INTRODUCTION

When a hydrophilic surfactant is dissolved in water, it usually forms spherical or rod-like micelles. The spherical or rod-like micellar solutions have low viscosity and show Newtonian flow behavior. However, under certain conditions such as the presence of counter ions, one-dimensional growth of micelles takes place and long flexible aggregates called wormlike micelles are formed. Wormlike micellar solutions show highly viscoelastic behavior at relatively low surfactant concentration, because wormlike micelles are entangled with each other and form a transient network. It is well known that long-chain cationic surfactants such as hexadecyltrimethylammonium bromide (CTAB) or erucyl bis(hydroxyethyl)methylammonium chloride (EHAC) form wormlike micelles in the presence of inorganic salts or hydrotropes such as sodium salicylate (NaSal) or sodium p-toluenesulfonate (Na-TS). The presence of counterions reduces the repulsive interaction between charged head groups and decreases the spontaneous curvature of the aggregates, and consequently one-dimensional micellar growth takes place.

Recently, it was reported that viscoelastic solutions of wormlike micelles are formed in salt-free condition when lipophilic nonionic cosurfactants such as poly(oxyethylene)alkyl ethers or alkanolamides are added to the dilute micellar solution of hydrophilic cationic, anionic, or non-ionic surfactants. In those systems lipophilic cosurfactant molecules incorporated in the hydrophilic spherical

Rheological Properties of Wormlike Micellar Solutions Being Available in Wide Temperature Range in Sucrose Palmitate Systems

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Abstract: We investigated the melting point of the hydrated solid and rheological property of wormlike micellar solutions in the water/sucrose monopalmitate (C16SE)/tri (oxyethylene) dodecyl ether (C12EO3) system when a part of C16SE was substituted with the surfactants which have lower Krafft point than C16SE. The melting point of the hydrated solid of the water/C16SE/C12EO3 system is around 34°C. When C16SE is substituted with sodium dodecyl sulfate (SDS), the melting point of the hydrated solid decreases below 5°C at α (weight fraction of SDS in C16SE+SDS mixture) being greater than 0.3 and the zero shear viscosity (η0) increases from the original nonionic system. When C16SE is substituted with octa (oxyethylene) dodecyl ether (C12EO8), the melting point of the hydrated solid decreases down to 24°C and the maximum zero shear viscosity (η0 max) decreases with the increase in α (weight fraction of C12EO8 in C16SE+C12EO8 mixture). η0 max is dramatically increased by the substitution of C16SE with SDS. With further increase of α, η0 max decreases gradually. The dynamic rheology data of highly viscous wormlike micellar solutions fit well to the Maxwell’s mechanical model of viscoelastic material, indicating the formation of rigid network of entangled wormlike micelles. Shear (plateau) modulus G0 is almost unchanged, whereas relaxation time τR shows similar behavior to η0 max. Hence, the behavior of η0 max can be explained from the behavior of τR by considering the equation relating these quantities, η0=G0τR. Since τR is proportional to the length of wormlike micelles, the behavior of η0 max can be explained in terms of the change in the length of wormlike micelles caused by the addition of SDS.

Key words: worm-like micelle, rheology, melting temperature of hydrated solid, sucrose fatty acid ester

1 INTRODUCTION

When a hydrophilic surfactant is dissolved in water, it usually forms spherical or rod-like micelles. The spherical or rod-like micellar solutions have low viscosity and show Newtonian flow behavior. However, under certain conditions such as the presence of counter ions, one-dimensional growth of micelles takes place and long flexible aggregates called wormlike micelles are formed. Wormlike micellar solutions show highly viscoelastic behavior at relatively low surfactant concentration, because wormlike micelles are entangled with each other and form a transient network. It is well known that long-chain cationic surfactants such as hexadecyltrimethylammonium bromide (CTAB) or erucyl bis(hydroxyethyl)methylammonium chloride (EHAC) form wormlike micelles in the presence of inorganic salts or hydrotropes such as sodium salicylate (NaSal) or sodium p-toluenesulfonate (Na-TS). The presence of counterions reduces the repulsive interaction between charged head groups and decreases the spontaneous curvature of the aggregates, and consequently one-dimensional micellar growth takes place.

