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Characteristics of rodlike micelles of cetyltrimethylammonium chloride in aqueous NaCl solutions: their flexibility and the scaling laws in dilute and semidilute regimes

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Abstract: Static light scattering has been measured for aqueous NaCl solutions of cetyltrimethylammonium chloride (CTAC) at 25 °C. While spherical micelles are formed above the critical micelle concentration for 0–1.5 M NaCl solutions, rodlike micelles are formed at NaCl concentrations higher than 1.18 M.

The aggregation number of rodlike micelles increases markedly with increasing NaCl concentration, and it is as large as 11400 in 4.0 M NaCl. Long rodlike micelles are semiflexible and behave like wormlike chains. Their contour length and persistence length have been calculated as 630 and 46.4 nm, respectively, in 4.0 M NaCl.

Rodlike micelles overlap and entangle together to form a network in semidilute solutions above a threshold micelle concentration. The radius of gyration of the blob can be scaled for its molecular weight with the exponent, 0.55, coinciding with that for isolated rodlike micelles in dilute solutions. The scaling laws for the reciprocal envelope of light scattered in the semidilute regime and for the molecular weight and the radius of gyration of the blob are also discussed with reference to the micelle concentration.

Key words: Light scattering, cetyltrimethylammonium chloride, semiflexible rodlike micelle, semidilute solutions, scaling law.

Introduction

The size and shape of surfactant micelles generally depend on the strucutre of surfactant, nature of counterion, concentrations of surfactant and added salt, and temperature. Molecules of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), in water at 35 °C associate together only into spherical micelles above a critical micelle concentration, and rodlike micelles are formed in aqueous solutions above 0.06 M NaBr [1].

Such a salt-induced sphere-rod transition was observed at 0.12 M for tetradecyltrimethylammonium bromide (TTAB) [2] and at 1.8 M for dodecyltrimethylammonium bromide (DTAB) [3] in aqueous NaBr solutions at 25 °C. Tetradecyltrimethylammonium chloride (TTAC) forms rodlike micelles at the threshold salt concentration, 2.7 M, higher than TTAB [2], and dodecyltrimethylammonium chloride (DTAC) cannot associate into rodlike micelles even in 4.0 M NaCl [4].

The size of rodlike micelles strikingly increases with an increase in salt concentration: rodlike micelles can have molecular weight more than 10^6 in solutions at higher salt concentrations [1, 2]. Long rodlike micelles are semiflexible [5–9], and their flexibility has been discussed on the basis of a wormlike chain model [10]. Rodlike micelles entangle together and behave like a network in semidilute solutions. The analysis of its behavior based on the scaling law [11] has been carried out for alkyltrimethylammonium bromide [2, 12, 13].

There are few investigations associated with the size and shape of micelles of cetyltrimethylammonium chloride (CTAC) [14–19]. Reiss-Husson and Luzzati [14] found the micelle aggregation number, 84, for CTAC in aqueous solution at 27 °C by the small-angle X-ray scattering technique. Hayter and Penfold [15] determined the structure and charge of ionic micelles by small-angle neutron scattering, and reported that CTAC micelles have aggregation number 90–125 in water and 0.1 M NaCl, depending on the micelle concentration. Roelants et al. [16] deduced the aggregation number of CTAC micelles by the fluorimetric method, and Roelants et al. [18] and Malliaris et al. [19] observed its temperature dependence by the same technique. Dorshow et al. [17] measured dynamic light scattering for 0.02–3 M NaCl solutions of CTAC and observed changes in the diffusion coefficient with concentrations of surfactant and salt as well as with temperature.

In this work we will measure static light scattering on aqueous NaCl solutions of CTAC and demonstrate that rodlike micelles are formed above the threshold NaCl concentration of sphere-rod transition. Rodlike micelles become very long in aqueous solutions of high NaCl concentrations. They are semiflexible, and their flexibility is evaluated on the basis of the wormlike chain model. We will also discuss the scaling laws for entangled rodlike micelles in semidilute solutions under the approximation of the blob model.

Experimental

The sample of CTAC was the same as that previously used [20]. Commercial CTAC was recrystallized three times from an ethanol-acetone mixture, and the purity of the recrystallized sample was checked by gas chromatography. NaCl was ignited for 1 h, and water was redistilled from alkaline potassium permanganate.

Light scattering was measured on a Dynamic Light Scattering Spectrophotometer DLS-700, designed and built by Otsuka Denshi Co., Inc., Osaka, and equipped with a personal computer. A cell housing was filled with di-n-butyl phthalate and kept at 25 ± 0.05 °C.

Details of measurement have already been described [1, 2]. The argon-ion laser beam at 488 nm was vertically polarized, and the scattered light in vertical and horizontal polarizations was collected on a photomultiplier. Solvents and solutions were filtered five times through a Millipore membrane filter with pore sizes of 0.025 to 0.65 μm.

