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# Viscosity boosting effect of added ionic surfactant in nonionic wormlike micellar aqueous solutions

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#### ABSTRACT

We have investigated the viscosity boosting effect of ionic surfactant on nonionic wormlike micellar solutions formed in the water/sucrose oleate ( $C_{18:1}SE$ ) system. The zero-shear viscosity increases one order of magnitude from that of a binary water/ $C_{18:1}SE$  system by substituting the nonionic surfactant with ionic surfactant. The viscosity boosting effect depends on hydrophobic chain length and the ionic species of ionic surfactant. On increasing ionic surfactant composition, relaxation time increases; however, the plateau modulus is approximately constant. Zero-shear viscosity is a product of the relaxation time and the plateau modulus; hence we consider that the increase in the relaxation time is responsible for the viscosity boosting. Ionic surfactant added to nonionic wormlike micelles gives an electric double layer and it causes an electrostatic excluded volume effect. Therefore the diffusion constant of wormlike micelles, which can relax by reptation, may decrease due to the growth of the electric double layer and thus the relaxation time increases. However, excess addition of ionic surfactant causes reduction of viscosity. This may be attributed to the geometry change of wormlike micelles to spherical micelles due to the large repulsion between the hydrophilic groups of ionic surfactant.

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#### 1. Introduction

Surfactant molecules in water and other solvents can form various self-assembled structures such as micelles and liquid crystals due to their hydrophobic interaction. The micellar shapes may vary from spherical to wormlike, depending on composition, temperature, and other factors. When micelles grow and become wormlike, the aggregates are much like polymers, and as polymers they are semiflexible and may entangle each other [1]. The aqueous solutions then become highly viscoelastic. The formation of wormlike micelles has been reported in many systems. The addition of simple salts such as sodium chloride (NaCl) or potassium bromide (KBr) to ionic surfactants such as cetvltrimethylammonium bromide (CTAB) or sodium dodecyl sulfate (SDS) [2-6] results in the screening of the electrostatic interactions between the charged head groups, and thus in the one-dimensional growth of the aggregates. Strongly binding counterions such as sodium salicylate [5,7-10], sodium *p*-toluensulfonate [11,12], which contain an aromatic phenyl group, also promote the formation of long wormlike micelles when they are added in CTAB or cetylpyridinium chloride solutions. As examples of other systems, which are in salt-free conditions, the cationic-anionic surfactant systems [13-15] form wormlike micelles arising from the charge neutralization at the micellar surface. Recently, wormlike micelle formation was also reported in the systems with hydrophilic ionic + lipophilic nonionic surfactant [16–25], and hydrophilic nonionic + lipophilic nonionic surfactant [22,26–33]. Although hydrophilic surfactants are prone to form spherical or rod-like micelle in aqueous solutions due to strong repulsion between their head groups, lipophilic cosurfactants decrease the repulsion when they are incorporated in the layer; hence, the growth of wormlike micelle is induced.

The rheological property of the wormlike micellar solutions has been investigated in terms of the surfactant species, concentration, temperature, etc.; however, the effect of surface charge on rheology of micelles has not been reported in detail. Uchiyama et al. [34] have reported that in the mixed surfactant systems SDSpoly(oxyethylene) alkylethers, the viscosity of the solution arises with increase in the mole fraction of SDS. However, the maximum values of viscosity in these systems are not high, suggesting the presence of spherical or rod-like micelles. Similar results were reported in other publications [35-37]. Nishida et al. [38,39] reported that polyelectrolyte solutions exhibit a drastic increase in viscosity due to the contribution of the intermolecular electrostatic interaction arising from surface charge. Therefore, we expect an increase in viscosity in nonionic wormlike micellar solutions on increase of the surface charge. There are many works about formation of nonionic wormlike micelles by adding lipophilic surfactant such as poly(oxyethylene) alkylether, etc., to sugar surfactant [26–28] or poly(oxyethylene) cholesteryl ether [22,29,32,33]

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or polysorbate 80 [30] aqueous solutions. According to Yamamoto et al. [40], the addition of the ionic surfactant SDS to the wormlike micelle solutions with sucrose hexadecanoate/poly(oxyethylene) alkylether causes a drastic increase in the viscosity. Hence, it is suggested that the addition of ionic surfactant in nonionic wormlike micellar solutions has a viscosity boosting effect. However, the aforementioned systems are complicated systems, so we have employed simpler systems to elucidate whether the viscosity boosting effect is truly caused by the addition of ionic surfactants to nonionic wormlike micelles.