Recently, it was reported that viscoelastic solutions of wormlike micelles are formed in salt-free condition when lipophilic nonionic cosurfactants such as poly(oxyethylene)alkyl ethers or alkanolamides are added to the dilute micellar solution of hydrophilic cationic, anionic, or non-ionic surfactants. In those systems lipophilic cosurfactant molecules incorporated in the hydrophilic spherical
micelles reduce the repulsive interaction among hydrophilic surfactant molecules\cite{39,30}, which results in the decrease in the curvature of surfactant layer.

Sucrose fatty acid esters, derived from sugar and fatty acids, are nontoxic and biodegradable, which makes them suitable for food industries, cosmetics, and pharmaceutical formulations. Sucrose mono fatty acid esters form spherical or slightly elongated micelles in water in the dilute region\cite{31}. Highly viscous wormlike micellar solutions can also be obtained by mixing a sucrose mono fatty acid ester and a lipophilic nonionic cosurfactant\cite{13,32}. Maestro et al.\cite{30} reported the formation of wormlike micelles from sucrose monopalmitate (C16SE) with a lipophilic nonionic surfactant having a small head group such as short-chain poly(oxyethylene) dodecyl ether (C12EO\textsubscript{n}) or glycerol monolaurate (ML). The viscosity of the micellar solution of aqueous C16SE system is increased up to 400 Pa·s by mixing those lipophilic cosurfactants. Although these nonionic wormlike micellar solutions with sucrose fatty acid esters seem promising for practical applications, a rather high melting point of the hydrated solid is around room temperature is inconvenient for the practical use.

In this work, we substituted a part of C16SE with sodium dodecyl sulfate SDS that has lower Krafft point (around 9°C) than C16SE in order to avoid hydrated solid deposition from the wormlike micellar solutions.

2 EXPERIMENTAL

2.1 Materials

Poly(oxyethylene) dodecyl ethers (C\textsubscript{12}EO\textsubscript{n}, n = 3 and 8) were purchased from Nikko Chemicals Co. Sodium dodecyl sulfate (SDS>98.5%) was purchased from Sigma Aldrich Japan Co. Sucrose palmitate (C16SE, ester content >99%) was supplied by Mitsubishi Chemical Co.

2.2 Measurements of the melting point of the hydrated solid

After the sample was cooled, the temperature of the sample was gradually increased in a water bath and the melting point of the hydrated solid was determined visually.

2.3 Rheological measurements

After mixing the components, the samples were left in a water bath at measurement temperature for at least 24 h to ensure equilibration before the rheological measurements. Rheological measurements were performed in an AR-G2 rheometer (TA Instruments) using cone-plate (two sizes: 40- and 60-mm diameters, each having a cone angle of 1 rad). Dynamic frequency-sweep measurements were performed in the linear viscoelastic regime of the samples, which was pre-determined by dynamic strain-sweep measurements.

