

Viscoelastic behavior of aqueous surfactant micellar solutions

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Abstract

A cationic surfactant, cetyltrimethylammonium *p*-toluenesulfonate (CTApTS), forms long threadlike micelles in aqueous solution. The threadlike micelles make concentrated entanglement networks, so that the solution shows pronounced viscoelastic behavior as concentrated polymer systems do. However, a mechanism for a process responsible for the longest relaxation time of the threadlike micellar system is different from that of semi-dilute to concentrated polymer systems. The threadlike micellar system exhibits unique viscoelasticity described by a Maxwell model. The longest relaxation time of the threadlike micellar system is not a function of the concentration of CTApTS, but changes with that of *p*-toluenesulfonate (*p*TS⁻) ions in the bulk aqueous phase supplied by adding sodium *p*-toluenesulfonate (NapTS). The rates of molecular motions in the threadlike micelles are not influenced by the concentration of *p*TS⁻ anions, therefore, molecular motions in the threadlike micelles (*micro-dynamics*) are independent of the longest relaxation mechanism (*macro-dynamics*). A nonionic surfactant, oleyldimethylamineoxide (ODAO), forms long threadlike micelles in aqueous solution without any additives. The aqueous threadlike micellar system of ODAO also shows Maxwell type viscoelastic behavior. However, the relaxation mechanism for the longest relaxation process in the system should be different from that in the threadlike micellar systems of CTApTS, since the system of ODAO does not contain additive anions. Because increase in the average degree of protonation of head groups of ODAO molecules in micelles due to adding hydrogen bromide causes the relaxation time remarkably longer, changes in *micro-structure* and *micro-dynamics* in the threadlike micelle are closely related to *macro-dynamics* in contrast with the threadlike micellar system of CTApTS.

Keywords : viscoelasticity, storage modulus, loss modulus, relaxation time relaxation, relaxation strength, surfactant, micelle, wormlike micelle, threadlike micelle, dielectric relaxation, rotational relaxation, fluorescence anisotropy, fluorescence probe molecules, fluidity

1. Introduction

It is well known that some cationic surfactant molecules, such as cetyltrimethylammonium bromide (CTAB), form long wormlike threadlike micelles in aqueous solution with adequate additives like sodium *p*-toluenesulfonate (NapTS) or sodium salicylate (NaSal) by prior works by Imai *et al.* (2000a; 2000b; 2001), Shikata *et al.* (1987; 1988); Hoffmann *et al.* (1994). In the threadlike micelles, counterions are completely exchanged from bromide (Br⁻) anions to the additive anions such as a *p*-toluenesulfonate ion (*p*TS⁻) or salicylate ion (Sal⁻). The molar ratio of CTA⁺ relative to additive anions in the formed threadlike micelles is kept at

unity, and excess additive anions remain in the bulk aqueous phase. Since the formed threadlike micelles are usually enormously long, they easily make concentrated entanglement networks. Thus, threadlike micellar solutions show pronounced viscoelastic behavior caused by entanglement formation between formed threadlike micelles as well as semi-dilute to concentrated polymer systems. However, a mechanism for the viscoelastic relaxation process of the threadlike micellar system observed in the longest relaxation time region related to entanglement release between two threadlike micelles is different from that of the polymer system, in which the polymer molecules release entanglements by use of the *reptation* process well discussed theoretically by Doi and Edwards (1986).

Many threadlike micellar systems formed by cationic surfactants exhibit unique viscoelasticity which can be perfectly described well by a Maxwell model with only one set of

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relaxation time (τ_m) and plateau modulus (G_0) as given by equation (1) as first reported by Shikata *et al.* (1987).

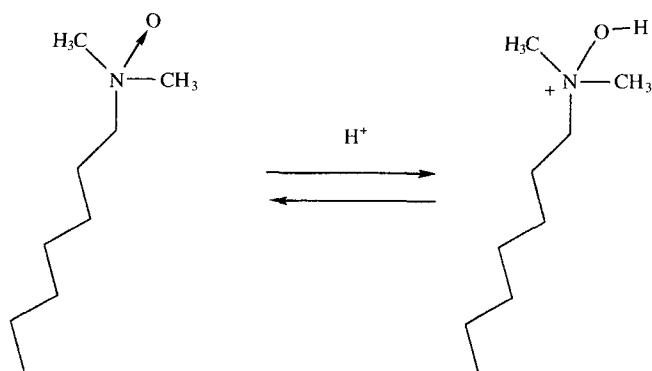
$$G' = \frac{G_0}{1 + \omega^2 \tau_m^2}, \quad G'' = \frac{G_0 \omega \tau_m}{1 + \omega^2 \tau_m^2} \quad (1)$$

It is well known that the relaxation time, τ_m , of the threadlike micellar system of CTAB is not a function of the concentration (c_D) of CTAB, but of excess additive anions (c_S^*), pTS^- or Sal^- , in the bulk aqueous phase.

Cetyltrimethylammonium *p*-toluenesulfonate (CTApTS) is also a cationic surfactant which forms long threadlike micelles in aqueous solution showing strong viscoelastic behavior described by the Maxwell model given by equation (1) without any additives as reported by Soltero *et al.* (1995; 1996) and Shikata *et al.* (2002). Because aqueous CTApTS systems do not contain Br^- , the system is very useful to investigate the contribution of the presence of Br^- to viscoelastic behavior and also to rates of molecular motions in the threadlike micelles.

By the way, nonionic surfactants bearing an amineoxide type head group, such as dodecyl dimethylamineoxide (DDAO), tetradecyldimethylamineoxide (TDAO), and oleyldimethylamineoxide (ODAO), alter their characters as nonionic surfactants into those of cationic surfactants in aqueous solution depending on the average degree of protonation ($\langle\alpha\rangle$) of their head groups ($N \rightarrow O$) controlled by adding simple acids such as hydrogen chloride (HCl) and hydrogen bromide (HBr) as reported by Maeda *et al.* (2001), Kawasaki *et al.* (2002) and Itatani and Shikata (2001). Scheme 1 schematically represents the protonation process of the amineoxide type surfactant caused by the presence of acid, H^+ .

The shape of DDAO micelles in aqueous solution which is a spherical shape at low $\langle\alpha\rangle$ values changes into short rods around $\langle\alpha\rangle=0.5$ at a relatively high concentration of NaCl as reported by Kaimoto *et al.* (1994). The shape of TDAO micelles in aqueous solution at high salt concentrations changes into a long threadlike shape around $\langle\alpha\rangle=0.5$, and the aqueous TDAO micellar solutions show pronounced viscoelasticity around the condition making long threadlike micelles as confirmed by Maeda *et al.* (2001).



