

Viscosity Behavior of Semiflexible Rodlike Micelles of Alkyltrimethylammonium Halides in Dilute and Semidilute Solutions

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The relative viscosity of aqueous micellar solutions of tetradecyltrimethylammonium bromide (TTAB) and cetyltrimethylammonium chloride (CTAC) and bromide (CTAB) in the presence of concentrated NaCl or NaBr has been measured under different shear rates. The viscosity displays strong shear dependence, characteristic of the pseudoplastic non-Newtonian flow. The persistence length of semiflexible rodlike micelles can be evaluated from the intrinsic viscosity at zero shear rate, based on the wormlike cylinder chain model, the values being 53, 77, and 53 nm for TTAB, CTAC, and CTAB, respectively. Semiflexible rodlike micelles overlap together above the threshold micelle concentration, $(c - c_0)^*$, and entangle together above the threshold micelle concentration, $(c - c_0)_\eta^*$. The relative viscosity of solutions at micelle concentrations above $(c - c_0)_\eta^*$ can be analyzed, according to the reptation model and the scaling law, and it follows the relation $\eta_{rel}^0 \sim [(c - c_0)/(c - c_0)_\eta^*]^x$ with $x = 2.2-3.0$.

Introduction

We have demonstrated by light-scattering measurements that tetradecyl- and cetyltrimethylammonium halides in aqueous solutions associate together into rodlike micelles, when the salt is added beyond the threshold salt concentration, C_s^* .¹⁻⁴ The C_s^* value is 0.12 M for TTAB in NaBr at 25 °C, 1.18 M for CTAC in NaCl at 25 °C, and 0.06 M for CTAB in NaBr at 35 °C.

Rodlike micelles of these surfactants have semiflexible character, if their contour length is much longer than the length of Kuhn's segments. Their flexibility is characterized by the persistence length defined for the wormlike chain model of Kratky and Porod,⁵ which can be calculated from the radius of gyration and the contour length of micelles.¹⁻⁴ The persistence length of semiflexible chains should also be evaluated from the intrinsic viscosity at zero shear rate.⁶

In semidilute solutions above the threshold micelle concentration, $(c - c_0)^*$, rodlike micelles overlap and entangle together like a network and the behavior of solutions must be described by the correlation length or the mesh size of a network, ξ .⁷ The characteristics of entangled rodlike micelles of TTAB and CTAC^{1,2,4} can be represented by the scaling law for parameters from light scattering.⁷ It is also known that the viscosity behavior of entangled chains in aqueous solutions is different from that of isolated chains.⁷⁻¹⁰

Although the viscosity of aqueous micellar solutions was measured by many workers,¹¹⁻²⁶ almost all of the investigations

were carried out by a capillary viscometer with a finite shear rate and for Newtonian flow,^{11-15,17,21-24,26} and only a few data were concerned with the high viscosity of aqueous micellar solutions and its shear dependence.^{16,18-20,25}

Ozeki and Ikeda¹⁶ measured the reduced viscosity of aqueous solutions of dodecyltrimethylammonium chloride by using a modified capillary viscometer, and they reported that the non-Newtonian viscosity manifested for solutions of high NaCl concentrations. Hoffmann et al.¹⁸⁻²⁰ measured the viscosity at very low shear rates by means of rotational viscometers and pointed out that the solutions of tetradecylammonium trifluoroacetate were viscoelastic.¹⁸ Candau et al.²⁵ performed the viscosity measurement of 0.1 M KBr solutions of TTAB and CTAB on capillary and rotational viscometers and found a high viscosity for CTAB at high concentrations.

In the present work we measure the relative viscosity at different shear rates of aqueous micellar solutions of TTAB, CTAC, and CTAB in the presence of concentrated sodium salts and obtain the intrinsic viscosity of rodlike micelles at zero shear rate. We estimate the flexibility of rodlike micelles, based on the theory of wormlike cylinder chain proposed by Yamakawa and Fujii.⁶ Furthermore, we discuss the viscosity behavior of aqueous solutions of rodlike micelles in dilute and semidilute regimes, based on the reptation model and the scaling law.⁷⁻¹⁰

Experimental Section

Materials. Samples of TTAB, CTAC, and CTAB are the same as previously purified and used.¹⁻⁴ The purity of recrystallized samples was checked by gas chromatography, on which there was only one peak arising from each sample. NaCl and NaBr were ignited for 1 h. Water was redistilled from alkaline potassium permanganate.