3 RESULTS AND DISCUSSIONS

3.1 Zero shear viscosity and the melting point of the hydrated solid of water/C16SE/SDS/C12EO\textsubscript{n} system

We investigated the change of zero shear viscosity (\(\eta_0\)) when a part of C16SE is substituted with SDS. Here, we define the weight fraction of SDS in C16SE+SDS mixture as \(\alpha\), and the weight fraction of C12EO\textsubscript{n} in total surfactants as \(W_1\). At \(\alpha=0\), \(\eta_0\) first increases dramatically upon addition of a small amount of C12EO\textsubscript{n}. The increase in \(\eta_0\) suggests the formation of entangled, wormlike micelles. Micellar growth is attributed to the decrease in surfactant layer curvature with the incorporation of C12EO\textsubscript{n} into the palisade layer of the surfactant aggregate. It can be explained through the packing parameter, \(\nu/\alpha f\), where \(\nu\) and \(\alpha\) are the effective length and the volume of a lipophilic tail and \(\alpha_s\), the cross-sectional area of the headgroup at the hydrophile-lipophile interface. This parameter determines the interfacial curvature of the aggregate. If \(\alpha f\) is larger than \(\nu\), as is the case for sucrose alkanoate surfactants, micelles tend to be spherical or slightly elongated, because the tails are packed in the core of the aggregate but the headgroups need a big surface to be accommodated and, as a result, a large curvature is required at the interface. When C12EO\textsubscript{n}, which has a much smaller headgroup, is added, it forms mixed micelles with the sucrose surfactant. The mean \(\alpha_s\) in the mixed micelle is reduced because of smaller \(\alpha_s\) of C12EO\textsubscript{n}, and hence, the curvature decreases. This induces the transformation of rod-like micelles to giant wormlike micelles in order to reduce the number of endcaps with higher curvature. However, upon further addition of C12EO\textsubscript{n}, \(\eta_0\) passes through a maximum and then decreases. This behavior can be attributed to micellar branching which causes the formation of slipping points that allows faster relaxation, leading to a reduction in \(\eta_0\). The \(\eta_0\) behavior observed for different \(\alpha\) is similar to the case for \(\alpha=0\). However, \(W_1\) giving the maximum \(\eta_0(\eta_0^{\max})\) shifts towards higher \(W_1\) values upon increasing \(\alpha\). Moreover, above \(\alpha=0.3\), the increase of \(\eta_0\) at low \(W_1\) is gradual. Especially, a plateau region appears at \(\alpha=0.8\). These indicate that SDS is more hydrophilic than C16SE, making the curvature more positive. Hence, more C12EO\textsubscript{n} is needed to induce an one-dimensional micellar growth.

The melting point of the hydrated solid of the water/C16SE/SDS/C12EO\textsubscript{n} system is shown in Table 1. Above those melting temperature we could have micellar solutions. Note that the rheological measurements at \(\alpha=0\) was performed for samples in a supercooled state, since the melting point of the hydrated solid exceeds 25°C as shown in Table 1.

At \(W_1=0\), the melting point of the hydrated solid at \(\alpha=0\)
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Table 1 The Melting Point of the Hydrated Solid Phase of the Water/C_{16}SE/SDS/C_{12}EO3 System at W_{1} = 0 and W_{1} giving \( \eta_{0}^{\text{max}} \).

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>At ( W_{1} = 0 )</th>
<th>At ( W_{1} ) giving ( \eta_{0}^{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40°C</td>
<td>34°C (( W_{1} = 0.06 ))</td>
</tr>
<tr>
<td>0.1</td>
<td>22°C</td>
<td>21°C (( W_{1} = 0.24 ))</td>
</tr>
<tr>
<td>0.3</td>
<td>&lt;5°C</td>
<td>15°C (( W_{1} = 0.35 ))</td>
</tr>
<tr>
<td>0.6</td>
<td>&lt;5°C</td>
<td>&lt;5°C (( W_{1} = 0.45 ))</td>
</tr>
<tr>
<td>0.8</td>
<td>&lt;5°C</td>
<td>&lt;5°C (( W_{1} = 0.5 ))</td>
</tr>
</tbody>
</table>

Fig. 1 Zero Shear Viscosity (\( \eta_{0} \)) as a Function of \( W_{1} \) (weight fraction of C_{12}EO3 in total surfactant) in the Water/C_{16}SE/SDS/C_{12}EO3 System at Several \( \alpha \) (weight fraction of SDS in C_{16}SE+SDS mixture) at 25°C. The weight ratio of C_{16}SE+SDS to water is fixed at 1/9. Open circle (\( \alpha = 0 \)), filled square (\( \alpha = 0.1 \)), open triangle (\( \alpha = 0.3 \)), filled circle (\( \alpha = 0.6 \)), open diamond (\( \alpha = 0.8 \)). Solid lines are just for guide.

is 40°C. When C_{16}SE is substituted with SDS, the melting point of the hydrated solid decreases dramatically and becomes lower than 5°C above \( \alpha = 0.3 \). As we expected, the melting point of the hydrated solid decreases by substituting a part of C_{16}SE with a surfactant having lower Krafft point. At the \( W_{1} \) giving \( \eta_{0}^{\text{max}} \), which is obtained from Fig. 1, the melting point of the hydrated solid decreases from 34°C to below 5°C above \( \alpha = 0.6 \).