In this paper, we report the viscosity boosting effect of adding ionic surfactant to sucrose oleate (C18:1SE) wormlike micellar aqueous solution. C<sub>18:1</sub>SE has an ability to form wormlike micelles by itself in aqueous solution. For reference, the viscosity of sucrose alkanoate 10% aqueous solutions is shown in Table 1, showing that increasing the carbon chain length the viscosity of the solutions increases. C<sub>18:1</sub>SE aqueous solution show about 100 Pa s, which is a rather high value, and therefore, it is suitable to use C<sub>18-1</sub>SE wormlike micellar solutions to verify the viscosity boosting effect of ionic surfactants. We employed different ionic surfactants such as SDS, CTAB, CTAC, DTAB, and DDAB. It has been known that the viscosity of wormlike micellar solutions is boosted by employing longer hydrophobic chains [16,19,23,32], appropriate cosurfactant head group size [17,18,26,29], etc. Our attempt in this paper is a novel approach in which surface charge is given to nonionic wormlike micelles. By this approach we expect to increase the effective volume of micelles, followed by the viscosity boosting.

#### 2. Experimental

#### 2.1. Materials

Sucrose oleate ( $C_{18:1}$ SE, monoester content > 70%) was obtained as a gift from Mitsubishi-Kagaku Foods Co., Tokyo. Sodium dodecyl sulfate (SDS, purity > 99%) was obtained from Sigma–Aldrich. Dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), and didodecyldimethylammonium bromide (DDAB) were obtained from Tokyo Chemical Industry Co., Ltd.

#### 2.2. Rheological measurement

The samples were homogenized and left in a water bath at least 48 h to ensure equilibration before performing measurements. Rheological measurements were performed in a stress-controlled rheometer, AR-G2 (TA Instruments Co.), at 25 °C using cone-plate (two sizes: 40 and 60 mm diameters, each having a cone angle of 1°) geometry depending on the viscosity of the sample.

#### 3. Results and discussion

3.1. Dynamic rheological properties of water/C<sub>18:1</sub>SE/ionic surfactant systems

We have prepared several samples at various molar fractions of ionic surfactant within total surfactant, [ionic surfactant/

Table 1	
The zero-shear viscosity of sucrose alkanoate 10% aqueous solutions (25 $^{\circ}\text{C}$ ).	

Sucrose alkanoate	Zero-shear viscosity [Pa s]	
Sucrose dodecanoate	0.002 [26]	
Sucrose tetradecanoate	0.01	
Sucrose hexadecanoate	0.4	
Sucrose oleate	100	

 $(C_{18:1}SE + ionic surfactant)] (=X_1)$ , in the water/ $C_{18:1}SE$ /ionic surfactant systems. SDS, DTAB, CTAB, CTAC, and DDAB were employed as ionic surfactants. The weight fraction of total surfactant was fixed to 0.1. As we described in the Introduction, the binary water/ $C_{18:1}SE$  system gives a highly viscous micellar solution. When we substitute  $C_{18:1}SE$  with ionic surfactants except for DDAB, viscosity boosting effects can apparently be observed, so we have performed a more detailed rheological study.

Fig. 1 shows the result of oscillatory measurement of highly viscous samples. (a) SDS system  $X_1 = 0, 0.041, 0.12$ , (b) DTAB system  $X_1 = 0.039, 0.076, 0.11$ , (c) CTAB system  $X_1 = 0.033, 0.13, 0.23$ , (d) CTAC system  $X_1 = 0.037, 0.11, 0.17$  are given.