Moreover, ODAO forms long threadlike micelles in aqueous solutions even at $\langle\alpha\rangle=0$ without any additives and form concentrated entanglement networks to show pronounced viscoelastic behavior as reported by Hoffmann *et al.* (1992), Hashimono *et al.* (1991), Kawasaki *et al.* (2002) and Shikata and Itatani (2002). It seems that the shape of micelles of amineoxide type surfactants is highly dependent on the length of alkyl tails even at the same $\langle\alpha\rangle$ value. Aqueous ODAO threadlike micellar solutions also show the Maxwell type viscoelastic behavior with one set of τ_m and G_0 as aqueous CTAB threadlike micellar systems do. However, the longest relaxation time which is directly related to entanglement release mechanism is highly dependent on the value of $\langle\alpha\rangle$ in the system and should be completely different from that in the threadlike CTAB micellar systems, since the threadlike micellar system of ODAO does not contain additive anions like pTS^- .

In this article, viscoelastic features in a long time region related to the entanglement release mechanisms, in other words, *macro-dynamics* of these aqueous threadlike micellar systems of cationic and nonionic surfactants, CTApTS and ODAO, are compared with each other. Moreover, rates of molecular motions for surfactants and additives in the micellar interior (*micro-dynamics*), which can be detected by using dielectric relaxation and fluorescence anisotropy relaxation measurements, are compared in both aqueous threadlike micellar systems. Then, the relationship between the *micro-* and *macro-dynamics* is also discussed in these systems.

2. Experimental section

2.1. Materials

Cetyltrimethyl *p*-toluenesulfonate (CTApTS) is a CTA^+ type cationic surfactant of which counterion is pTS^- . CTApTS was purchased from Sigma Chemical Co. (St. Luis) and was purified by re-crystallization from a mixture of chloroform and diethylether. NapTS was purchased from Wako Pure Chemicals Ltd. (Osaka) and was used without further purification. DDAO and ODAO were kindly gifted from Nippon Oil & Fats Co. Ltd. (Tokyo). TDAO was synthesized from tetradecyldimethylamine, which was obtained from Wako Pure Chemicals Ltd., by the oxidation reaction using hydrogen peroxide according to the standard method performed by also Kaimoto *et al.* (1994). DDAO and TDAO were purified by re-crystallization from a mixture of methanol and acetone. ODAO was used without further purification. Highly de-ionized water with the specific resistance higher than 18 M Ω cm obtained by a MilliQ system was used as a solvent for sample solutions.

The concentrations of CTApTS (c_D) were ranged from 30 to 100 mmol kg $^{-1}$ and those of NapTS (c_S) were from 0 to 300 mmol kg $^{-1}$ in aqueous CTApTS and NapTS solutions

(CTApTS:NaP₃TS/W). The concentrations of ODAO (c_D) were ranged from 20 to 200 mmol kg⁻¹ in aqueous solutions (ODAO/W). The values of $\langle\alpha\rangle$ were changed from 0 to 1.0 by adding HBr in aqueous solutions of DDAO, TDAO and ODAO at 100 mmol kg⁻¹; the value of $\langle\alpha\rangle$ in this study was conventionally defined as $[\text{HBr}]/c_D$.

A fluorescence probe molecule, sodium 2-hydroxy-3-naphthoate (NaHN), was purchased from Wako Pure Chemical Ltd. and was used without purification. The concentrations of NaHN in sample solutions were kept on the order of 0.1 mmol kg⁻¹ and were less than 1% of c_D .

2.2. Methods

Dynamic viscoelastic measurements for sample solutions were carried out in a frequency (ω) range from 1×10^{-3} to 1×10^2 rad s⁻¹ using a stress controlled rheometer (ViscoAnalyser DAR-100, Reologica) equipped with cone-plate geometry. Measuring temperature was 25°C for the CTApTS:NaP₃TS/W system, and was changed from 10 to 35°C for the ODAO/W system. Storage and loss moduli (G' and G'') were determined as functions of ω under the condition of the linear viscoelastic response.

Dielectric relaxation measurements were performed using two measuring systems. In a low ω range from 6.28×10^6 to 6.28×10^9 rad s⁻¹, an RF LCR meter (4287A, Agilent Technology) equipped with a hand made electrode cell possessing the vacant electric capacitance of $C_0=0.23 \times 10^{-12}$ F was used. On the other hand, in a high ω range from 3.2×10^7 to 1.26×10^{11} rad s⁻¹, a dielectric measurement system composed of a network analyzer (8720ES, Hewlett Packard) and a co-axial probe (85070B, Hewlett Packard) was employed. Measuring temperature was 25°C for the CTApTS:NaP₃TS/W system, and was changed from 10 to 35°C for the ODAO/W system as in viscoelastic measurements. In the measuring system for the low range dielectric constant and loss, ϵ and ϵ'' , were evaluated in the manner; $\epsilon=CC_0^{-1}$ and $\epsilon''=\sigma(C_0\omega)^{-1}$, where C and σ represent the electric capacitance and conductance of sample solutions, respectively. The other system for the high ω range evaluated the values of ϵ and ϵ'' automatically by using a program developed by Hewlett Packard. Because the medium, water, possesses high ϵ ($\epsilon_w = 78$ in a ω range lower than 6×10^9 rad s⁻¹ at 25°C) and electric conductance due to the contribution of ionic species, the essential dielectric contribution, $\Delta\epsilon'$ and $\Delta\epsilon''$, of solutes were estimated using equations (2) and (3) as proposed by Shikata and Imai (1998) and Itatani and Shikata (2001)

$$\Delta\epsilon' = \epsilon' - \phi\epsilon'_w \quad (2)$$

$$\Delta\epsilon'' = \epsilon'' - \phi\epsilon''_w - \frac{\sigma_{dc}}{C_0\omega} \quad (3)$$

where ϵ'_w , ϵ''_w , ϕ and σ_{dc} represent the dielectric con-

stant and loss for water, the fractional contribution of water to dielectric behavior of the sample solution, and direct current conductance of the sample solution, respectively.

Steady state fluorescence anisotropy (r) for the probe molecule, NaHN, in the sample solution was estimated at 25°C using a fluorescence photometer (F-4500, Hitachi) which was equipped with two polarizing plates in front of excitation and emission windows, respectively. The fluorescence lifetime (τ_{life}) of the probe molecule in the sample solution was determined at 25°C by a single photon correlation method using an NAES 550 (Horiba) equipped with a high pressure hydrogen flash lamp which generated excitation pulses with a half width about 2 ns. The values of τ_{life} were precisely calculated from time courses of fluorescence decays and excitation pulses using deconvolution software supplied by Horiba. The rotational relaxation time (τ_ϕ) of the probe molecule in the sample solutions was evaluated using a Perrin's equation (4)

$$\frac{1}{r} = \frac{1}{r_0} \left(1 + \frac{3\tau_{life}}{\tau_\phi} \right) \quad (4)$$

where r_0 represents the instantaneous fluorescence anisotropy of a probe molecule. In the case of NaHN, the value of r_0 was estimated to be 0.34 by Shikata *et al.* (1997).