The results of Fig. 1 and Table 1 show that it is possible to obtain viscous wormlike micellar solution being stable below room temperature by substituting a part of C_{16}SE with SDS, which has lower Krafft point than C_{16}SE.

Figure 2 shows \( \eta_{0} \) of the water/C_{16}SE/SDS/C_{12}EO3 system at \( \alpha = 0.3 \) at different temperatures. When the temperature increases, the trend of the \( \eta_{0}-W_{1} \) curves remains essentially the same. However, \( W_{1} \) giving the \( \eta_{0}^{\text{max}} \) slightly shifts towards lower value with the increase in temperature. This trend is consistent with the fact that as the temperature increases, the extent of hydration of the EO groups of C_{12}EO3 molecules decreases and the cross-sectional area of the amphiphile, \( \alpha_{s} \), decreases. Such a change in the surfactant properties would decrease the spontaneous curvature of the surfactant layer, and hence, less C_{12}EO3 is needed to induce a micellar growth. A similar observation was reported in the wormlike micellar solutions of the water/AES (alkyl ethoxylate sulfate)/C_{12}EO3 system^{38}. From the viewpoint of the curvature energy, formation of saddle-shaped micellar joints with the regions having negative Gaussian curvature should be considered. When the spontaneous curvature of the surfactant layer decreases (with increasing temperature), the energy cost associated with the formation of the surfactant layer with negative Gaussian curvature becomes lower. As a result, the formation of the junction becomes more favorable. Hence, micellar free ends favor fusion with the cylindrical part of their own or other micelles, and micellar branching is triggered at lower values of \( W_{1} \). Moreover, Fig. 2 indicates that the \( \eta_{0}^{\text{max}} \) decreases with the increase in temperature. This can be explained by the Eq.1 shown later, which indicates that when the flow activation energy is constant, \( \eta_{0} \) is proportional to \( \frac{1}{T} \) exponentially.

The Arrhenius plot of \( \eta_{0} \) at \( \alpha = 0.3 \) (\( W_{1} = 0.35 \)) is shown in Fig. 3. \( \eta_{0} \) decreases exponentially with temperature. This exponential decay of the viscosity with temperature is in accordance with the well-known equation for wormlike micelles^{39}.

Fig. 2 Effect of Temperature on the Zero Shear Viscosity (\( \eta_{0} \)) of the Water/C_{16}SE/SDS/C_{12}EO3 Systems at \( \alpha = 0.3 \). Arrows indicate \( W_{1} \) giving maximum \( \eta_{0} \). Filled circle (25°C), open diamond (30°C), filled square (40°C), open triangle (50°C). Lines guide for the eyes.

where $E_a$ is the flow activation energy, $R$ is the universal gas constant, and $A$ is a constant. The activation energy describes the energy that is necessary to move individual micelles in an environment of surrounding micelles. The activation energy is therefore given by the interactions between individual aggregates. From the slope of the straight line fit in Fig. 3, we calculate the flow activation energy $E_a$ to be 123 kJ mol$^{-1}$. This value of $E_a$ is comparable to those reported for other wormlike micelles.$^{2, 11, 35}$.

3.2 Zero shear viscosity and the melting point of the hydrated solid of the water/C$_{16}$SE/C$_{12}$EO$_8$/C$_{12}$EO$_3$ system