Measurement. The viscosity was measured on a Haake Rotovisco RV12 concentric-cylinder rotational viscometer equipped

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TABLE I: Characteristics of Rodlike Micelles

	C_s , M	$10^2(c - c_0)_n^*$, g cm^{-3}	$10^{-2}[\eta]$, $\text{cm}^3 \text{g}^{-1}$	k'	$10^2(c - c_0)_n^*$, g cm^{-3}	a_n , nm	10^{-4} M	L_c , nm	a_{LS} , nm	$10^2(c - c_0)_n^*$, g cm^{-3}	x	ν_n
TTAB in NaBr (25 °C)	2.0	>1.3	1.49	0.35 ₄	1.00	71	124	219	56	0.49		
	2.5	0.93	1.68	0.31 ₈	0.90	49	164 ^a	289			2.41	0.75
	3.0	0.80	2.17	0.35 ₆	0.71	58	185	327	60	0.29	2.36	0.76
	3.5	0.65	2.62	0.32 ₅	0.63	46	252 ^a	444			2.29	0.77
	4.0	0.46	3.02	0.31 ₅	0.44	40	333	588	37	0.28	2.16	0.80
CTAC in NaCl (25 °C)	3.5	0.60	2.72	0.34 ₅	0.40	83	199 ^a	343			2.58	0.72
	4.0	0.38	4.21	0.36 ₄	0.40	71	366	564	46	0.21	2.98	0.67
CTAB in NaBr (35 °C)	0.3	~1.1	1.27	0.31 ₉	1.04	45	197	280	42	0.59	2.53	0.73
	0.5	0.70	2.64	0.33 ₄	0.57	60	347	494	53	0.27	2.19	0.79

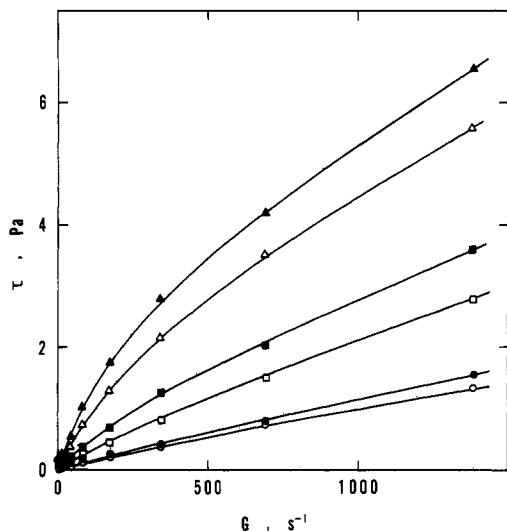
^a Interpolated.

Figure 1. Plot of shear stress against shear rate for 0.5 M NaBr solutions of CTAB at 35 °C. Micelle concentrations ($10^{-2} \text{ g cm}^{-3}$): \circ , 0.30; \bullet , 0.41; \square , 0.62; \blacksquare , 0.81; \triangle , 1.04; \blacktriangle , 1.20.

with the temperature vessel, which was kept at constant temperature. The coaxial double cylinder sensor NV was used, the inner cup of which was temperature-controlled. The shear stress, τ , was measured at each shear rate, G , and the viscosity, η_G , at shear rate G was obtained from the flow equation

$$\tau = \eta_G G \quad (1)$$

The shear rate was changed from 5.41 to 1385 s^{-1} . The relative viscosity, $\eta_{rel,G}$, is given by

$$\eta_{rel,G} = \eta_G / \eta_0 \quad (2)$$

where η_0 is the viscosity of solvent and it is independent of the shear rate.

Results

The relation between shear stress and shear rate is illustrated in Figure 1 for 0.5 M NaBr solutions of CTAB at 35 °C. The stronger upward curvature is found for more concentrated solutions, which is characteristic of the non-Newtonian flow of pseudoplastic type or the structural viscosity.

Figure 2 shows the double logarithmic plot of shear stress against shear rate. The linear relation holds at high shear rates, but the deviation from the linearity occurs at low shear rates, which is larger for more concentrated solutions. The similar dependence of shear stress on shear rate has been reported for non-Newtonian flow of poly- γ -benzyl-L-glutamate in *m*-cresol.²⁷⁻³⁰

Generally, the power law equation

$$\tau = \alpha G^n \quad (3)$$

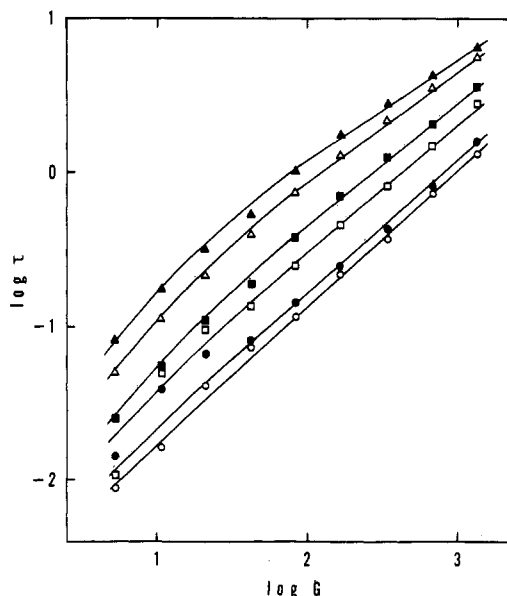


Figure 2. Double logarithmic plot of shear stress against shear rate for 0.5 M NaBr solutions of CTAB at 35 °C. The symbols are the same as in Figure 1.