For a dilute solution of micelles at a surfactant concentration, c (g cm^{-3}), light scattering at a small scattering angle, θ, is generally described by the Debye equation,

$$\frac{K(c-c_o)}{R_\theta - R_\theta^o} = \frac{1}{M}\left(1 + \frac{1}{3} R_G^2 \mu^2\right) + 2B(c - c_o), \quad (1)$$

where K is the optical constant, and μ is the magnitude of scattering vector. R_θ and R_θ^o are the reduced scattering intensities for solutions at c and the critical micelle concentration, c_o, respectively. M and R_G are the average molecular weight and radius of gyration of micelles, and B is the second virial coefficient.

Specific refractive index increment, $(\partial \tilde{n}/\partial c)_{C_s}$, of a solution at constant salt concentration, $C_s(M)$, was measured at 25 ± 0.05 °C on a Differential Refractometer RM-102 of Otsuka Denshi Co., Inc., with light of 488 nm extracted from an iodine lamp. The apparatus was calibarted by using aqueous solutions of sucrose. Observed values of the specific refractive index increment were constant over the surfactant concentrations up to 2×10^{-2} g cm^{-3}.

Results

Figure 1a illustrates the increment of the reduced scattering intensity in the 90° direction for aqueous NaCl solutions of CTAC. With increasing surfactant concentration beyond the critical micelle concentration, the increment of the reduced scattering intensity increases almost linearly for 0–1.0 M NaCl solutions and with curvatures for 1.5–4.0 M NaCl solutions. The intensity is generally stronger for solutions of higher NaCl concentrations.

As seen in Figure 1b, the angular dissymmetry in the 60° direction, $z_{60} = R_{60}/R_{120}$, is 1.00 ± 0.02 for 0–1.0 M NaCl solutions, indicating no angular dependence of the reduced scattering intensity. Then the particle scattering factor representing the internal interference is unity.

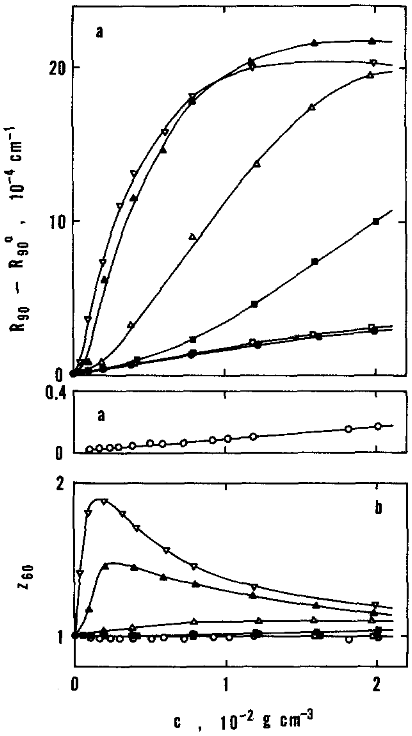

Fig. 1. The plots of (a) the increment of reduced scattering intensity in the 90° direction and (b) the dissymmetry of the scattered light in the 60° direction as a function of the surfactant concentration for aqueous NaCl solutions of CTAC at 25 °C. NaCl concentration (M): (○) 0; (●) 0.5; (□) 1.0; (■) 1.5; (△) 2.0; (▲) 3.0; (▽) 4.0

On the other hand, the angular dissymmetry is larger than unity for 1.5–4.0 M NaCl solutions, and the angular dependence is observed for these solutions: the reciprocal angular envelope increases linearly with increasing $\sin^2 (\theta/2)$, and its extra-polation to zero scattering angle gives the light scattering free from internal interference. As the surfactant concentration increases, the angular dissymmetry for 3.0 and 4.0 M NaCl solutions increases and decreases through a maximum.

Figure 2 represents the Debye plots at 90° scattering angle for 0–1.0 M NaCl solutions and at 0° for 1.5–4.0 M NaCl solutions. The intercept at zero micelle concentration for 0–1.5 M NaCl solutions provides the reciprocal of the micelle molecular weight, and the positive slope against the micelle concentration, $c - c_0$, for 0–1.0 M NaCl solutions gives the second virial coefficient. Numerical values of the micelle molecular weight and the second virial coefficient are listed in Table 1, together with values of the specific refractive index increment and the critical micelle concentration. The critical micelle concentration decreases with an increase in NaCl concentration, and it is less than 10^{-5} g cm^{-3} for solutions above 2.0 M NaCl.