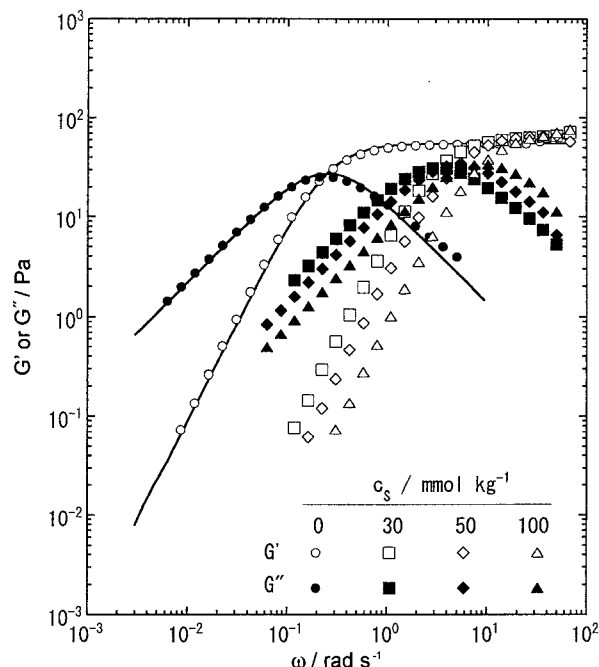


Fig. 1. Frequency, ω dependence of storage and loss moduli, G' and G'' , for the CTApTS:NaP₃TS/W system at $c_D = 100$ mmol kg⁻¹ and 25°C. Solid lines represent the best fitting curves for G' and G'' curves at $c_S = 0$ mmol kg⁻¹ calculated by using the Maxwell model with $G_0 = 55$ Pa and $\tau_m = 4.0$ s.

3. Result and discussion

3.1. Macro-dynamics

Cationic surfactant system

The CTApTS:Na p TS/W system shows pronounced viscoelasticity that can be perfectly described by a Maxwell model as shown in Figure 1. Solid lines in Figure 1 represent the ω dependence of G' and G'' for a Maxwell model well fitted to the data at $c_S=0$ mmol kg $^{-1}$; $G_0=55$ Pa and $\tau_m=4.0$ s. The value of plateau modulus, G_0 , is proportional to the square of CTAB concentration, c_D , irrespective of Na p TS concentration, c_S , as shown in Figure 2. It has been well known that the values of plateau moduli observed in semi-dilute to concentrated polymer solutions are also proportional to the square of the polymer concentration as described in literature, for example, a textbook written by Ferry (1980). Essentially the same relationship between G_0 and c_D has been recognized also in a CTAB:NaSal/W system by Shikata *et al.* (1987). Thus, the origin of viscoelasticity for the threadlike micellar system should be entanglement between long threadlike micelles as well as in semi-dilute to concentrated polymer systems. On the other hand, the longest relaxation times, τ_m , for the system exactly evaluated from the peak frequencies of G'' curves are strongly dependent on c_S as seen in Figure 1.

The concentration of excess (or free) pTS^- ions (c_S^*) in the bulk aqueous phase can be estimated by using the formula of $c_S^*=c_S-c_D$, because the molar ratio of CTA $^+$ rel-

ative to pTS^- in threadlike micelles is close to unity just like in solid salts. The molar ratio between CTA $^+$ and Sal $^-$ in threadlike micelle formed in aqueous solution of CTAB and NaSal is also reported to be unity by Shikata *et al.* (1988), therefore, interaction between CTA $^+$ and pTS^- or Sal $^-$ to form threadlike micelles is stoichiometric.

The value of τ_m for the CTApTS:Na p TS/W system remarkably depends on c_S^* as seen in Figure 3. In the same figure, the relationship between τ_m and c_S^* for the CTAB:Na p TS/W system is also plotted with open symbols. When c_S^* is higher than 0.02 mol kg $^{-1}$, the dependence of τ_m on c_S^* for the CTApTS:Na p TS/W system becomes identical with that for the CTAB:Na p TS/W system irrespective of c_D . This suggests that the slowest relaxation process or *macro-dynamics* of threadlike micelles formed by CTA $^+$ is governed only by the value of c_S^* and is independent of the presence of Na $^+$ and/or Br $^-$ ions at the condition of $c_S^* > 0.02$ mol kg $^{-1}$. A similar trend has been also observed in aqueous CTAB and NaSal solutions (CTAB:NaSal/W) by Shikata *et al.* (1987; 1988), however, the relationship between τ_m and c_S^* for the CTAB:NaSal/W system is considerably different from that of the CTApTS:Na p TS/W system as shown with a solid line in Figure 3. Since the strength of interaction between CTA $^+$ and Sal $^-$ is higher than that between CTA $^+$ and pTS^- , the difference in

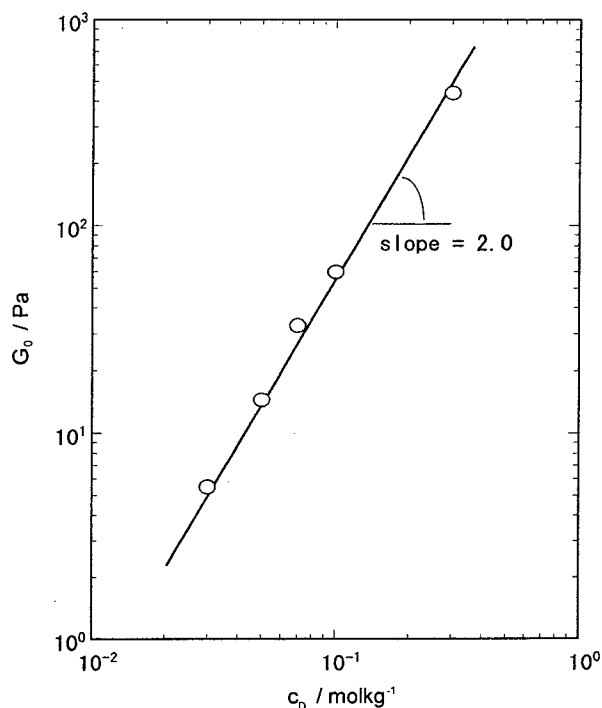


Fig. 2. Relationship between the plateau modulus, G_0 , and c_D for the CTApTS:Na p TS/W system.

