different salt concentrations is plotted against the aggregation number in the double logarithmic scale, as shown in Fig. 5. The relation between them is linear and scaled as eq. (14). The exponent, ν, is 0.55 for C_{14}TAB, C_{16}TAC and C_{16}TAB. This value is far from unity for rigid thin rod,[48] indicating the semiflexibility of rodlike micelles in dilute solutions.

The double logarithmic plot of the radius of gyration vs. the aggregation number of blobs in semidilute solutions is shown in Fig. 6, in which the straight lines are drawn with the exponent for 0.55. The scaling law of eq. (7) holds for C_{14}TAB and C_{16}TAC, independent of the salt concentrations, indicating that the scaling laws of rodlike micelles of C_{14}TAB and C_{16}TAC in dilute solution are not perturbed even under the entangled condition.

Figure 7 shows the double logarithmic plot of the reduced values of the reciprocal envelope of light scattering in the zero direction, together with the molecular weight and the radius of gyration of blobs, for semidilute solutions of C_{14}TAB and C_{16}TAC against the reduced micelle concentration. Slopes of 1.54, − 1.54, and − 0.85 at high reduced micelle concentrations can be derived on the basis of eqs. (28), (24), and (23), respectively, with $\nu = 0.55$, and drawn by the dotted lines. The plots gradually approach straight lines with the theoretically predicted slope, as the reduced micelle concentration increases.

The application of the scaling law for long rodlike micelles entangled together was made by Candau et al.[2,18] They measured the intensity of scattered light and the diffusion coefficient for semidilute solutions of alkyltrimethylammonium bromides with surfactant concentrations up to 0.6 M and observed that the scaling law against the volume fraction of surfactant holds for aqueous KBr solutions of C_{16}TAB above the overlap threshold micelle concentration: the scaling law was excellently consistent with that theoretically predicted for real chains in good solvent.[25]

We have demonstrated the relation $R_G \sim M^{0.70}$ for rodlike micelles of dimethyloleylamine oxide in aqueous solutions, independent of NaCl and HCl concentrations.[24] The exponent, 0.70, is still smaller than that for rigid rods, indicating the semiflexibility of rodlike micelles of dimethyloleylamine oxide.

ELECTRON MICROSCOPIC OBSERVATION

We have observed by electron microscopy the specimens regenerated from aqueous solutions of alkyltrimethylammonium halides.[26] Solutions of surfactants were prepared at concentrations of 0.1×10^{-2} g cm^{-3} in water and 0.5×10^{-2} g cm^{-3} in 0.5 M sodium halide, and incubated at 25 or 35 °C. An aliquot of each solution was put on a carbon-coated electron microscope grid. After an excess of the solution was removed by soaking, the specimen on the grid was negatively stained with 1 % solution of uranyl acetate. Electron micrographs were taken at a numerical magnification of 50,000 with a JEM 100C Electron Microscope, operated at 80 kV.

The electron micrographs of specimens prepared from aqueous solutions of alkyltrimethylammonium halides are presented in Fig. 8(1). They display globular images with considerably uniform diameter, which may be assigned to spherical micelles. Micelles are dispersed randomly and their radius of 2 - 3 nm is comparable to the radius evaluated, as shown in Table I. Spherical micelles of C_{14}TAB have rather large diameter. This might be interpreted as a result of the collapse of micelle structure during drying. Electron micrographs of spherical micelles were presented for surfactants with alkyl chain length of C_{14} to C_{22} by Bachmann et al.,[49] who prepared the specimens by the freeze-drying method.