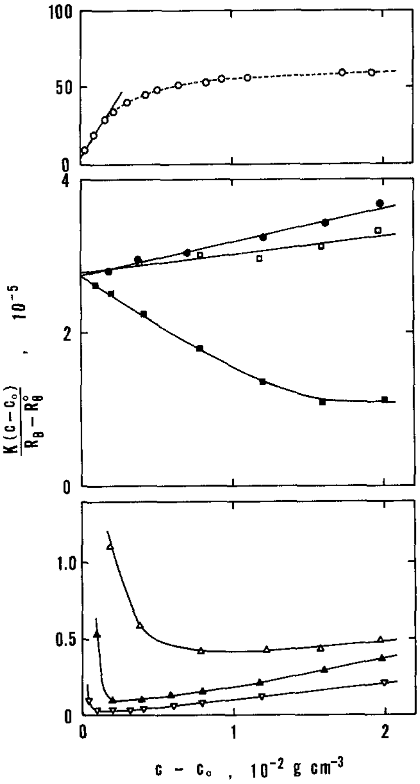

Fig. 2. The Debye plots of light scattering at the scattering angle, θ, as a function of the micelle concentration for aqueous NaCl solutions of CTAC at 25 °C. $\theta = 90°$ for 0–1.0 M NaCl solutions; $\theta = 0°$ for 1.5–4.0 M NaCl solutions. The symbols represent the same NaCl concentrations as in Figure 1

Table 1. Characteristics of spherical micelles of CTAC in aqueous NaCl solutions at 25 °C

C_s (M)	$(\partial \tilde{n}/\partial c)_{C_s}$ (cm^3 g^{-1})	c_0 (10^{-2} g cm^{-3})	M (10^4)	m	B (10^{-3} cm^3 g^{-1})
0	0.160	0.080	2.58	80.7	78.2
0.5	0.159	0.010	3.66	114	0.22
1.0	0.158	0.005	3.56	111	0.11
1.5	0.157	0.002	3.70	115	

The micelle molecular weight for 0–1.5 M NaCl solutions ranges from 25800 to 37000, corresponding to the micelle aggregation number, $m = M/320.0$, from 81 to 115. This indicates the formation of spherical micelles.

Our value for the aggregation number of spherical micelles of CTAC is close to values at dilute micelle concentrations measured by the small-angle X-ray scattering [14], small-angle neutron scattering [15], and fluorimetric method [16]. However, values in the other literature, evaluated by the fluorimetric method [17, 18], are larger than ours.

The second virial coefficient is very large and positive for CTAC in water, indicating that it arises mainly from the electrostatic repulsion of micelles. The value of the second virial coefficient decreases with an increase in NaCl concentration and it should be much less than 10^{-4} cm^3 g^{-1} at NaCl concentrations above 1.5 M, owing to weakening of the electrostatic repulsion in the presence of NaCl.

The Debye plot of CATC in water deviates downward from the initial straight line around the micelle concentration of 0.32×10^{-2} g cm^{-3}. Similar break points were observed for miceller solutions of the other alkyltrimethylammonium halides in water [1, 2, 21]. The corresponding micelle concentration was 0.64×10^{-2} g cm^{-3} for TTAC, 0.77×10^{-2} g cm^{-3} for TTAB, and $(0.3–0.4) \times 10^{-2}$ g cm^{-3} for CTAB. This phenomenon may be interpreted as weakening of the intermicellar repulsion, owing to stronger binding of counterion on the micelle above this micelle concentration.

The Debye plots for 2.0–4.0 M NaCl solutions decrease with an increase in the micelle concentration, and they reach a constant value for 1.5 M NaCl solution and increase beyond a minimum for 2.0–4.0 M NaCl solutions with further increasing micelle concentration. This behavior implies that, while surfactant molecules associate together into spherical micelles at the critical micelle concentration, rodlike micelles are formed with increasing micelle concentration. Rodlike micelles overlap and entangle at the micelle concentrations above the minimum, as will be discussed later. Corresponding to this minimum, a maximum for the angular dissymmetry is manifest for 3.0 and 4.0 M NaCl solutions, as seen in Figure 1b.

The constant or minimum value of the Debye plot corresponds to the reciprocal of the molecular weight of rodlike micelle, since the contribution of the intermicellar interaction should be very small at the dilute micelle concentration where the molecular weight of rodlike micelles have been evaluated. The slope of the straight line for reciprocal angular envelope of light scattering at the same micelle concentration gives the radius of gyration of rodlike micelles. Numerical values of the molecular weight, the aggregation number, and the radius of gyration of rodlike micelles are listed in Table 2.

Discussion

Formation of rodlike micelles

The micelle molecular weight of CTAC in aqueous NaCl solutions is plotted against the molar concentration of counterion in a double logarithmic scale in Figure 3. With an increase in molar concentration of counterion, the molecular weight of rodlike micelles steeply increases, while that of spherical micelles gradually varies. Both spherical and rodlike micelles follow the linear relations given by

$$\log M = \alpha \log (C_o + C_S) + \beta . \qquad (2)$$

The same relations hold for spherical and rodlike micelles of the other alkyltrimethylammonium halides in sodium halide solutions [1–4], as seen in Figure 3. The values of α and β are summarized in Table 3.