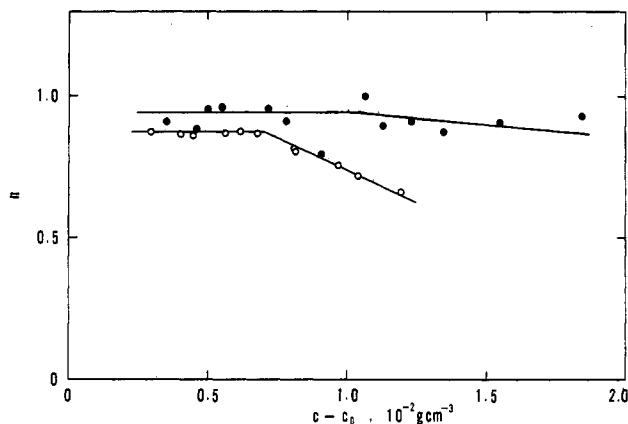


Figure 3. n value at high shear rates as a function of micelle concentration for 0.3 and 0.5 M NaBr solutions of CTAB at 35 °C: \bullet , 0.3 M; \circ , 0.5 M.

holds for flows of solution,²⁸ where α and n are constants. The n value is unity for the Newtonian flow, and it is smaller than unity for the pseudoplastic non-Newtonian flow. The n value at high shear rates can be taken from the double logarithmic plot of shear stress against shear rate for 0.3 and 0.5 M NaBr solutions of CTAB at 35 °C, and it is plotted in Figure 3 against micelle concentration, $c - c_0$, where c is the surfactant concentration and c_0 is the critical micelle concentration. The n value decreases at micelle concentrations above $\sim 1.1 \times 10^{-2} \text{ g cm}^{-3}$ in 0.3 M NaBr and $0.70 \times 10^{-2} \text{ g cm}^{-3}$ in 0.5 M NaBr. These micelle concentrations correspond to the threshold values above which the non-Newtonian flow becomes remarkable, and we designate them as $(c - c_0)_n^*$.

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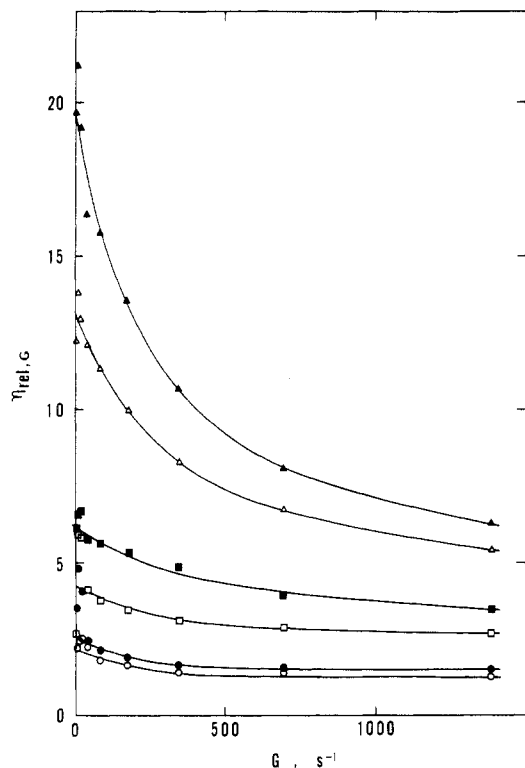


Figure 4. Relative viscosity as a function of shear rate for 0.5 M NaBr solutions of CTAB at 35 °C. The symbols are the same as in Figure 1.

A similar dependence of shear stress on shear rate can be observed for 3.5 and 4.0 M NaCl solutions of CTAC and for 2.0 to 4.0 M NaBr solutions of TTAB at 25 °C. The $(c - c_0)_n^*$ values obtained for all the systems examined are summarized in Table I. The $(c - c_0)_n^*$ value decreases with increasing salt concentration.

Figure 4 gives the relative viscosity, $\eta_{rel,G}$, as a function of shear rate for 0.5 M NaBr solutions of CTAB at 35 °C. The relative viscosity decreases with an increase in shear rate, indicating the shear-thinning. The extrapolation to zero shear rate of the curve gives the relative viscosity at zero shear rate, η_{rel}^0 ($\equiv \lim_{G \rightarrow 0} \eta_{rel,G}$).

The dependence of viscosity parameters on shear rate or shear stress was reported for poly- γ -benzyl-L-glutamate in *m*-cresol²⁷⁻²⁹ and in toluene³¹ and for DNA in aqueous solution,^{32,33} and discussed on the basis of theoretical aspect.^{27-29,33} The experimental and theoretical profiles provide a plateau at low shear rates or stresses and an inverse sigmoidal decrease at high shear rates or stresses. On the contrary, our results do not give any plateau region within experimental shear rates.