We also attempted to decrease the melting point of the hydrated solid in water/C$_{16}$SE/C$_{12}$EO$_3$ mixture by using C$_{12}$EO$_8$ instead of SDS. Figure 4 shows a plot of $\eta_0$ as a function of $W_1$ for the water/C$_{16}$SE/C$_{12}$EO$_8$/C$_{12}$EO$_3$ system at several $\alpha$; in this case, $\alpha$ represents the weight fraction of C$_{12}$EO$_8$ in C$_{16}$SE+C$_{12}$EO$_8$ mixture. At every $\alpha$, $\eta_0$ first increases on addition of a small amount of C$_{12}$EO$_3$, and upon further addition of C$_{12}$EO$_3$, $\eta_0$ passes through a maximum and then decreases. However the $\eta_0$ max dramatically decreases with the increase in $\alpha$. The $\eta_0$ max for $\alpha$=0.0 is about 100 Pa s and it becomes less than 10 Pa s at $\alpha$=0.1, then finally decreases almost by three orders of magnitude at $\alpha$=0.3, at which the fluidity of the sample is high. This is attributed to the fact that the wormlike micelles are not formed in the water/C$_{12}$EO$_3$/C$_{12}$EO$_3$ system. Additionally, $W_1$ giving the $\eta_0$ max shifts towards higher value upon increasing $\alpha$. It indicates that C$_{12}$EO$_3$ is more hydrophilic than C$_{16}$SE, making the curvature more positive. Hence, more C$_{12}$EO$_3$ is needed to induce an one-dimensional micellar growth. Phase separation takes place at higher $W_1$ as $\alpha$ increases. It also suggests that C$_{12}$EO$_8$ makes the curvature more positive.

The melting point of the hydrated solid of the water/C$_{16}$SE/C$_{12}$EO$_8$/C$_{12}$EO$_3$ system is shown in Table 2. When a part of C$_{16}$SE is substituted with C$_{12}$EO$_8$ at $W_1$ = 0, the melting point of the hydrated solid of the water/C$_{16}$SE/C$_{12}$EO$_3$ system decreases gradually and reaches 24 $^\circ$C at $\alpha$=0.3. At the $W_1$ giving $\eta_0$ max, the melting point of the hydrated solid decreases from 34 $^\circ$C to 24 $^\circ$C with the increase in $\alpha$. It is possible to decrease the melting point of the hydrated solid to around room temperature by substituting a part of C$_{16}$SE with C$_{12}$EO$_8$. However, the C$_{12}$EO$_8$ is less effective than SDS to decrease the melting point of the hydrated solid. Moreover the $\eta_0$ max decreases dramatically in the mixed nonionic surfactant system. Thus, we can conclude that SDS is more favorable for

\[
\eta_0 = A \exp \left( \frac{E_a}{RT} \right)
\]
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extending the available temperature range of wormlike micelles compared with C_{12}EO_{8}.

3.3 Dynamic frequency sweep measurement for the water/C_{16}SE/SDS/C_{12}EO_{3} system

Viscoelastic properties of the water/C_{16}SE/SDS/C_{12}EO_{3} systems at $\alpha$=0 ($W_{1}=0.06$), 0.1 ($W_{1}=0.24$) and 0.8 ($W_{1}=0.48$) were investigated by frequency sweep measurements. Each $W_{1}$ value is the fraction of C_{12}EO_{3} giving $\eta_{0}^{\text{max}}$. The results are shown in Fig. 5. The dynamic rheology data show variation of the storage modulus $G'$ which reflects the elastic property, and loss modulus $G''$ which reflects the viscous property as a function of oscillation frequency $\omega$. At high $\omega$, the sample exhibits elastic behavior ($G'$ shows a plateau value and dominates over the $G''$), whereas at low $\omega$ the sample shows viscous behavior ($G''$ exceeds $G'$). In the low $\omega$ region the data points of $G'$ and $G''$ fit well to the Maxwell’s mechanical model of viscoelastic material described by the following equations, which considers a single process for stress relaxation characterized by relaxation time, $\tau_{R}$.