While the slope, α, for spherical micelles is close to 0.1 for all surfactants, that for rodlike micelles is an order of magnitude higher than for spherical micelles. The α value for rodlike micelles is two to three times larger for chloride derivatives than for bromide derivatives, and it is strongly indicative of different degrees of counterion binding. It is noted that the linear relation, (2), with a slope, 0.31, holds for rodlike micelles of dimethyloleylamine oxide in aqueous solutions, irrespective of different NaCl and HCl concentrations [9].

The threshold NaCl concentration, C_S^*, for the sphere-rod transition of CTAC micelles is 1.18 M, and the micelle molecular weight, M^*, and aggregation num-

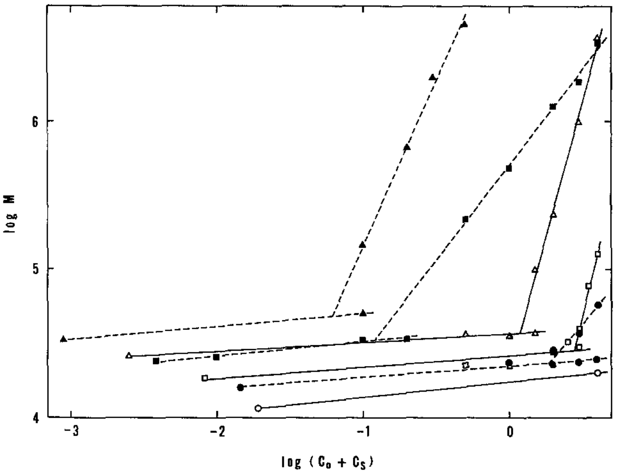

Fig. 3. The double logarithmic plot of M vs. $(C_o + C_S)$ for micelles of alkyltrimethylammonium halides in corresponding aqueous sodium halide solutions. (○) DTAC at 25 °C; (●) DTAB at 25 °C; (□) TTAC at 25 °C; (■) TTAB at 25 °C; (△) CTAC at 25 °C; (▲) CTAB at 35 °C

Table 2. Characteristics of rodlike micelles of CTAC in aqueous NaCl solutions at 25 °C

C_2 (M)	$(\partial \tilde{n}/\partial c)_{C_S}$ (cm^3 g^{-1})	$(c - c_o)$[a] (10^{-2} g cm^{-3})	M (10^4)	m	R_G (nm)	L_c (nm)	$(c - c_o)^*$ (10^{-2} g cm^{-3})	$(C - C_o)^*$ (M)
1.5	0.157	2.01	9.88	309	13.5	17.0	1.59	0.050
2.0	0.156	0.793	23.7	739	21.5	40.8	0.95	0.030
3.0	0.149	0.205	98.9	3090	52.4	170	0.27	0.0085
4.0	0.112	0.197	366	11400	88.8	630	0.21	0.0065

[a]) The molecular weight and the radius of gyration of rodlike micelles were obtained at given surfactant concentrations.

Table 3. Values of α and β in Equation (2)

	Temperature (°C)	Spherical			Rodlike			Reference
		α	β		α	β		
DTAC	25	0.105	4.26	$m \leq 76$	–	–	–	4
DTAB	25	0.085	4.37	$m \leq 79$	1.11	4.10	$m > 78$	3
TTAC	25	0.09	4.42	$m \leq 102$	3.99	2.70	$m > 96$	2
TTAB	25	0.11	4.62	$m \leq 101$	1.28	5.71	$m > 98$	2
CTAC	25	0.06	4.56	$m \leq 115$	3.66	4.31	$m > 116$	this work
CTAB	35	0.09	4.78	$m \leq 137$	2.07	7.22	$m > 132$	1

ber, m^*, at the threshold NaCl concentration are 37300 and 116 respectively. The C_s^* value of CTAC is an order of magnitude higher than that of CTAB [1], but it is a half of that of TTAC [2], both manifesting the strong effect of counterion species and alkyl chain length on the threshold salt concentration.

Dorshow et al. [17] investigated dynamic light scattering for aqueous NaCl solutions of CTAC. According to them, the positive dependence of the diffusion coefficient on the surfactant concentration indicates the intermicellar repulsive interaction at low NaCl concentrations. With increasing NaCl concentration, the intermicellar repulsive interaction diminishes by the counterion binding, and when it vanishes, the micellar growth from sphere to rod is induced. Such an NaCl concentration for CTAC falls between 1 and 2 M at 25 °C [17], which is consistent with our threshold NaCl concentration, 1.18 M, for the sphere-rod transition.