Since the critical micelle concentration is very low for all solutions examined,¹⁻³ the viscosity at the critical micelle concentration, η_{cmc} , can be identified with η_0 . Then

$$\eta_{rel,cmc}^0 = \eta^0 / \eta_{cmc} \approx \eta^0 / \eta_0 = \eta_{rel}^0 \quad (4)$$

For dilute solutions the Huggins equation holds as follows

$$\frac{\eta_{rel}^0 - 1}{c - c_0} = \frac{\eta_{sp}^0}{c - c_0} = [\eta] + k'[\eta]^2(c - c_0) \quad (5)$$

where η_{sp}^0 means the specific viscosity at zero shear rate, $[\eta]$ is the intrinsic viscosity at zero shear rate, and k' is a hydrodynamic interaction coefficient known as the Huggins constant.

The relative viscosity can also be related to the micelle concentration by the Mead-Fuoss equation for dilute solutions

$$\frac{\ln \eta_{rel}^0}{c - c_0} = [\eta] - \beta[\eta]^2(c - c_0) \quad (6)$$

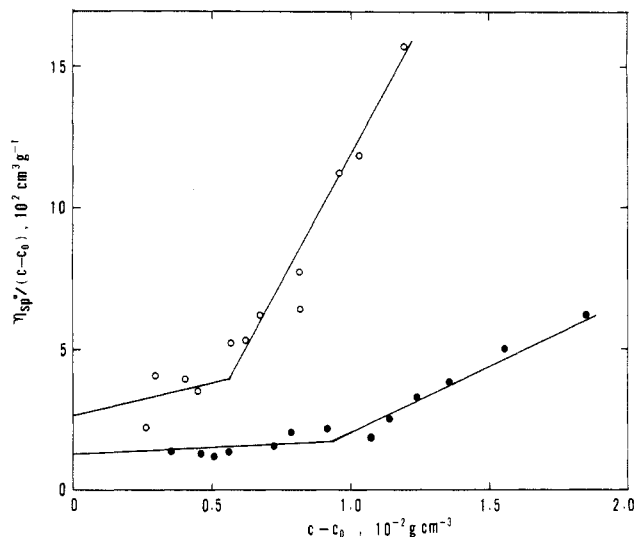


Figure 5. Plot of the reduced viscosity against micelle concentration for 0.3 and 0.5 M NaBr solutions of CTAB at 35 °C: ●, 0.3 M; ○, 0.5 M. Initial straight lines at lower micelle concentrations were drawn on the basis of the values of $[\eta]$ and k' in Table I.

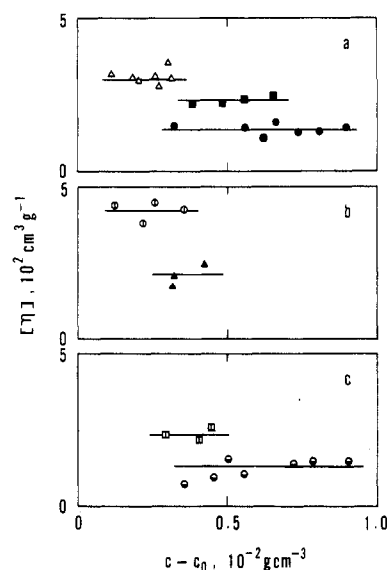


Figure 6. Plot of the intrinsic viscosity against micelle concentration. Salt concentration (M): (a) TTAB, (●) 2.0; (■) 3.0; (Δ) 4.0; (b) CTAC, (▲) 3.5; (⊙) 4.0; (c) CTAB, (⊙) 0.3; (⊓) 0.5.

The hydrodynamic interaction coefficient, β , is connected with the Huggins constant as

$$k' + \beta = \frac{1}{2} \quad (7)$$

Then, from eq 5-7

$$\frac{2(\eta_{sp}^0 - \ln \eta_{rel}^0)}{(c - c_0)^2} = [\eta]^2 \quad (8)$$

Figure 5 represents the plot of the reduced viscosity against micelle concentration for 0.3 and 0.5 M NaBr solutions of CTAB at 35 °C. The intrinsic viscosity can be calculated from observed values at lower micelle concentrations, according to eq 8. When the obtained value of the intrinsic viscosity is inserted in eq 5, the Huggins constant can be evaluated.

By means of the same procedure, values of $[\eta]$ and k' for the other systems can be derived, as illustrated in Figure 6 for $[\eta]$ values. They are constant, independent of the micelle concentrations we examined, and the averaged numerical values are given in Table I. While the intrinsic viscosity increases with an increase in salt concentration, the Huggins constant is 0.32-0.36, which is of the same magnitude as that for flexible polymer chains in good solvents, 0.35.³⁴

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Solutions examined are prepared at salt concentrations higher than the C_s^* value for each surfactant, and the surfactant concentrations range over $(0.12\text{--}1.9) \times 10^{-2} \text{ g cm}^{-3}$, which is much higher than the critical micelle concentration ($<10^{-5} \text{ g cm}^{-3}$) for prepared salt solutions.¹⁻³ Then the obtained intrinsic viscosities and the Huggins constants may be attributed to those for rodlike micelles. That they are not dependent on the micelle concentration means negligible micelle growth within the micelle concentrations we studied here.