In Fig. 1, all the systems show that the storage modulus G' is smaller than the loss modulus G'' at low frequency, and the system behaves as a liquid. With increasing frequency, G' exceeds G'', suggesting solid-like behavior. The viscoelastic behavior of the entangled wormlike micelles in low shear frequency range often follows the Maxwell model of viscoelastic fluids with a single relaxation time  $\tau_{\rm R}$ , described by the equations [41,42].

$$G' = \frac{\omega^2 \tau_{\rm R}^2}{1 + \omega^2 \tau_{\rm R}^2} G_0,\tag{1}$$

$$G'' = \frac{\omega \tau_{\rm R}}{1 + \omega^2 \tau_{\rm R}^2} G_0, \tag{2}$$

where  $G_0$  is the plateau modulus that is a measure of the degree of entanglement at a given temperature, and is given by G' at high  $\omega$ . The relaxation time,  $\tau_R$ , can be estimated as  $(\omega_R)^{-1}$  where  $\omega_R$  is the frequency at which two moduli are equal. The  $\tau_R$  apparently increases and then decreases for all the systems with increasing  $X_1$ . In other words,  $\tau_R$  gives a maximum at a certain  $X_1$ .

#### 3.2. Zero-shear viscosity of water/ $C_{18:1}$ SE/ionic surfactant systems

The complex viscosity  $|\eta^*|$  is related to the storage and loss modulus by the relation:

$$\eta^*| = \frac{\left(G^{\prime 2} + G^{\prime 2}\right)^{1/2}}{\omega}.$$
(3)

This quantity  $|\eta^*|$  is related to the zero-shear viscosity  $(\eta_0)$  by the relation:

$$|\eta^*| = \frac{\eta_0}{\left(1 + \omega^2 \tau_{\rm R}^2\right)^{1/2}}.$$
(4)

From Eqs. (3) and (4)  $\eta_0$  can be obtained by using the relation

$$\eta_0 = G_0 \tau_{\rm R}.\tag{5}$$

Fig. 2 shows the zero-shear viscosity ( $\eta_0$ ) plots against the molar fractions of ionic surfactant ( $X_1$ ) in total surfactants.

It is clearly seen that in the system with SDS, with increase in  $X_1$ the viscosity increases one order of magnitude at a maximum value of  $\eta_0$  ( $\eta_0^{\text{max}}$  = 1500 Pa s), and then decreases. Such a viscosity boosting effect by ionic surfactant addition in nonionic wormlike micelles is reported elsewhere [40]. A similar behavior of  $\eta_0$  is observed in other systems except for the DDAB system. But cationic surfactant systems except for the DDAB systems show a plateau region at the early stage of ionic surfactant addition.  $\eta_0^{\text{max}}$  in the CTAB and CTAC systems are higher than in the other systems, giving 3000 and 2700 Pa s, respectively. The mechanism of these dramatic changes of  $\eta_0$  by adding ionic surfactant is explained in Section 3.3. The effects of hydrophobic chain length and number, counterion, and head group type on the viscosity behavior are individually explained in Section 3.4. The decrease in the  $\eta_0$  at higher  $X_1$  can be understood rather easily in terms of critical packing parameter or end-cap energy. The increased repulsion between head groups



**Fig. 1.** Variation of *G'* (open plots), *G''* (closed plots) as a function of  $\omega$  at various molar fractions of ionic surfactant. The solid lines are the best fit to Eqs. (1) and (2). (a) SDS system  $X_1 = 0$  ( $\Delta$ ,  $\blacktriangle$ ), 0.041 ( $\bigcirc$ ,  $\oplus$ ), 0.12 ( $\square$ ,  $\blacksquare$ ); (b) DTAB system  $X_1 = 0.039$  ( $\triangle$ ,  $\bigstar$ ), 0.076 ( $\bigcirc$ , $\oplus$ ), 0.11 ( $\square$ ,  $\blacksquare$ ); (c) CTAB system  $X_1 = 0.033$  ( $\triangle$ ,  $\bigstar$ ), 0.13 ( $\bigcirc$ ,  $\oplus$ ), 0.23 ( $\square$ ,  $\blacksquare$ ); (d) CTAC system  $X_1 = 0.037$  ( $\triangle$ ,  $\bigstar$ ), 0.11 ( $\bigcirc$ ,  $\oplus$ ), 0.11 ( $\bigcirc$ ,  $\blacksquare$ ).