Evidence for the binding of Br^- on the micelle stronger than Cl^- was provided by Dorshow et al. [17] and Sepúlveda and Cortés [22]. Then the C_s^* value of chloride derivatives is higher than that of bromide derivatives. Zana [23] reported a decrease in degree of ionization from 0.35 to 0.16 upon increasing alkyl chain length of alkyltrimethylammonium bromides from C_8 to C_{16}. This causes the induction of sphere-rod transition at a lower salt concentration for a surfactant with longer alkyl chain.

Characteristics of rodlike micelles

It has been established that long rodlike micelles are not rigid, and their flexibility has been estimated for ionic and nonionic surfactants [2, 5–9]. A rodlike micelle can be represented by the wormlike chain of Kratky and Porod [10], which is characterized by the contour length, L_c, and the persistence length, a. Then the mean-square radius of gyration, $\langle R_G^2\rangle_o$, and the mean-square end-to-end distance, $\langle r^2\rangle_o$, for rodlike micelles are expressed by [10, 24]

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

and

$$\frac{\langle r^2\rangle_o}{2a^2} = \frac{L_c}{a} - 1 + e^{-L_c/a}, \quad (4)$$

where the suffix, o, means that the parameters stand for the unperturbed chains without the excluded volume effect.

The contour length of a rodlike micelle can be calculated by

$$L_c \approx M/M_L, \quad (5)$$

where M_L is the molecular weight per length of a micelle. On the basis of simple geometrical assumption, the value of M_L has been obtained as 5800 nm^{-1} for CTAC [2].

According to Equations (3)–(5) and assuming $\langle R_G^2\rangle_o \approx R_G^2$, the contour length, the persistence length and the end-to-end distance for rodlike micelles of CTAC can be evaluated from the observed values of the molecular weight and the radius of gyration of corresponding micelles.

The contour length of rodlike micelles of CTAC in 4.0 M NaCl is as long as 630 nm, as seen in Table 2, and its persistence length is 46.4 nm. The number of Kuhn's statistical segments, $L_c/2a$, is 6.8 and the end-to-end distance is 233 nm which is 1/3 of the contour length, indicating semiflexibility. On the other hand, the contour length of CTAC micelles in 3.0 M NaCl is 170 nm, which is only twice the length of Kuhn's segments, $2a = 93$ nm. For such short rodlike micelles, the evaluation of the persistence length is impossible.

In the previous work [2], we have evaluated the persistence lengths of long rodlike micelles of TTAB and CTAB in aqueous NaBr solutions. They are approximately constant, independent of the NaBr concentration, and amount, on the average, to 51 and 47 nm for TTAB and CTAB, respectively, when the contour length is much longer than the length of Kuhn's segments.

If the contour length is sufficiently long, the flexibility of rodlike micelles of alkyltrimethylammonium halides seems to be independent of their contour length, the alkyl chain length, and the counterion species, either chloride or bromide, and their persistence length ranges over 37–60 nm. The threshold values of the molecular weight and the contour length, above which the flexibility of rodlike micelles can be evaluated, are about 10^6 and 200 nm, respectively, for alkyltrimethylammonium halides.

The flexibility of rodlike micelles of ionic surfactant would be reduced by the electrostatic repulsion between surface charges. The charge density on a micelle is determined by the binding of counterion on its surface. The counterion binding would be independent of salt concentration, if the salt concentration is high, although the contour length of rodlike micelles increases with an increase in salt concentration. Then the flexibility may be independent of the contour length of long rodlike micelles formed at high salt concentrations.

The counterion binding is larger for the bromide derivative than for the chloride derivative, and for a surfactant of longer alkyl chain [17, 22, 23]. Then micelles of a surfactant with bromide counterion or with longer alkyl chain may be more flexible than those with chloride counterion or with shorter alkyl chain. However, comparison of the thickness of rodlike micelles [20] would reveal the opposite effect on the flexibility: the diameter increases in the order TTAB < CTAC < CTAB, and hence, the contribution of diameter to the flexibility decreases in this order. As a result of cancellation of these two opposite effects, long rodlike micelles of TTAB, CTAC and CTAB are all flexible to a similar degree, within the error of analysis.

The persistence length of rodlike micelles was frist estimated by Appell et al. [5], who assigned a value, 20 nm, for micelles of cetylpyridinium bromide in aqueous NaBr solution. The persistence length for rodlike micelles of dodecyldimethylammonium chloride in aqueous NaCl solutions was reported by three groups as 82 [6], 45 [8], and 35 [2] nm, and that of dodecyldimethylammonium bromide was 45 [8] and 31 [2] nm. The persistence length of rodlike micelles of dimethyloleylamine oxide was estimated to be as long as 100–200 nm, depending on the concentration of added HCl [7, 9].