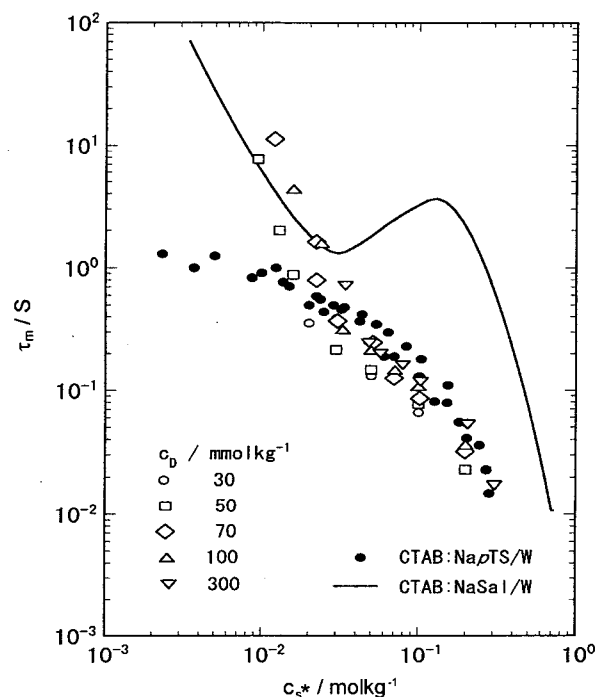


Fig. 3. Dependence of the relaxation time, τ_m , on the concentration of free pTS^- in the bulk aqueous phase, c_S^* , for the CTApTS:Na p TS/W system. The dependence of τ_m on c_S^* in the CTAB:NaSal/W system reported by Shikata *et al.* (1988) is also plotted in the same figure with a solid line as a reference.

strength of the interaction should be an essential reason for the difference in the relationship between τ_m and c_S^* in these systems.

Unique viscoelastic behavior, which has been found in many threadlike micellar systems and is perfectly described by the Maxwell model, has been discussed and interpreted on the basis of proposed models. Cates (1987) proposed a *living polymer* mode for the unique viscoelasticity in threadlike micellar systems, and Turner *et al.* (1992; 1993) modified the *living polymer* model. However, the calculated relaxation time, τ_m , through the *living polymer* model does not correctly express the dependence of τ_m on c_S^* seen in Figure 3.

Shikata *et al.* (1988) also proposed a model called a *phantom crossing* model to explain the dependence of τ_m on c_S^* for the CTAB:NaSal/W system without inconsistency. In the *phantom crossing* model, it is assumed that two threadlike micelles make an entanglement point and the two micelles fuse each other at the entanglement point to form a tentative cross-shaped branching point. After a lifetime of the branching point equal to the viscoelastic relaxation time, τ_m , has passed, individual two threadlike micelles regenerate erasing the entanglement (branching) point since the cross-shaped branching is unstable energetically. This process looks as if two phantoms cross through each other at their collision. Because threadlike micelles are formed by inter-molecular interaction between surfactant molecules not by covalent chemical bonding, it is possible for micelles to make such branching points and to bring about the crossing through reaction at entanglements as depicted schematically in Figure 4. Supposing excessive free additive pTS^- in the bulk aqueous phase operates as a catalyst for the crossing through reaction at entanglement points, the dependence of τ_m on c_S^* for the CTAPTS:NaP₃TS/W system can be understood systematically.

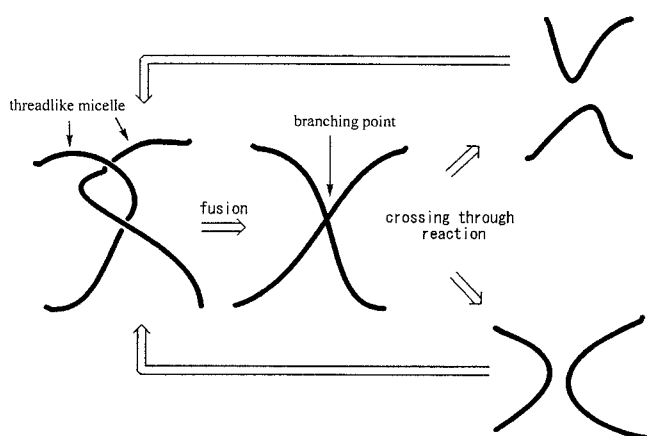


Fig. 4. Schematic representation for a *phantom crossing* model possible in threadlike micellar systems.

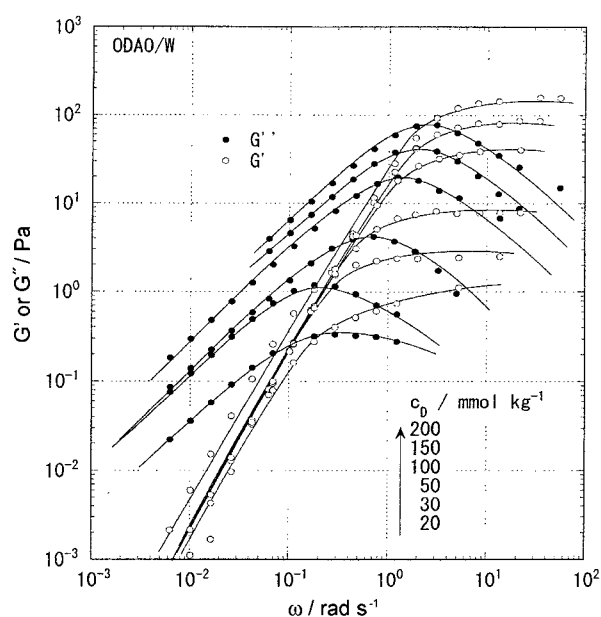


Fig. 5. Dependence of G' and G'' on ω for the ODAO/W system with varying c_D from 20 to 200 mmol kg^{-1} at $\langle\alpha\rangle=0$ and 15°C.

Nonionic surfactant system

The dependence of G' and G'' on ω for aqueous ODAO solutions with various c_D at $\langle\alpha\rangle=0$ (without HBr) is shown in Figure 5. The solutions at c_D lower than 50 mmol kg^{-1} possess relaxation functions of which ω dependence is fairly broad and are not described with a Maxwell model. The relaxation functions for the solutions at c_D higher than 50 mmol kg^{-1} look sharp and are well described by the Maxwell model with only one set of τ_m and G_0 . The values of ω where G'' curves possess maximums, corresponding to the reciprocals of the longest relaxation times, shift towards a high ω side with increasing c_D . The value of $\langle\alpha\rangle$ for the ODAO/W system in Figure 5 were not controlled by adding HBr, however, some amineoxide groups of ODAO molecules are protonated by H^+ generated from water molecules since the value of pH for the solutions were slightly higher than 7.0.