**Fig. 2.** Variation of the zero-shear viscosity  $\eta_0$  with the molar fraction of ionic surfactants ( $X_1$ ).

causes the geometry change of wormlike micelles to rodlike or spherical micelles with large curvatures. This curvature change is explained in terms of CPP (critical packing parameter [43]). The CPP is defined as

$$CPP = \nu / (l_{\max} \cdot a). \tag{6}$$

where *v* is the volume of the hydrophobic chain,  $l_{\text{max}}$  is the length of the hydrophobic chain, and *a* is the area per molecule at the hydrophile–lipophile interface. For CPP = 1/3, the aggregates are spherical and for 1/3 < CPP < 1/2, the aggregates are rodlike or wormlike structures. The CPP of C<sub>18:1</sub>SE is assumed at about  $\frac{1}{2}$ , resulting in the formation of wormlike micelles in aqueous solution. However,

CPP of SDS [44], which is ionic surfactant, is about 1/3 due to large repulsion between the head groups. Therefore addition of ionic surfactant varies the average CPP from 1/2 to 1/3 and the wormlike micelles become rodlike or spherical micelles, and hence the viscosity decreases. From the viewpoint of the end-cap energy, the increased electrostatic repulsion between the head groups favors the formation of end caps by decreasing the scission energy required to form two new ends. This change leads to increase of the translation entropy. Accordingly we can explain the reduction of viscosity after  $\eta_0^{max}$ . However the viscosity boosting at  $X_1$  before reaching  $\eta_0^{max}$  cannot been explained in terms of CPP and translational entropy.

#### 3.3. Origin of viscosity boosting effect

The values of  $G_0$  and  $\tau_R$  for the viscoelastic systems may be estimated from the Maxwell fit to the experimental data in Fig. 1. Fig. 3a and b show the variation of the  $\tau_R$  and  $G_0$  values with the molar fraction of each added ionic surfactant.

In the range of viscosity boosting in Fig. 2, the relaxation time also increases while the plateau modulus decreases. From Eq. (5), the zero-shear viscosity is a product of relaxation time and plateau modulus; hence we can consider that the increase in relaxation time is responsible for the viscosity boosting. Since *G'* and *G''* follow the Maxwell model, these systems have a single relaxation time. Cates and Candau [42] have described in detail a model for the relaxation mechanism in wormlike micellar solutions, reversible scission reaction and reptation. The reversible scission is described by the time for breakage of a micellar chain  $\tau_{\rm br}$ , which is



**Fig. 3.** (a) Variation of the relaxation time  $\tau_R$  with the molar fraction of ionic surfactants ( $X_1$ ); (b) variation of the plateau modulus  $G_0$  with the molar fraction of ionic surfactants ( $X_1$ ).

inversely proportional to the length of the chain. Thus, for a chain with length equal to the average length  $\bar{L}$ , the breakage time is

$$\tau_{\rm br} = 1/kL,\tag{7}$$

where k is a constant depending on temperature. In the reptation model [45], relaxation of chain conformations occurs by the gradual disengagement of any given chain, by curvilinear diffusion along its own contour, from a tube-like environment. The time for the reptation is described by the equation

$$\tau_{\rm rep} = L^2/D,\tag{8}$$

where D denotes the curvilinear diffusion constant of the chain in its tube. The Cates model predicts that the relaxation time is given by

$$\tau_{\rm R} = (\tau_{\rm br} \cdot \tau_{\rm rep})^{1/2} = (\bar{L}/k \cdot D)^{1/2}.$$
(9)

It is found that if the breaking time is smaller than the reptation time ( $\tau_{\rm br} \ll \tau_{\rm rep}$ ), the system shows a single relaxation. In Fig. 1 the experimental data of *G'* and *G''* can be fitted to Maxwell model in the range of small frequency. This pattern is characteristic of wormlike micelles. On the other hand, in the high frequency the experimental data deviate from Maxwell model, showing an upturn in the *G''* due to the presence of some "faster" relaxation processes, including the Rouse mode of local motion. This pattern is also observed in many wormlike micellar solutions [16,17,19,22,23,27,29,32].