As an alternative procedure, the logarithm of the relative viscosity was plotted against shear rate and extrapolated to zero shear rate in order to obtain the logarithmic relative viscosity at zero shear rate, $(\ln \eta_{rel})^0 (= \lim_{G \rightarrow 0} \ln \eta_{rel,G})$, the exponent of which provides the relative viscosity at zero shear rate. The viscosity parameters obtained through the same process from these values coincide with those from the procedure described above within an error of analysis.

The plots in Figure 5 increase with increasing micelle concentration, according to the straight line with values of $[\eta]$ and k' in Table I, and they deviate upward above a certain micelle concentration from the initial linear increase. This phenomenon can be interpreted as the entanglement of rodlike micelles above the micelle concentration, $(c - c_0)_{\eta}^*$, which may be called the threshold micelle concentration of entanglement of rodlike micelles. The $(c - c_0)_{\eta}^*$ values for all systems examined are included in Table I.

Discussion

Flexibility of Rodlike Micelles. It has already been confirmed by light-scattering measurements¹⁻⁴ and electron microscopic observations^{3,4} that rodlike micelles of TTAB, CTAC, and CTAB are not rigid but semiflexible. A theoretical equation for the intrinsic viscosity at zero shear rate of solutions of semiflexible polymer chains without the excluded volume effect was derived by Yamakawa and Fujii,⁶ who applied the Oseen-Burgers procedure of hydrodynamics to a wormlike cylinder with a contour length L_c and a diameter in a cross section or a thickness d .

According to their theory

$$[\eta] = \phi(2aL_c)^{3/2}/M \quad (9)$$

$$L_c = M/M_L \quad (10)$$

where a is a flexibility parameter called the persistence length, M is the molecular weight, and M_L is the molecular weight per unit contour length. The function ϕ depends on the contour length, thickness, and persistence length, and its numerical values are given by Yamakawa and Fujii.⁶

Equation 9 is applicable for the intrinsic viscosity of solutions of semiflexible rodlike micelles obtained at zero shear rate. The values of M for TTAB, CTAC, and CTAB were directly obtained from the light-scattering measurements¹⁻³ or evaluated from their interpolation. The values of M_L and d were calculated under the appropriate assumption given elsewhere,¹ and the values found in this way for TTAB, CTAC, and CTAB are 5670, 5800, and 7030 nm^{-1} for M_L and 4.2₀, 4.5₂, and 4.7₂ nm for d , respectively. Then an optimum value of the persistence length suitable to the observed $[\eta]$ value can be obtained for each system by the computer simulation.

The values of the persistence length, a_{η} , evaluated from the intrinsic viscosity are summarized in Table I, together with the values of M and L_c , and compared with the values, a_{LS} , from light-scattering parameters.^{1,4} They may be taken as independent of the ionic strength and averaged as 53, 77, and 53 nm for TTAB, CTAC, and CTAB, respectively. These values are in agreement with the averaged a_{LS} values of 51, 46, and 47 nm for TTAB, CTAC, CTAB, respectively.^{1,2,4}

The present results support the independence of persistence length of rodlike micelles of alkyltrimethylammonium halides on alkyl chain length and counterion species. The reason for this

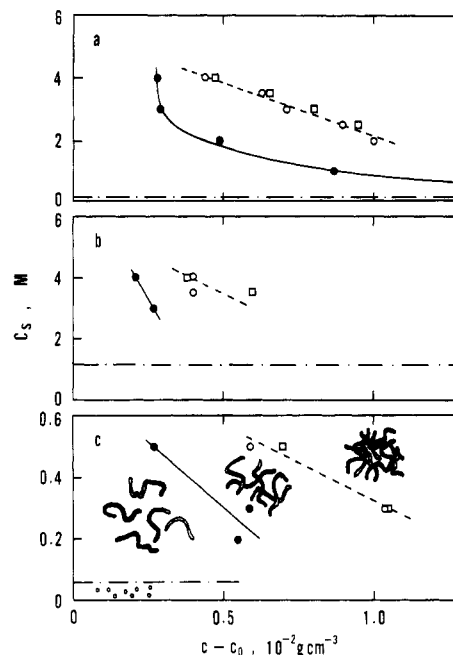


Figure 7. Diagram of threshold concentrations for sphere-rod transition, for overlap and entanglement of rodlike micelles, and for non-Newtonian flow: ---, C_s^* ; ●, $(c - c_0)^*$; ○, $(c - c_0)_{\eta}^*$; □, $(c - c_0)_{\eta}^*$. (a) TTAB, (b) CTAC, (c) CTAB.