The ω dependence of G' and G'' for the system at $c_D=100 \text{ mmol kg}^{-1}$ with various $\langle\alpha\rangle$ values is shown in Figure 6. A very slight change of the $\langle\alpha\rangle$ value from 0 to 0.1 induces a remarkable increase in τ_m from 0.15 to 40 s, whereas the value of G_0 is independent of $\langle\alpha\rangle$. At the condition of $\langle\alpha\rangle=0.15$, phase separation occurred in the ODAO/W system to segregate precipitation. The value of G_0 for the system is perfectly proportional to the square of c_D at the condition of $c_D > 50 \text{ mmol kg}^{-1}$, as in the aqueous threadlike micellar system of cationic surfactants described above and in concentrated polymer systems.

These viscoelastic features in the ODAO/W system involve that the origin of the elasticity is entanglement

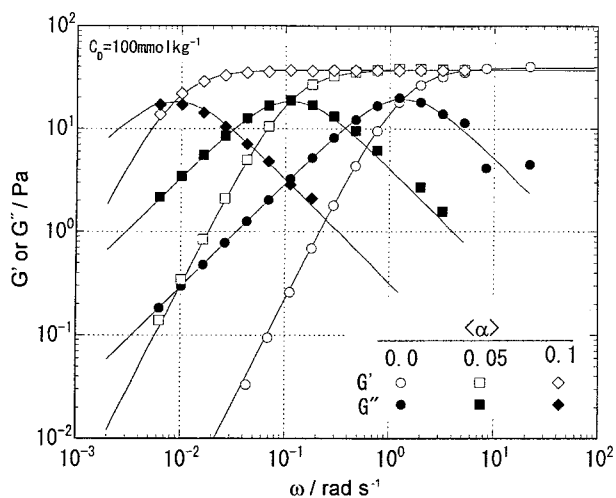


Fig. 6. Dependence of G' and G'' on ω for the ODAO/W system with varying $\langle\alpha\rangle$ at $c_D=100 \text{ mmol kg}^{-1}$ and 15°C .

between threadlike micelles and the τ_m value is controlled only by $\langle\alpha\rangle$.

The fact that the ODAO/W system exhibits the Maxwell type relaxation behavior suggests that the mechanism of entanglement release in the system is also explained by the *phantom crossing* model. However, the ODAO/W system does not contain a large amount of excessive free ions like $p\text{TS}^-$ working as a catalyst for the crossing through reaction of threadlike micelles in the system. Therefore, a factor that controls the crossing through reaction in a different way from that in the CTApTS:NapTS/W system is operating in the ODAO/W system.

Because amineoxide groups of surfactants are stoichiometrically protonated in a low $\langle\alpha\rangle$ region as confirmed by Itatani and Shikata (2001), the value of $\langle\alpha\rangle$ directly corresponds to the composition of protonated ODAO molecules in micelles, which should be related to the *micro-structure* and *micro-dynamics* of micelles.

3.2. Micro-dynamics

Cationic surfactant system

Dielectric spectra, $\Delta\epsilon'$ and $\Delta\epsilon''$, as functions of ω for the CTApTS:NapTS/W system at $c_D=100 \text{ mmol kg}^{-1}$ and several c_S from 30 to 100 mmol kg^{-1} are shown in Figure 7. Solid lines in Figure 7 represent fitting curves assuming all the experimental spectrum is reproducible by the sum of four sets of Debye type relaxation functions as given in equation (5): τ_i and $\Delta\epsilon_i$, $i=1$ to 4.

$$\Delta\epsilon' = \sum_{i=1}^4 \frac{\Delta\epsilon_i}{1 + \omega^2 \tau_i^2} \quad \Delta\epsilon'' = \sum_{i=1}^4 \frac{\Delta\epsilon_i \omega \tau_i}{1 + \omega^2 \tau_i^2} \quad (5)$$

Agreement between experimental data and fitting curves is perfect in all the sample solution examined. Figure 8 shows the c_S dependencies of τ_i and $\Delta\epsilon_i$ used for the fitting curves

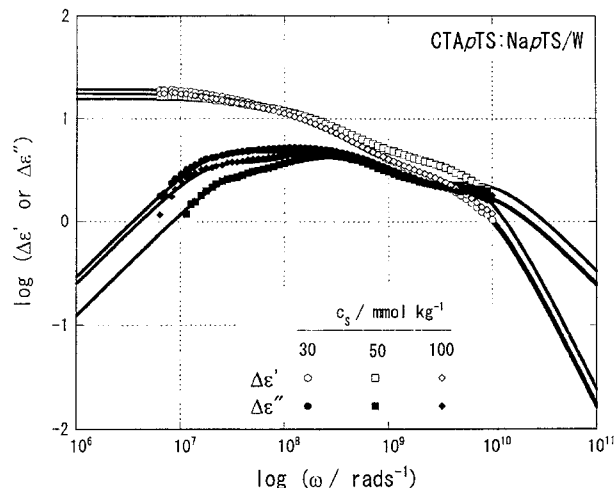


Fig. 7. Dielectric relaxation spectra, $\Delta\epsilon'$ and $\Delta\epsilon''$ vs ω for the CTApTS:NapTS/W system with varying c_S at $c_D=100 \text{ mmol kg}^{-1}$ and 25°C . Solid lines represent the best fitting curves for spectra calculated by equation (5).

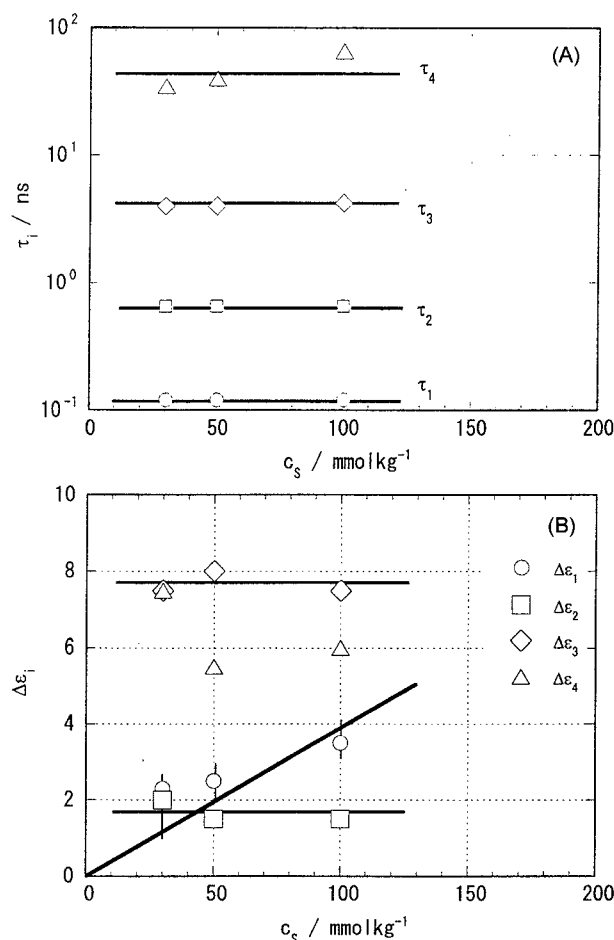


Fig. 8. Dependencies of $\Delta\epsilon_i$ (A) and τ_i (B), $i=1$ to 4, on c_S for the best fitting curves shown in Figure 7.

in Figure 7.