Behavior of rodlike micelles in semidilute solutions

At a certain threshold micelle concentration, defined by

$$(c - c_o)^* = M/[(4/3)\,\pi R_G^3 N_A]\,, \tag{6}$$

rodlike micelles contact with one another. The values of $(c - c_o)^*$ (g cm^{-3}) and $(C - C_o)^*$ (M) for rodlike micelles of CTAC are shown in Table 2. The threshold micelle concentration decreases with increasing NaCl concentration.

When micelle concentration exceeds this threshold value, rodlike micelles overlap and entangle together to form a network, which is characterized by an average mesh size, ξ, or the correlation length [11]. When M_ξ represents the molecular weight of a blob, i. e., a unit of mesh, and ξ_G is the radius of gyration of a blob,

$$c - c_o = M_\xi/[(4/3)\,\pi \xi_G^3 N_A]\,. \tag{7}$$

The reduced intensity of light scattered in the θ direction from such semidilute solutions of micelles may be expressed by

$$R_\theta - R_\theta^o = K(c - c_o)\, M_\xi \left(1 - \frac{1}{3}\,\xi_G^2 \mu^2\right), \tag{8}$$

if blobs behave ideally [2].

The values of M_ξ and ξ_G for entangled rodlike micelles of CTAC can be obtained from light scattering for semidilute solutions of CTAC above the threshold micelle concentration of overlap. Applying Equation (5) and replacing M and L_c with M_ξ and $L_{c,\xi}$, the contour length of a blob, $L_{c,\xi}$, can be calculated. Their numerical values are listed in Table 4. With increasing micelle concentration, values of m_ξ, ξ_G and $L_{c,\xi}$ decrease and thus blobs become smaller. The angular dissymmetry and the Debye plot pass a maximum and a minimum, respectively, near the threshold micelle concentration of overlap, where blobs are identical with micelles themselves. The similar behavior of entangled rodlike micelles in semidilute solutions has been found for TTAB in aqueous NaBr solutions (2).

Table 4. Characteristics of entangled rodlike micelles of CTAC in aqueous NaCl 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)	ξ_G (nm)	$L_{c,\xi}$ (nm)
2.0	1.22	1.29	23.4	22.0	40.4
	1.58	1.67	23.0	22.1	39.7
	1.97	2.09	20.5	21.0	35.2
3.0	0.398	1.46	94.7	52.1	163
	0.592	2.18	75.3	47.7	130
	0.803	2.95	64.5	43.8	111
	1.18	4.33	46.8	37.7	80.5
	1.60	5.88	34.2	32.5	58.9
	1.98	7.29	26.8	28.7	46.1
4.0	0.317	1.53	302	79.9	519
	0.409	1.98	248	72.5	426
	0.613	2.96	173	62.4	298
	0.787	3.80	133	53.1	229
	1.20	5.78	84.4	43.1	145
	1.99	9.61	46.9	35.3	80.9

The scaling law

The property of rodlike micelles which entangle together to form a network in semidilute solutions can be described by the scaling law, as proposed for entangled polymer chains [11]. In dilute micellar solutions, the radius of gyration of a micelle is related to the number of surfactant molecules in a micelle and hence the micelle molecular weight by

$$R_G \cong b(M/M_1)^\nu \sim M^\nu , \qquad (9)$$

where b is the length of a micelle per surfactant and M_1 is the molecular weight of monomeric surfactant. Similarly, in semidilute micellar solutions, the radius of gyration of a blob is given by

$$\xi_G \cong b(M_\xi/M_1)^\nu \sim M_\xi^\nu , \qquad (10)$$

where M_ξ/M_1 is the number of surfactant molecules in a blob. The exponent, ν, for polymer chain is 0.5 for the ideal random coil [11] and unity for rigid thin rod [25]. Although the exponent in Equation (9) may not always be identical with that in Equation (10), we find them to be equal in our case, as will be seen below.

Figure 4 shows the double logarithmic plot of the radius of gyration and the molecular weight for rodlike micelles of CTAC formed in dilute solutions at different NaCl concentrations. The radius of gyration varies with the molecular weight as $R_G \sim M^{0.55}$. The value of the exponent of 0.55 is consistent with that rodlike micelles of CTAC are not rigid but semiflexible.

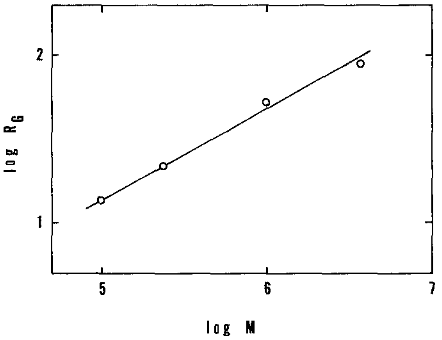

Fig. 4. The double logarithmic plot of R_G vs. M for rodlike micelles of CTAC at 25 °C

The double logarithmic plot of ξ_G vs. M_ξ for entangled rodlike micelles of CTAC is given in Figure 5. Data are on a straight line with a slope of 0.55. The same scaling law holds for both dilute and semidilute regimes, regardless of the NaCl concentrations.