The relaxation time is related to the length and the diffusion constant of wormlike micelles according to Eq. (9). However, the increase in  $\tau_R$  does not seem to be due to the growth of wormlike micelles because addition of ionic surfactant should cause

the geometry change of wormlike micelles to rodlike or spherical micelles as we already explained in Section 3.2, in which the average CPP decreases by the addition of ionic surfactant. Hence we consider that the decrease of *D* and *k* leads to the increase in relaxation time rather than the growth of wormlike micelles. Incorporation of ionic surfactant in nonionic wormlike micelles gives the electric double layer around the wormlike micelles due to the dissociation of the ionic surfactants. When the electric double layers are overlapped, repulsion occurs between them due to the osmotic pressure resulting from the difference of counterion concentration in crossover field and other. Therefore, the formation of the electric double layer has an effect of increasing the effective volume of wormlike micelles, which can be called the electrostatic excluded volume effect [39,46,47]. In the range of viscosity boosting the plateau modulus decreases with increasing  $X_1$ , suggesting strengthening of the electrostatic repulsion among the wormlike micelles. The increase in the effective volume inhibits diffusion of wormlike micelles in the entanglement network and results in interrupting the reptation process. The constant k may change by the addition of ionic surfactant; however, Eq. (9) can be applied only when it is assumed that  $\tau_{\rm br} \ll \tau_{\rm rep}$ ; therefore, we consider that the change of constant *k* can be ignored.

Fig. 4 shows the variation of *tan*  $\delta$  given by Eq. (10) as a function of  $\omega$  at various  $X_1$ .

$$\tan \delta = \frac{G'}{G'}.\tag{10}$$

Smaller  $tan \delta$  indicates larger elasticity. The  $tan \delta$  values decreases with  $\omega$  for all the samples. As  $X_1$  increases from 0 to 0.041, the  $tan \delta$  values becomes lower below  $\omega = 10^1$  rad s<sup>-1</sup>, indicating that the elastic property strengthens. On the other hand, at  $X_1 = 0.12$  the elastic property is stronger at low  $\omega$  whereas weaker at high  $\omega$  compared to the sample at  $X_1 = 0$  which has lower viscosity than the sample at  $X_1 = 0.12$  should be shorter than at  $X_1 = 0$  by considering CPP, which reflects smaller  $G_0$  values or smaller degree of entanglement for  $X_1 = 0.12$ . The lower elasticity at high  $\omega$  for the sample at  $X_1 = 0.12$  could be attributed to the above difference of micelle length.

For summarizing our explanation for Figs. 2–4, we can almost visualize the structural change of micelles and those networks along the addition of ionic surfactant. The number of entanglement or the network density continuously decreases by shortening the length of micelles, which leads to the decrease in viscosity at high ionic surfactant composition. However, at the early stage of ionic



**Fig. 4.** Variation of  $tan \delta$  as a function of  $\omega$  in the system with SDS at  $X_1 = 0$  ( $\blacktriangle$ ), 0.041 ( $\blacklozenge$ ), 0.12( $\blacksquare$ ).

surfactant addition, the viscosity increases due to thickening of the effective volume of wormlike micelles, which overcomes the shortening effect of micelles.

One can find a similar phenomenon and a mechanism for the viscosity boosting in polyelectrolyte systems [38,39]. However, decreasing the viscosity in the present systems cannot be explained by the reason for polyelectrolyte systems. In the polyelectrolyte solutions, shielding the surface charge with increasing the ionic strength causes a decrease in the viscosity. But in the present systems, all the added ionic surfactant molecules are incorporated in wormlike micelles and, therefore, the shape of micelles can be varied from long wormlike cylinders toward spheres.