$$G'(\omega) = \frac{\omega^{2} \tau_{R}^{2}}{1+\omega^{2} \tau_{R}^{2}} G_{0}$$  \hspace{1cm} (2)

$$G''(\omega) = \frac{\omega \tau_{R}}{1+\omega^{2} \tau_{R}^{2}} G_{0}$$  \hspace{1cm} (3)

where, $G_{0}$ is called shear (plateau) modulus that can be obtained from the $G'$ value at infinite $\omega$. Such viscoelastic behavior indicates the formation of rigid network of entangled wormlike micelles\(^6\). The relaxation time, $\tau_{R}$, can be evaluated from the relation:

$$\tau_{R} = \frac{1}{\omega C}$$  \hspace{1cm} (4)

where $\omega C$ is the frequency at which $G'$ and $G''$ intersect and it is also called crossover frequency. Nevertheless, the data deviates from this model at high frequencies. This deviation is thought to have arisen from a transition of the relaxation mode from ‘slower’ reptation to other ‘breathing’ or ‘Rouse’ modes of cylindrical micelles, analogous to polymer chain\(^3\). Once $G_{0}$ and $\tau_{R}$ are available, $\eta_{0}$ can be calculated using following relation\(^3\):\(^6\):

$$\eta_{0} = G_{0} \tau_{R}$$  \hspace{1cm} (5)

$\eta_{0}$ obtained from this equation coincides with the $\eta_{0}$ measured by steady rate sweep tests. The complex viscosity, $|\eta'|$, is related to the storage and loss moduli by the relation\(^3\):\(^6\):

$$|\eta'| = \frac{(G'^{2} + G''^{2})^{1/2}}{\omega}$$  \hspace{1cm} (6)

$|\eta'|$ exponentially as a function of oscillatory shear frequency for the water/C_{16}SE/SDS/C_{12}EO_{3} system at $\alpha$=0 ($W_{1}=0.06$), 0.1 ($W_{1}=0.18$) and 0.8 ($W_{1}=0.48$) are plotted in Fig. 6.

![Fig. 5 Frequency Sweep Measurements for the Water/C_{16}SE/SDS/C_{12}EO_{3} System at $\alpha$=0 ($W_{1}=0.06$), 0.1 ($W_{1}=0.24$) and 0.8 ($W_{1}=0.48$). The weight ratio of C_{16}SE+SDS to water is fixed at 1/9. Circle ($\alpha$ = 0), square ($\alpha$ = 0.1), diamond ($\alpha$ = 0.8). Filled symbols correspond to $G'$, whereas the open symbols $G''$. Lines represent the Maxwellian fit.](image1)

![Fig. 6 The Complex Viscosity as a Function of Oscillatory Shear Frequency for the Water/C_{16}SE/SDS/C_{12}EO_{3} System at $\alpha$=0 ($W_{1}=0.06$), 0.1 ($W_{1}=0.18$) and 0.8 ($W_{1}=0.48$). Circle ($\alpha$ = 0), square ($\alpha$ = 0.1), diamond ($\alpha$ = 0.8).](image2)
The shear thinning behavior is observed in all samples, suggesting the formation of wormlike micelles. The plateau region at $\alpha=0.1$ is larger than those at $\alpha=0.8$ and 0. This trend corresponds with the result of $\eta_0$ measured by steady rate sweep tests which shows that $\eta_0^{\text{max}}$ at $\alpha=0.1$ is larger than that at $\alpha=0.8$ and 0 (see Fig. 1).

Cole-Cole plot, which is the plot of $G''(\omega)/G''_{\text{max}}$ against $G'(\omega)/G'_{\text{max}}$, is another way to verify the viscoelastic wormlike micellar behavior. $G''_{\text{max}}$ can be calculated using following relation:

$$G_0 \equiv 2G''_{\text{max}} \quad (7)$$

A Maxwell material is characterized by a semicircle centered at $G'(\omega)/G'_{\text{max}}=1$ in the Cole-Cole plot\(^\text{37}\). From the data shown in Fig. 7, it can be seen that the shape of the curve at $\alpha=0$ and 0.1 follows a semicircular behavior indicating the presence of viscoelastic wormlike micelles in the solution. The shape of the curve at $\alpha=0.8$ deviates from semicircle around $G''_{\text{max}}=2$, suggesting the poor viscoelastic behavior.