We have investigated the behavior of rodlike micelles of TTAB in aqueous NaBr solutions and obtained the exponents of 0.54 for dilute regime and of 0.55 for semidilute regime [2], which are close to the values for CTAC.

From Equations (6) and (9), it can be shown that the threshold micelle concentration of overlap is scaled as

$$(c - c_o)^* \sim MR_G^{-3} \sim M^{-(3\nu-1)} \sim R_G^{-(3\nu-1)/\nu} . \qquad (11)$$

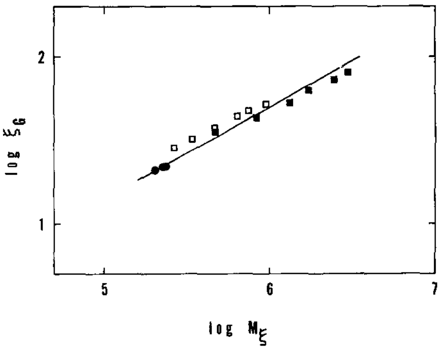

Fig. 5. The double logarithmic plot of ξ_G vs. M_ξ for entangled rodlike micelles of CTAC at 25 °C. NaCl concentration (M): (●) 2.0; (□) 3.0; (■) 4.0

In semidilute solutions, where the number of blobs in a micelle is M/M_ξ, the radius of gyration of a micelle is described by

$$R_G \cong \xi_G (M/M_\xi)^\nu . \qquad (12)$$

From a requirement that the number of surfactant molecules in a blob does not depend on the micelle molecular weight but does on the micelle concentration, the scaling law

$$M_\xi / M_1 \sim (c - c_o)^x \qquad (13)$$

should hold for blobs, or, from the relation (10),

$$\xi_G \sim (c - c_o)^{x\nu} . \qquad (14)$$

Since $\xi_G \approx R_G$ at $(c - c_o) \approx (c - c_o)^*$, Equations (9), (11), and (14) are combined to give

$$M^\nu \sim (c - c_o)^{*x\nu} \sim M^{-x\nu(3\nu - 1)} . \qquad (15)$$

Therefore, it follows that

$$x = -1/(3\nu - 1) . \qquad (16)$$

Then, in semidilute solutions,

$$\xi_G \sim (c - c_o)^{-\nu/(3\nu - 1)} \qquad (17)$$

from Equation (14) or, combined with Equation (11),

$$\xi_G / R_G \sim [(c - c_o)/(c - c_o)^*]^{-\nu/(3\nu - 1)} . \qquad (18)$$

From Equations (12) and (18),

$$M_\xi / M \cong (\xi_G / R_G)^{1/\nu} \sim [(c - c_o)/(c - c_o)^*]^{-1/(3\nu - 1)} . \qquad (19)$$

If blobs behave ideally, the osmotic pressure, Π, for semidilute solutions of micelles should be proportional to the number density of blobs in solution, leading to the concentration dependence:

$$\Pi / kT \sim (c - c_o)/M_\xi \sim \xi_G^{-3} \sim (c - c_o)^{3\nu/(3\nu - 1)} \qquad (20)$$

where Equations (7) and (17) have been substituted. This relation follows the demonstration by Daoud et al. [26], based on the assumption that the osmotic pressure behaves like some power of the micelle concentration. The same relation was derived by des Cloiseaux [27], whose derivation is based on the impenetrable sphere approximation for the second virial coefficient.

Since the light scattered from a micellar solution in the 0° direction is given by the relation,

$$\frac{K(c - c_o)}{R_o - R_o^o} = \frac{1}{kT} \left(\frac{\partial \Pi}{\partial (c - c_o)} \right)_T , \qquad (21)$$

then

$$\frac{K(c - c_o)}{R_o - R_o^o} \sim (c - c_o)^{1/(3\nu - 1)} \qquad (22)$$

or

$$\left(\frac{K(c - c_o)}{R_o - R_o^o} \right) \Big/ \left(\frac{K(c - c_o)}{R_o - R_o^o} \right)_{(c - c_o) = (c - c_o)^*} \sim \left(\frac{(c - c_o)}{(c - c_o)^*} \right)^{1/(3\nu - 1)} \qquad (23)$$

for semidilute solutions.