## 3.4. Difference in viscosity boosting effect in various ionic surfactant systems

In Fig. 2 unlike the SDS added system,  $\eta_0$  of the system with cationic surfactants such as CTAB, CTAC, and DTAB do not increase in the range of  $X_1$ , 0–0.04. After rising above a certain level, the  $\eta_0$  begins to increase with  $X_1$ . It would appear that difference of the degree of dissociation between anionic surfactants and cationic surfactants has some effect on the surface charge of the wormlike micelles. According to Sasaki et al. [48] and Asakawa et al. [49], the degree of dissociation of counterion of SDS is higher than that of cationic surfactants CTAB, CTAC, and DTAB. Therefore the system with SDS having higher dissociation degree than cationic surfactants gives a maximum relaxation time at lower molar fraction of ionic surfactant and, consequently, the  $\eta_0$  for the SDS system increases at smaller substitutions of nonionic surfactant. Comparing the CTAB system with the CTAC system, before reaching the  $\eta_0^{\text{max}}$ , the CTAC system shows higher viscosity than the CTAB system; however, in the range of decreasing  $\eta_0$  the CTAC system shows a steeper decrease in  $\eta_0$ . According to Ref. [49], degree of dissociation of CTAC is higher than that of CTAB. Therefore, a large degree of dissociation helps to increase the viscosity, but on the other hand it causes a steeper decrease in  $\eta_0$  resulting from the faster curvature change of wormlike micelles by larger electrostatic repulsion between the head groups.

In the systems with CTAB and CTAC, the maximum values of  $\eta_0$ are about 3000 Pa s, which is about two times higher than that of the SDS system and almost 10 times higher than that of DTAB system. The carbon number of alkyl chain for SDS and DTAB are 12 whereas that for CTAB and CTAC is 16. The effect of carbon chain length of the lipophilic cosurfactant on viscosity of wormlike micellar solutions has been studied [16,17,19,32]. Varade et al. [23] reported that in the system of water/sodium dodecyl tri(oxyethylene) sulfate/N-hydroxyethyl-N-methyldodecanamide or Nhydroxyethyl-N-methylhexadecanamide (NMEA-12 or -16), the  $\eta_0^{\text{max}}$  of the NMEA-16 added system is higher than in the NMEA-12 added system. It is known that longer chain amphiphilic molecules form thicker films and, thus, the bending elasticity of the films is high [50,51]. Based on this, we can expect wormlike micelles having greater stiffness in the case of longer chain CTAB or CTAC.

Contrary to single-chain ionic surfactant systems, the  $\eta_0$  shows a sudden decrease with addition of DDAB. DDAB has two alkyl chains as a lipophilic part and tends to form the lamellar phase, which indicates that the CPP for DDAB is about 1/2. Therefore, addition of DDAB causes structural changes of wormlike micelles to a branch type [52–54] or lamellar structure and such effect of geometrical packing change overcomes the electrostatic excluded volume effect, which plays an important role in the single-chain ionic surfactant systems.

#### 4. Conclusions

In this study we investigated the viscosity boosting effect of added ionic surfactant in nonionic wormlike micellar solutions formed in the water/sucrose oleate (C<sub>18:1</sub>SE) system. On increasing ionic surfactant composition, the zero-shear viscosity increases dramatically and it decreases after reaching the maximum value. Generally, in terms of CPP or end-cap energy, the addition of ionic surfactant should decrease the viscosity due to the increase in the repulsion between the head groups. Although decrease in viscosity has been also observed at high ionic compositions, a viscosity boosting effect occurs on small additions of ionic surfactant, which is about 30 times higher than that of binary water/ $C_{18:1}$ SE systems. We consider that the electrostatic excluded volume due to the formation of electric double layer is the main factor of increasing viscosity with addition of ionic surfactant. The electrostatic excluded volume effect would cause the increase in relaxation time through the decrease in the diffusion constant of wormlike micelles in the entangled system. In most previous reports regarding wormlike micelles, the surfactant head group interactions have been tuned through adding salts or lipophilic cosurfactants to obtain higher viscosities. However our approach is different from those previous reports. We attempted to boost the viscosity of a micellar solution by turning the surface charge density on the micelles. This novel approach has worked well and surprisingly it is possible to obtain higher viscosity despite that the micelles become shorter. This new findings should contribute to further manipulation methods of molecular assemblies, which is receiving the growing attention of people involved in nanotechnology.

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