Shikata *et al.* (2002) very recently have reported that aqueous NapTS solutions shows fairly strong dielectric relaxation behavior with a relaxation time of 0.1 ns and strength proportional to the concentration of NapTS. Since Na^+ bearing no dipoles completely dissociates into the bulk aqueous phase, free $p\text{TS}^-$ in the bulk aqueous phase should keep a dipole moment ($\mu_{p\text{TS}^-}$). Free $p\text{TS}^-$ possibly bears some tightly hydrated water molecules. The value of a relaxation time, τ_1 , found in the $\text{CTApTS}:\text{NapTS}/\text{W}$ system is close to the relaxation time in the aqueous NapTS solutions. Furthermore, the relaxation strength, $\Delta\epsilon_1$, for τ_1 mode in the $\text{CTApTS}:\text{NapTS}/\text{W}$ system is not different so much from that for the relaxation mode found in the aqueous NapTS solutions. From these the τ_1 mode in the system corresponds to the rotational relaxation of free $p\text{TS}^-$ in the bulk aqueous phase.

On the other hand, the relaxation mode of τ_3 is assigned to the rotational relaxation mode for ion pairs formed between ammonium head groups of CTA^+ and $p\text{TS}^-$ in threadlike micelles bearing a dipole moment (μ_{IP}) through discussion on the values of τ_3 and $\Delta\epsilon_3$. A spherical micellar system for an aqueous CTAB solution at the concentration of 100 mmol kg^{-1} shows pronounced dielectric relaxation behavior with only one set of a relaxation time and strength (*ca.* 0.8 ns and 19, respectively) due to the rotational relaxation mode for ion pairs formed between CTA^+ and Br^- as reported by Shikata *et al.* (1998). Because rotational motion of ion pairs in threadlike micelles is slightly slower than that in spherical micelles as shown by Shikata *et al.* (1999), the obtained value of τ_3 , *ca.* 4ns, is reasonable for the rotational relaxation mode of ion pairs formed between CTA^+ and $p\text{TS}^-$. The reason why the magnitude of $\Delta\epsilon_3$ is about a half value of that for the aqueous CTAB spherical micellar system is probably difference in separations between ions forming ion pairs and that in the shapes of micelles in each system.

Since the molecular motion of $p\text{TS}^-$ forming the ion pair with CTA^+ in threadlike micelles should be highly restricted, its (rotational) relaxation time should be ranged between the values of τ_1 and τ_3 , moreover, its relaxation strength should be less than the value of free $p\text{TS}^-$, $\Delta\epsilon_1$, at the condition of $c_s^*=c_D=100 \text{ mmol kg}^{-1}$, in which the concentration of free $p\text{TS}^-$ in the bulk aqueous phase is identical with that of $p\text{TS}^-$ forming ion pairs in threadlike micelles. Consequently, the relaxation mode of τ_2 is assigned to the rotational relaxation mode, *wobbling motion*, of $p\text{TS}^-$ in threadlike micelles.

Because threadlike micelles formed in the $\text{CTApTS}:\text{NapTS}/\text{W}$ system are electrically neutral, they keep no counterion clouds which are usually borne around ionic micellar particles such as those formed in aqueous CTAB solutions as reported by Shikata *et al.* (1998). Thus, one does not have to take account of the contribution of the

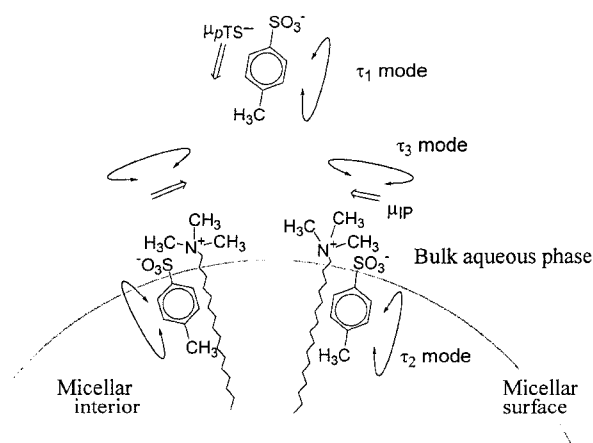


Fig. 9. Schematic representation for the τ_1 , τ_2 and τ_3 mode possibly taking place in threadlike micelles formed in the $\text{CTApTS}:\text{NapTS}/\text{W}$ system. $\mu_{p\text{TS}^-}$ and μ_{IP} represent dipole moments of $p\text{TS}^-$ and the ion pair formed between CTA^+ and $p\text{TS}^-$, respectively.

counterion clouds to the dielectric behavior. Then, the assignment for the slowest mode of τ_4 is not clear at present. It is likely that the τ_4 mode is related to relaxation processes in which the exchange of $p\text{TS}^-$ between two ion pairs in threadlike micelles. Figure 9 depicts schematically the relaxation modes of τ_1 , τ_2 , and τ_3 in threadlike micelles formed in the $\text{CTApTS}:\text{NapTS}/\text{W}$ system.

From Figure 8, it is obvious that relaxation times and strengths ($i=2$ and 3) for molecular motion, *micro-dynamics*, in the micellar interior are independent of the value of c_s (or c_s^*), whereas the longest relaxation time, τ_m , is considerably dependent on c_s^* as seen in Figure 3. Consequently, The rates of molecular motion observed in aqueous cationic micellar systems are not influenced by the value of c_s^* , therefore, the *micro-dynamics* in the micelles is independent of the *macro-dynamics*.