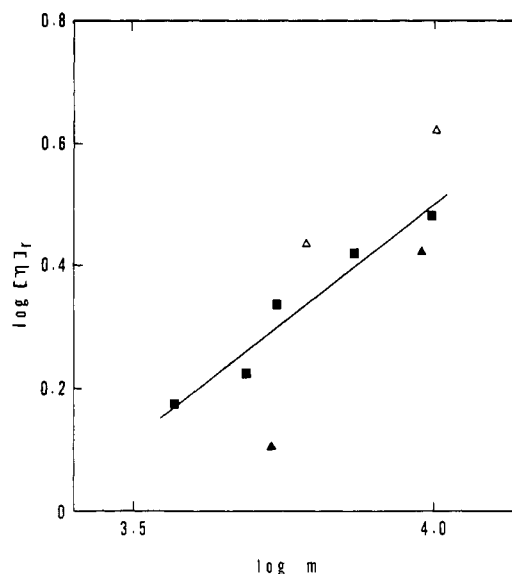


Figure 8. Double logarithmic plot of the intrinsic viscosity at zero shear rate against the aggregation number of rodlike micelles of TTAB, CTAC, and CTAB: ■, TTAB; △, CTAC; ▲, CTAB.

would come from the cancellation of two opposing factors for the flexibility. The flexibility of rodlike micelles of ionic surfactants is determined by their surface charge density and the thickness. The surface charge density or the degree of ionization is lower for surfactant micelles with long alkyl chain than for those with short alkyl chain,³⁵ and it is lower for bromide derivatives than for chloride derivatives.^{36,37} Then rodlike micelles of CTAB would be more flexible than those of TTAB and CTAC, because of weaker electrostatic repulsion between surfactants in a micelle. However, the thickness of rodlike micelles affects their flexibility in the order of TTAB > CTAC > CTAB.

Ozeki³⁸ evaluated the flexibility of rodlike micelles of dodecyltrimethylammonium chloride, by using values of the intrinsic

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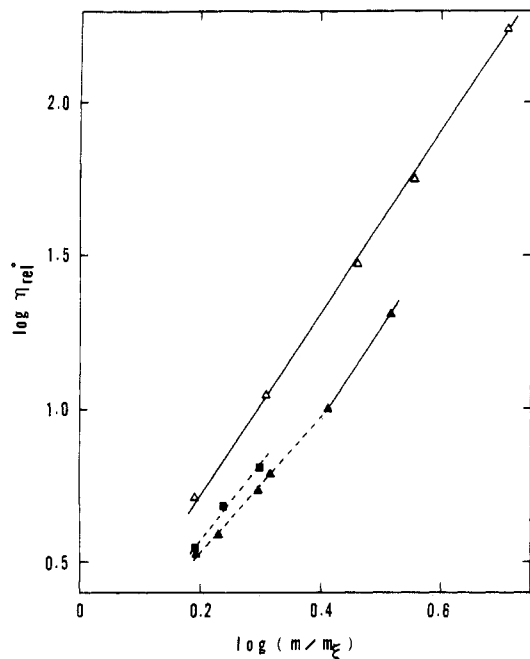


Figure 9. Relative viscosity at zero shear rate as a function of m/m_ξ for TTAB in 3.0 and 4.0 M NaBr and for CTAC in 4.0 M NaCl: \blacktriangle , TTAB in 3.0 M NaBr; \blacksquare , TTAB in 4.0 M NaBr; \triangle , CTAC in 4.0 M NaCl.

viscosity¹⁶ and eq 9. The persistence length, 22.5–30 nm, calculated by Ozeki for long rodlike micelles with the molecular weight larger than 10^6 is slightly smaller than 35 nm, which was evaluated by us from the data of light scattering.¹

The Scaling Law in Dilute and Semidilute Solutions. When the micelle concentration is increased, rodlike micelles overlap together above a certain micelle concentration, which can be defined by $(c - c_0)^* = M / [(4\pi/3)R_G^3 N_A]$, where N_A is the Avogadro's number and R_G is the radius of gyration of rodlike micelles. The $(c - c_0)^*$ values for TTAB, CTAC, and CTAB can be evaluated from values of the molecular weight, M , and the radius of gyration, R_G , obtained from light-scattering measurements,¹⁻³ and they are included in Table I.

The $(c - c_0)_\eta^*$ and $(c - c_0)_\eta^*$ values at each salt concentration for rodlike micelles of TTAB, CTAC, and CTAB are plotted in Figure 7 together with the $(c - c_0)^*$ values. The threshold salt

concentration of sphere-rod transition, C_s^* , is also illustrated in Figure 7. While the threshold micelle concentration of entanglement, $(c - c_0)_\eta^*$, is very close to the threshold value for non-Newtonian flow, $(c - c_0)_\eta^*$, it is higher than the threshold value of overlap, $(c - c_0)^*$. Three threshold values decrease with increasing salt concentration. This means that long rodlike micelles formed at higher salt concentrations overlap and entangle together at lower micelle concentrations.