Values of $\eta_0^{\text{max}}$ at several $\alpha$ obtained from Fig. 1 are plotted against $\alpha$ in Fig. 8. The $G_0$ and $\tau_0$ estimated from Fig. 5 are also plotted in Fig. 8. It is very striking that the $\eta_0^{\text{max}}$ dramatically increases by about 20 times. However, upon further addition of SDS, $\eta_0^{\text{max}}$ passes through a maximum at $\alpha=0.1$ and then decreases. In this system, $\eta_0^{\text{max}}$ is another way to verify the viscoelastic behavior of such systems in the low-frequency region follows the Maxwell model with a single relaxation time $\tau_\phi$ which is expressed as\(^\text{38}\)

$$\tau_\phi = \tau_0^{\text{rep}} \times \frac{1}{2} \quad (8)$$

$\tau_\phi$ and $\tau_0$ have the following proportionality relations\(^\text{39}\).

$$\tau_\phi \approx \bar{L}^3 \cdot \phi^\frac{3}{2} \quad (9)$$

$$\tau_0 \approx \bar{L}^{\frac{1}{3}} \quad (10)$$

where $\bar{L}$ is the average contour length of wormlike micelles and $\phi$ is the surfactant volume fraction. From the proportional relations of Eqs. 8, 9, and 10,

$$\tau_R \sim \bar{L} \cdot \phi^{-\frac{3}{2}} \quad (11)$$

When logarithm is taken, it is expressed as follows.

$$\ln \tau_R \sim \ln \bar{L} + \ln \phi^{-\frac{3}{2}} \quad (12)$$

From Eq. 12, increase in $\tau_R$ suggests that $\bar{L}$ increases or $\phi$ increases. In this system, $\phi$ is almost unchanged. However, when a part of $C_{16}\text{SE}$ is substituted with SDS, the micellar surface has charges and an electrical double layer is formed. It is likely that $\phi$ slightly increases due to the electrical double layers. Therefore, it is thought that the increase in $\eta_0^{\text{max}}$ is caused by the increase in $\bar{L}$ or $\phi$. $\bar{L}$ is expressed as:

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**References**

where $E_c$ is the end-cap energy required to form two hemispherical end-caps as a result of rod scission. For charged micelles in the absence of salt, the scission energy has an additional component, $E_a$, due to the repulsion of charges along the micelles that favor shorter micelles, $E_a$ is proportional to $\nu$. $\nu$ is the effective charge per unit length. It can be said from Eqs 12 and 13 that $\ln L$ of the first term of Eq 12 is proportional to $-\nu^2$, indicating the reduction of $\ln L$ with the increase in $\alpha$. Moreover the reduction rate of $\ln L$ becomes larger with the increase in $\nu$, that is, increase in $\alpha$. The decrease in $\tau_L$ above $\alpha=0.1$ suggests that the influence of a reduction in the contour length of wormlike micelles increases because the reduction rate of $\ln L$ increases with $\alpha$. Therefore, the decrease in $\eta_s^{\max}$ above $\alpha = 0.1$ can be explained by the reduction of $L$.

4 CONCLUSION

The formation of wormlike micelles with sucrose fatty acid esters are already reported, but high melting temperature of the hydrated solid is a problem caused by strong attraction among sucrose head groups due to strong hydrogen bonding. To solve the problem we partly substituted the sucrose fatty acid ester with other hydrophilic surfactant having lower Krafft temperature than the sucrose fatty acid ester. Wormlike micellar solutions are formed in the water/sucrose monopalmitate (C15SE)/tri(oxyethylene) dodecyl ether (C12EO3) system and a maximum zero-shear viscosity ($\eta_s^{\max}$) is found around 200 Pa·s at an appropriate mixing fraction of the two surfactants, but the hydrated solid phase is formed below 34°C. By the substitution of C15SE with SDS the melting temperature of the hydrated solid decreases dramatically and becomes below 5°C above $\alpha=0.3$, where $\alpha$ is the weight fraction of SDS in C15SE+SDS mixture. In addition, it was very striking that the maximum zero-shear viscosity dramatically increases by about 20 times. The dynamic rheology study for the highly viscous samples shows the Maxwell-type behavior that is typically observed for wormlike micellar solutions.

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