Nonionic surfactant system

Dielectric spectra, $\Delta\epsilon'$ and $\Delta\epsilon''$, as functions of ω for the ODAO/W system with several $\langle\alpha\rangle$ from 0 to 0.1 at 15°C are shown in Figure 10. The dielectric spectra are also reproducible with the sum of four Debye type relaxation functions as given by equation (5). The most significant change in the spectra should be an increase in relaxation strength of τ_3 mode found around $\omega=2\times 10^8 \text{ rad s}^{-1}$ with increasing $\langle\alpha\rangle$. Because the range of $\langle\alpha\rangle$ changed is not so wide, changes in the spectra in Figure 10 except for the τ_3 mode are negligibly small. In the cases of aqueous DDAO and TDAO solutions, increases in relaxation strength in dielectric spectra around $\omega=2\times 10^8 \text{ rad s}^{-1}$, *i.e.* τ_3 mode, with increasing $\langle\alpha\rangle$ are also observed in a low $\langle\alpha\rangle$ region as reported by Itatani and Shikata (2001). Thus, the increase in relaxation strength should be a general trend in all the aqueous solutions of amineoxide type surfactants

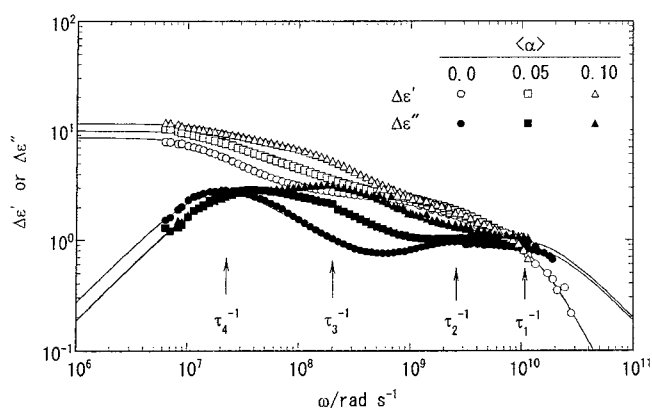


Fig. 10. Dielectric relaxation spectra, $\Delta\epsilon'$ and $\Delta\epsilon''$ vs ω for the ODAO/W system with varying $\langle\alpha\rangle$ values from 0 to 0.1 at $c_D=100 \text{ mmol kg}^{-1}$ and 15°C . Solid lines show the best fitting curves for spectra calculated by equation (5).

such as ODAO, DDAO and TDAO.

According to the previous study by Itatani and Shikata (2001), the τ_1 , τ_2 and τ_3 modes for amineoxide type surfactants in aqueous solution have been assigned as follows. The τ_1 mode corresponds to the rotational relaxation mode of unprotonated amineoxide head groups. The unprotonated head groups at $\langle\alpha\rangle=0$ possess coordination chemical bonding from a nitrogen atom to an oxygen atom bearing a dipole moment (μ_{NO}) which are detectable by dielectric relaxation measurements around $\omega=1\times 10^{10} \text{ rad s}^{-1}$ irrespective of the shape of micelles. The τ_2 mode around $\omega=5\times 10^{10} \text{ rad s}^{-1}$ is assigned to the rotational relaxation process for ion pairs bearing a dipole moment (μ_{IP}) formed between a protonated head group, *i.e.* $\text{N}^+\text{-OH}$, and Br^- supplied by adding HBr. Therefore, with increasing the value of $\langle\alpha\rangle$, the magnitude of $\Delta\epsilon_2$ increases, whereas that of $\Delta\epsilon_1$ decreases. However, changes in values of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are negligibly small since the range of $\langle\alpha\rangle$ change is small as seen in Figure 10. Hydrogen atoms belonging to *protonated* head groups are able to form hydrogen bonding to oxygen atoms of *unprotonated* or *protonated* head groups of surfactant molecules in micellar interior as proposed by Kaimoto *et al.* (1994). The formation of hydrogen bonding between two or three surfactants produces intermolecular associations, *dimers and trimers*, bearing rotational relaxation times much longer than those of individual surfactants in micelles. Consequently, the τ_3 mode is attributed to the rotational relaxation mode for the intermolecular associations with larger sizes due to the hydrogen bond formation.

Because the pH value of the ODAO/W system is slightly higher than 7.0 at $\langle\alpha\rangle=0$, a small part of amineoxide head groups are protonated to generate positive charges on the micellar surface even at the condition by H^+ dissociated from water molecules. Consequently, the surface of thread-

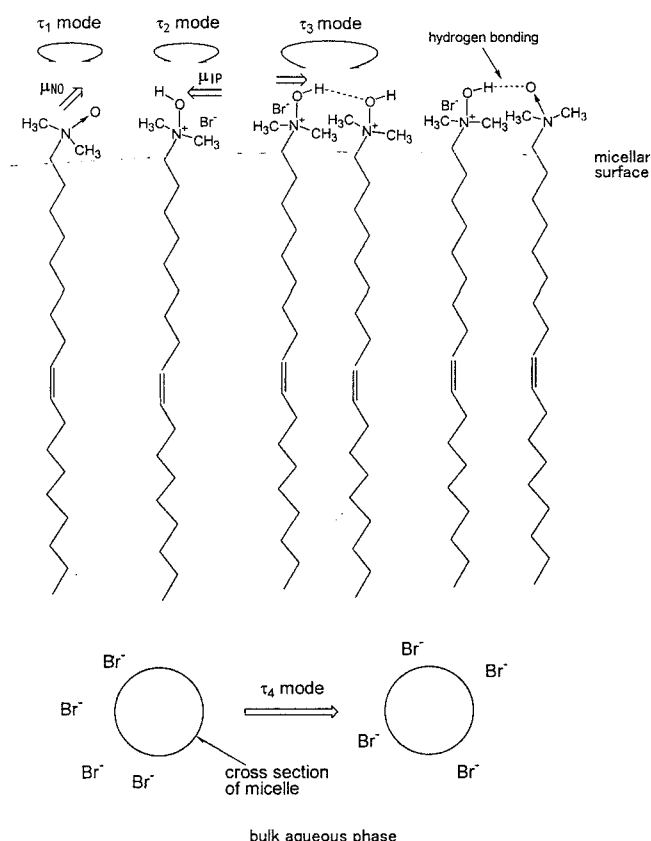


Fig. 11. Schematic representation for the τ_1 , τ_2 , τ_3 and τ_4 mode possibly taking place in threadlike micelles formed in the ODAO/W system. μ_{NO} and μ_{IP} represent dipole moments of the *unprotonated* head group and the ion pair formed between the *protonated* head groups and Br^- , respectively.

like micelles in the ODAO/W system is positively charged slightly irrespective of the $\langle\alpha\rangle$ value. Since electrically charged particles might bear counterion clouds in aqueous media, they usually show dielectric relaxation processes caused by the relaxation of counterion distribution around them as well discussed in aqueous polyelectrolyte solutions by Oosawa (1971). Thus, the τ_4 mode found in the ODAO/W system is assigned to the relaxation of counterion distribution around threadlike micelles in direction perpendicular to a long micellar axes as discussed by Itatani and Shikata (2001). Figure 11 schematically represents each relaxation mode in the threadlike micelle formed in the ODAO/W system.