In dilute solutions where micelles are isolated, the viscosity of rodlike micelles can be described like the Einstein equation:⁷

$$\eta^0 = \eta_{\text{cmc}}[1 + 2.5\psi] \quad (11)$$

The hydrodynamic volume fraction occupied by micelles is written by

$$\psi \sim (c - c_0)R_G^3/m \quad (12)$$

where m ($\equiv M/M_1$) is the aggregation number of rodlike micelles and M_1 is the molecular weight of surfactant. Then

$$[\eta] \equiv \frac{\eta^0 - \eta_{\text{cmc}}}{\eta_{\text{cmc}}(c - c_0)} \cong \frac{R_G^3}{m} \quad (13)$$

Using the scaling law of $R_G \sim m^{\nu, 2, 4, 7}$

$$[\eta] \sim m^{3\nu-1} \quad (14)$$

This relation is identical with the Mark-Houwink-Sakurada equation.

In this derivation, the hydrodynamic radius and the aggregation number are substituted by the radius of gyration and the aggregation number obtainable from light scattering, respectively. Although both do not always coincide,²⁹ this substitution does not interrupt the scaling law, if the former are proportional to the latter.

Figure 8 shows the double logarithmic plot of the intrinsic viscosity at zero shear rate against the aggregation number of rodlike micelles of TTAB, CTAC, and CTAB. The slope of straight line for rodlike micelles of TTAB in aqueous NaBr solutions at 25 °C is 0.75₄, and it leads to the $\nu_{[\eta]}$ value of 0.58. This value of ν is close to the ν_{LS} value of 0.55 from the scaling law for light scattering, $R_G \sim m^{\nu, 1, 4}$.

In semidilute solutions, rodlike micelles overlap and entangle together like a network. For entangled micelles, the reptation model⁷⁻¹⁰ proposed by de Gennes can be adopted. According to his model, the viscosity at zero shear rate is proportional to the

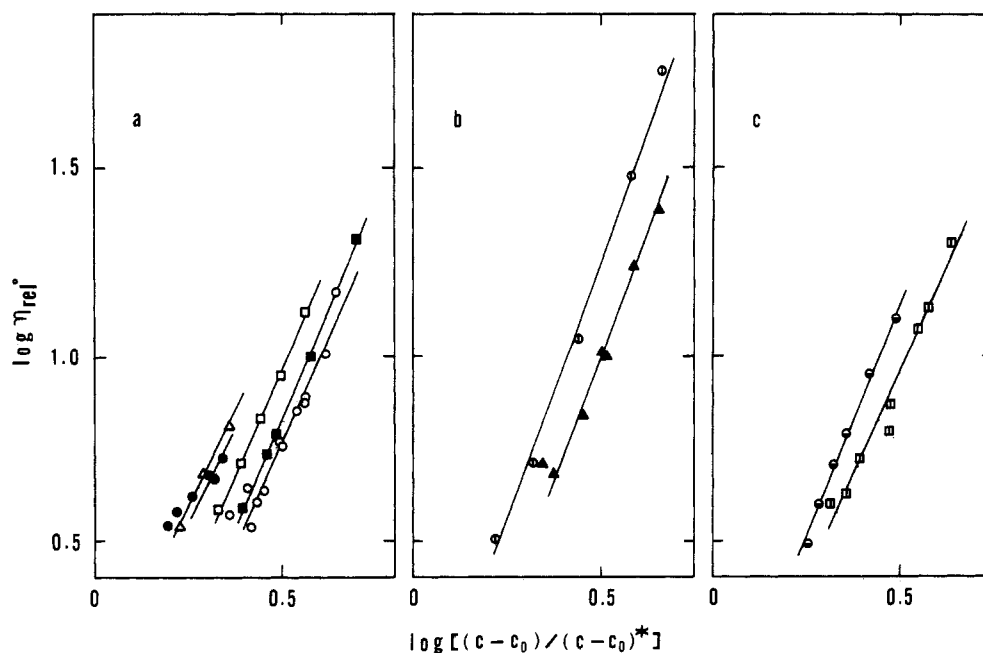


Figure 10. Relative viscosity at zero shear rate of entangled rodlike micelles as a function of $(c - c_0)/(c - c_0)^*$. Salt concentration (M): (a) TTAB, \bullet 2.0; \circ 2.5; \blacksquare 3.0; \square 3.5, \triangle 4.0; (b) CTAC, \blacktriangle 3.5; \circ 4.0; (c) CTAB, \circ 0.3; \square 0.5.

elastic modulus of a network, E , and to the terminal relaxation time, τ_t , which is the time for a chain to reptate out its tube length:

$$\eta^0 = E\tau_t \quad (15)$$

The elastic modulus is scaled as

$$E \sim T/\xi^3 \quad (16)$$

where T is temperature and ξ is the correlation length or the average mesh size of the network. If m_ξ represents the aggregation number of mesh, the terminal relaxation time is written by

$$\tau_t \cong \eta_{\text{cmc}}(m/m_\xi)^3(\xi^3/T) \quad (17)$$

From eq 15-17

$$\eta^0 \sim \eta_{\text{cmc}}(m/m_\xi)^3 \quad (18)$$

Utilizing the power law^{2,4} of

$$m_\xi/m \sim [(c - c_0)/(c - c_0)^*]^{-1/(3\nu-1)} \quad (19)$$

$$\eta_{\text{rel}}^0 = \eta^0/\eta_{\text{cmc}} \sim (m/m_\xi)^3 \quad (20)$$

$$\sim [(c - c_0)/(c - c_0)^*]^{3/(3\nu-1)} \quad (21)$$

It should be noticed that the scaling law associated with the viscosity behavior in semidilute solutions is realized by solutions of $(c - c_0) > (c - c_0)_\eta^* \geq (c - c_0)^*$ or $m_\xi < m_\eta^* \leq m$, where m_η^* is the aggregation number of mesh at the micelle concentration of $(c - c_0)_\eta^*$.