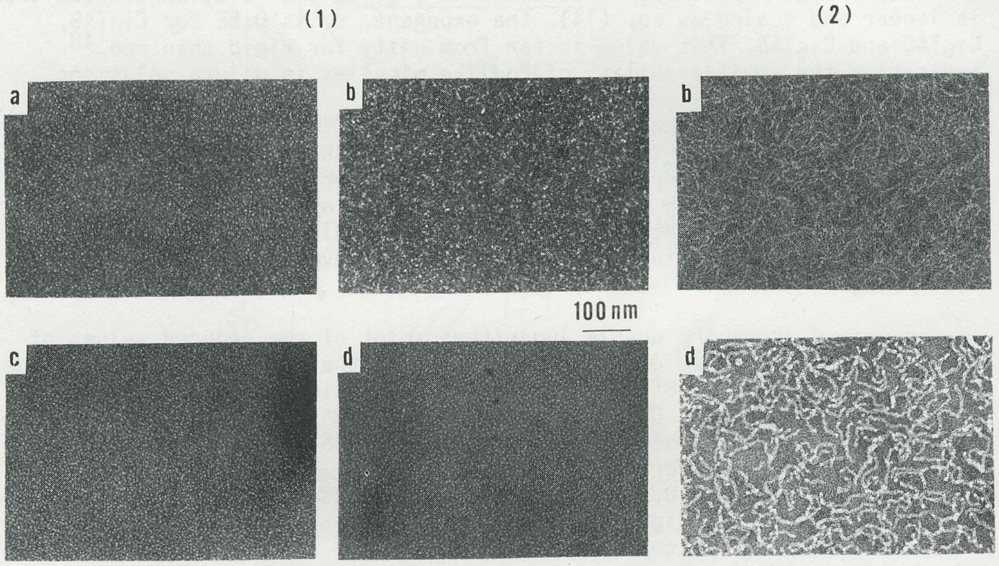

Figure 8. The electron micrographs of specimens regenerated from aqueous sodium halide solutions of alkyltrimethylammonium halides. (1), at surfactant concentration of 0.1×10^{-2} g cm^{-3} in water; (2) at 0.5×10^{-2} g cm^{-3} in 0.5 M NaBr. a, C_{14}TAC at 25°C; b, C_{14}TAB at 25 °C; c, C_{16}TAC at 25 °C; d, C_{16}TAB at 35 °C.

Figure 8(2) shows the electron micrographs of specimens from 0.5 M NaBr solutions of C_{14}TAB and C_{16}TAB. Both photographs present tortuous thread-like images with a uniform diameter, which can be identified as the semiflexible rodlike micelles. We have already reported similar images for semiflexible rodlike micelles of dimethyloleylamine oxide.[45]

The threshold NaCl concentration of sphere-rod transition is 2.7 M for C_{14}TAC and 1.18 M for C_{16}TAC, and the observation of rodlike micelles of C_{14}TAC and C_{16}TAC was disturbed by the deposition of crystalline NaCl.

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SUMMARY

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4. S. Hayashi ar

While rodlike micelles of C_{14}TAB have a diameter of 4 - 6 nm in cross-section, those of C_{16}TAB are rather thick in diameter, because of the collapse of micelle structure during drying. Images of rodlike micelles of C_{16}TAB with a smaller diameter were previously observed with a specimen from 0.5 M NaBr solution with surfactant concentration of 0.1 x 10^{-2} g cm^{-3}.[26] Although rodlike micelles of C_{14}TAB and C_{16}TAB are not well separated from one another, owing to their mutual penetration and entanglement, it is certain that rodlike micelles of C_{16}TAB are longer than those of C_{14}TAB, consistent with the results of light scattering.

Evidently we may safely attribute the observed images of electron micrographs to the spherical and semiflexible rodlike micelles in solution, although their structures in solution could sometimes be collapsed or perturbed during the process of preparation of specimen.

SUMMARY

Measurements of static light scattering have been carried out for aqueous NaCl solutions of C_{14}TAC and C_{16}TAC and for aqueous NaBr solutions of C_{14}TAB and C_{16}TAB at 25 or 35 °C. The double logarithmic plot of the micelle aggregation number against the ionic strength exhibits a transition point, where the salt-induced sphere-rod transition occurs. The threshold salt concentration of transition varies with the alkyl chain length and the counterion species, either chloride or bromide, caused by the change in degree of counterion binding.

Long rodlike micelles behave as semiflexible chains, and they can be described by the wormlike chain model. On the basis of geometrical considerations, the persistence length of a rodlike micelle has been calculated as 37 - 60 nm for C_{14}TAB, C_{16}TAC and C_{16}TAB, independent of surfactant species, if the rodlike micelle is much longer than the length of Kuhn's segments, 74 - 120 nm.

Rodlike micelles in semidilute solutions overlap one another above an overlap threshold micelle concentration and entangle together to form a network. The structural parameters and the scaling laws associated with the blobs which are units of the network have been evaluated and discussed for C_{14}TAB and C_{16}TAC micelles.

Electron micrographs for specimens regenerated from aqueous solution of surfactants show many globular images with a uniform diameter, which can be regarded as spherical micelles. On the other hand, specimens prepared from 0.5 M NaBr solutions of C_{14}TAB and C_{16}TAB display tortuous thread-like images with a uniform thickness, which may be identified with semiflexible rodlike micelles.

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