Figure 12 shows the rotational relaxation time (τ_θ) of the fluorescence probe, NaHN, in micelles formed by amineoxide type surfactants, such as DDAO, TDAO and ODAO, obtained at 25°C in aqueous solution at 100 mmol kg^{-1} as functions of $\langle\alpha\rangle$. The ODAO/W system forms threadlike micelles in all the condition examined. The DDAO/W system contains only spherical micelles, and the shape of

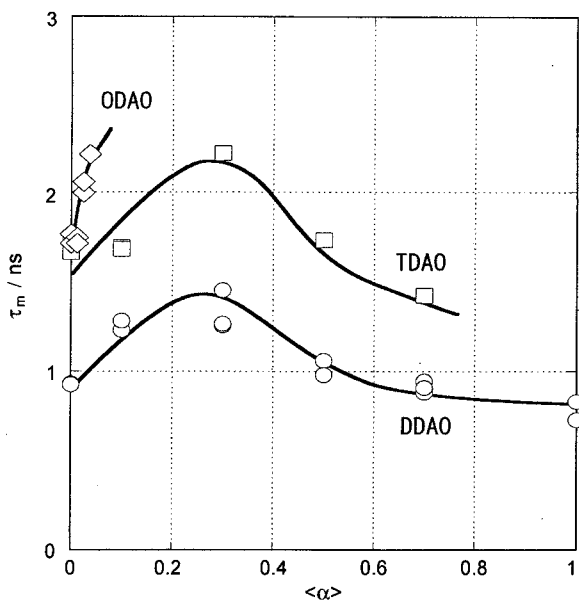


Fig. 12. Relationship between rotational the relaxation time, τ_ϕ , and the value of $\langle\alpha\rangle$ of a fluorescence probe molecule, NH, entrapped in micelles possessing various type of micellar shapes: spherical micelles in the DDAO/W system, spherical to short rodlike micelles in the TDAO/W system and threadlike micelles in the ODAO/W system.

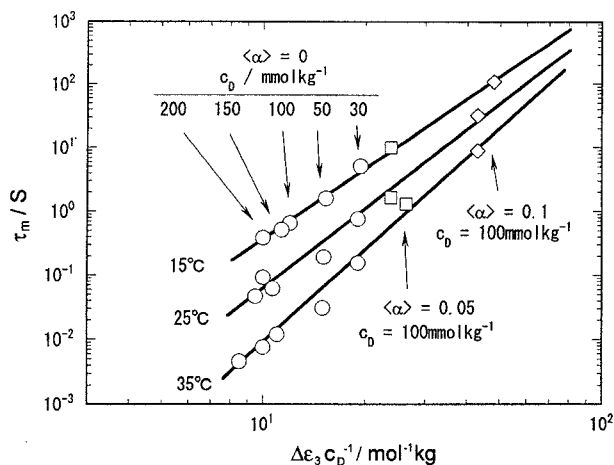


Fig. 13. Relationship between τ_m and the value of $\Delta\epsilon_3 c_D^{-1}$ for the ODAO/W system at varying temperatures.

micelles in the TDAO/W system changes from a spherical shape to a short rodlike shape with increasing $\langle\alpha\rangle$ as discussed by Kaimoto *et al.* (1994) and Maeda *et al.* (2001) in aqueous solution at low salt concentrations. Because the value of τ_ϕ is much shorter than the value of the rotational relaxation times for micelles in each system, it is more sensitive to fluidity in the micellar interior than differences in sizes and shapes of micelles. A change of the τ_ϕ value reflects a change in the fluidity in micelles, in other words,

micro-dynamics of micelles. A considerable increase in the value of τ_ϕ around $\langle\alpha\rangle=0.3$ found in every micellar system suggests that molecular motions in amineoxide type surfactant micelles is slowed down with increasing $\langle\alpha\rangle$ by the formation of inter-molecular associations due to hydrogen bonding initiated by *protonated* amineoxide head groups.

Because increase in the value of $\langle\alpha\rangle$ makes the mechanical relaxation time, τ_m , remarkably longer as described above, changes in the *micro-dynamics* of the micelle are closely related to the *macro-dynamics*, in contrast with the aqueous threadlike micellar system of cationic surfactants like CTAB or CTApTS. When we plot the relationship between the value of τ_m as a *macro-dynamic* parameter and the magnitude of $\Delta\epsilon_3$ as a *micro-dynamic* parameter at varying $\langle\alpha\rangle$ values and temperatures for the ODAO/W system in Figure 13, an empirical equation (6) is obtained.

$$\tau_m \propto \left(\frac{\Delta\epsilon_3}{c_D}\right)^{3.5-5} \quad (6)$$

The value of an exponent in equation (6) is slightly dependent on temperature. Probably, $\Delta\epsilon_3 c_D^{-1}$ is related to the number density of inter-molecular associations, *dimers* or *trimers*, of ODAO in threadlike micelles. It seems that the presence of such inter-molecular associations in threadlike micelles hinders the phantom crossing reaction, then, increase in the number density of inter-molecular associations lengthens the value of τ_m . It is interesting to note that the flexibility of threadlike micelles in the ODAO/W system is independent of the value of $\langle\alpha\rangle$ since the value of plateau modulus, G_0 , which reflects the density of entanglement points, is kept at a constant value irrespective of the $\langle\alpha\rangle$ value as shown in Figure 6.

4. Conclusions

Macro-dynamics measured by dynamic viscoelastic tests and *micro-dynamics* detected by dielectric relaxation and fluorescence anisotropy relaxation measurements were discussed for two aqueous surfactant systems forming threadlike micelles long enough to make entanglement networks as in semi-dilute to concentrated polymer systems. The first system was consisting of a cationic surfactant, CTApTS, and an additive, NapTS. The other system contained a nonionic surfactant, ODAO, and the average degree of protonation, $\langle\alpha\rangle$, was controlled by adding HBr.

The *micro-dynamics* (in the time scale on the order of 10^{-8} to 10^{-10} s) of threadlike micelles formed by CTApTS in aqueous solutions is essentially independent of the *macro-dynamics* (in the time scale longer than 10^{-2} s). On the other hand, the *micro-dynamics* of the threadlike micelle formed by ODAO in aqueous solution are closely related to the *macro-dynamics*, in contrast with the threadlike micellar systems formed by cationic surfactants.

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