In the derivation, the hydrodynamic correlation length and aggregation number are substituted by the corresponding correlation length and aggregation number obtained from light scattering. Then numerical values of m/m_ξ can be taken from the observed data or their interpolation,^{1,2} and the relative viscosity at zero shear rate for TTAB in 3.0 and 4.0 M NaBr and for CTAC in 4.0 M NaCl is plotted in Figure 9 against the m/m_ξ value at $m_\xi < m_\eta^*$. The linearity holds for CTAC in 4.0 M NaCl, and the data are on a line with a slope of 3.0, justifying eq 20.

There are experimental reports and theoretical discussions associated with the value of power index in eq 20. The experimental results for polymer solutions indicate that the power index is 3.4 or 3.5, instead of 3.0.^{8,10} Doi³⁹ points out that the fluctuation of the contour length of a chain must be taken into account, if $10 < m/m_\xi < 100$, and then the relative viscosity can be scaled as $\eta_{\text{rel}}^0 \sim (m/m_\xi)^{3.4}$. Nevertheless, our results for micellar solutions demonstrate the power index of 3.0 in the region of $m/m_\xi < 5.2$.

Figure 10 plots the relative viscosity at zero shear rate of entangled rodlike micelles against $(c - c_0)/(c - c_0)^*$ at $(c - c_0) > (c - c_0)_\eta^*$. All the plots exhibit a linear relation with a slope, x . The values of x are listed in Table I and they are between 2.2 and 3.0, independent of salt concentration, alkyl chain length, and counterion species.

The ν_η values evaluated from $x = 3/(3\nu - 1)$ are also listed in Table I. The values are 0.67-0.80 and are larger than $\nu_{[\eta]} = 0.58$ from the intrinsic viscosity and $\nu_{\text{LS}} = 0.55$ from light scattering.^{1,2,4} Since the ν value is 0.5 for ideal random coil chains of polymer⁷ and unity for rigid thin rods,⁴⁰ it can be inferred that blobs, units of a network formed by rodlike micelles, behave as a less flexible chain at the micelle concentrations higher than $(c - c_0)_\eta^*$. In this concentration region, the molecular weight of a blob, $M_\xi = M_1 m_\xi$ ranges over $(54-234) \times 10^4$ for TTAB in 3.0 and 4.0 M NaBr and CTAC in 4.0 M NaCl, of which smaller molecular weights correspond to a less flexible chain.^{1,2,4}

Candau et al.²⁵ observed a high viscosity value for 0.1 M KBr solutions of CTAB and compared it with the theoretical prediction for solutions of entangled polymer chains in semidilute region. Their result yielded a fairly high slope close to 8 on a double logarithmic plot of relative viscosity against the volume fraction of micellar surfactant.

Registry No. TTAB, 1119-97-7; CTAC, 112-02-7; CTAB, 57-09-0; NaCl, 7647-14-5; NaBr, 7647-15-6.

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Dynamic Investigation of a Concentrated Middle-Phase Microemulsion from Quasi-Elastic Light Scattering

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Dynamic light scattering is used to determine the diffusion coefficients of the light scatterers within a concentrated middle-phase microemulsion. These coefficients are derived from two models: the Kaler-Prager bicontinuous model and a model for interactive Brownian interface units derived from the Pusey-Fijnaut-Vrij model for concentrated liquid suspensions of polydisperse spheres. The diffusion coefficient of the Kaler-Prager bicontinuous model is determined; its value is the same as the apparent diffusion coefficient given by the cumulant analysis. This latter analysis diverges and clearly fails to fit the experimental data, while the former goes in poor agreement beyond two decades of the time scale. Experimental results are better fitted by the model for interactive Brownian interface units which gives the diffusion coefficients of the two diffusion modes that appear in the concentrated middle-phase microemulsion. The first diffusion coefficient, related to the collective diffusion mode of the interface units, is found 3 times higher than the second which is related to their self-diffusion mode.

Introduction

For some years, the structure of *concentrated* microemulsions has been the subject of numerous theoretical works and experimental works with techniques as different as small-angle neutron scattering,¹⁻⁵ small-angle X-ray scattering,⁶ light scattering,⁷⁻¹⁴

Hertzian spectroscopy,¹⁵ conductivimetry,¹⁶ It was found that this structure is either that of a dispersion of water (or oil) droplets

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