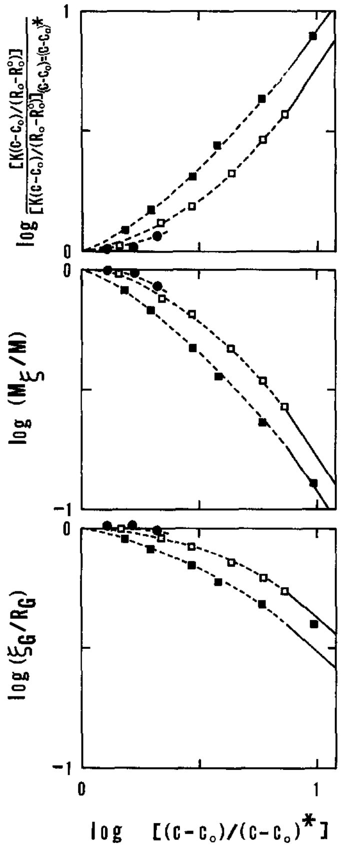

Fig. 6. The double logarithmic plot of the reduced values of (a) the reciprocal envelope of light scattering in the 0° direction, (b) the molecular weight and (c) the radius of gyration of the blob in semidilute NaCl solutions of CTAC as a function of the reduced micelle concentration. NaCl concentration (M): (●) 2.0; (□) 3.0; (■) 4.0

The reduced values of the reciprocal envelope of light scattering in the 0° direction, the molecular weight and the radius of gyration of the blobs for semidilute solutions of CTAC are plotted against the reduced micelle concentration in the double logarithmic scale in Figure 6. The theoretical lines with slopes of 1.54, -1.54, and -0.85, respectively, are drawn as the solid lines at high reduced micelle concentrations. They were evaluated from Equations (23), (19), and (18), respectively, using the value of $\nu = 0.55$. The plots gradually increase or decrease with an increase in logarithmic reduced micelle concentration and approach the straight lines predicted theoretically.

The behavior of rodlike micelles of alkyltrimethylammonium bromide in semidilute solutions has been investigated by Candau et al. [12, 13]. CTAB micelles in 0.1 M and 0.25 M KBr with surfactant concentrations up to 0.6 M obeyed two scaling laws above the threshold micelle concentration of overlap: the intensities of light scattering and diffusion coefficient were scaled against the volume fraction of surfactant, agreeing with the theoretical prediction for real chain in good solvent [11].

References

1. Imae T, Kamiy R, Ikeda S (1985) J Coll Interf Sci 108:215
2. Imae T, Ikeda S (1986) J Phys Chem 90:5216
3. Ozeki S, Ikeda S (1982) J Coll Interf Sci 87:424
4. Ozeki S, Ikeda S (1981) Bull Chem Soc Jpn 54:552
5. Appell J, Porte G, Poggi Y (1982) J Coll Interf Sci 87:492
6. Flamberg A, Pecora R (1984) J Phys Chem 88:3026
7. Imae T, Ikeda S (1984) Coll & Polym Sci 262:497
8. Van De Sante W, Persoons A (1985) J Phys Chem 89:404
9. Imae T, Ikeda S (1985) Coll & Polym Sci 263:756
10. Kratky O, Porod G (1949) Roc Trav Chim 68:1106
11. de Gennes PG (ed) (1979) Scaling Concepts in Polymer Physics, Cornell Univ Press, Ithaca London
12. Candau SJ, Hirsch E, Zana R (1984) J Phys, Paris 45:1263
13. Candau SJ, Hirsch E, Zana R (1985) J Coll Interf Sci 105:521
14. Reiss-Husson E, Luzzati V (1964) J Phys Chem 68:3504
15. Hayter JB, Penfold J (1983) Coll & Polym Sci 261:1022
16. Roelants E, Geladé E, Van Der Auweraer M, Croonen Y, De Schryver FC (1983) J Coll Interf Sci 96:288
17. Dorshow RB, Bunton CA, Nicoli DF (1983) J Phys Chem 87:1409
18. Roelants E, Geladé E, Smid J, De Schryver FC (1985) J Coll Interf Sci 107:337
19. Malliaris A, Le Morgne J, Zana R (1985) J Phys Chem 89:2709
20. Abe A, Imae T, Ikeda S (1987) Coll & Polym Sci 265:637
21. Ekwall P, Mandell L, Solyom P (1971) J Coll Interf Sci 35:519
22. Sepúlveda L, Cortés J (1985) J Phys Chem 89:5322
23. Zana R (1980) J Coll Interf Sci 78:330
24. Benoit H, Doty P (1953) J Phys Chem 57:958
25. Geiduschek EP, Holtzer A (1958) Advan Biol Med Phys 6:431
26. Daoud M, Cotton JP, Farnoux B, Jannink G, Sarma G, Benoit H, Duplessix R, Picot C, de Gennes PG (1975) Macromolecules 8:804
27. des Cloiseaux J (1975) J Phys, Paris 36:281

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