Effect of C_{12}EO_{n} mixed surfactant systems on the formation of viscoelastic worm-like micellar solutions in sucrose alkanoate– and CTAB–water systems

Sandra Engelskirchen\textsuperscript{a}, Durga P. Acharya\textsuperscript{b,∗}, Miguel Garcia-Roman\textsuperscript{c}, Hironobu Kunieda\textsuperscript{b}

\textsuperscript{a} Institut für Physikalische Chemie, Luxemburger Str. 116, Universität zu Köln, 50939 Köln, Germany
\textsuperscript{b} Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
\textsuperscript{c} Departamento de Ingeniería Química, Facultad de Ciencias, Universidad de Granada, Avda. Fuentenueva s/n, 18071 Granada, Spain

Received 14 April 2005; received in revised form 29 October 2005; accepted 26 December 2005
Available online 8 February 2006

Abstract

With successive addition of mixed polyoxyethylene dodecylether (C_{12}EO_{n}) surfactant with an average EO number of 3 to the aqueous solution of hexadecyltrimethylammonium bromide (CTAB) and sucrose monohexadecanoate (P1695), one-dimensional micellar growth occurs and the viscosity increases sharply leading to the formation of viscoelastic solutions of worm-like micelles. Steady and oscillatory shear rheological measurements show that in the aqueous CTAB system, the extent of micellar growth decreases with increasing the dispersion in EO chain in the mixture in following order C_{12}EO_{3} > C_{12}EO_{2} + C_{12}EO_{4} > C_{12}EO_{0} + C_{12}EO_{4} > C_{12}EO_{1} + C_{12}EO_{5}. With C_{12}EO_{0} + C_{12}EO_{6} no micellar growth occurs but a phase separation is observed. In P1695 system, the viscoelastic solution is formed at relatively lower concentration of mixed C_{12}EO_{n} and the extent of micellar growth decreases in the following order: C_{12}EO_{3} \approx C_{12}EO_{2} + C_{12}EO_{4} > C_{12}EO_{1} + C_{12}EO_{5} > C_{12}EO_{0} + C_{12}EO_{6}. The effect of the dispersion of EO chain length on the micellar growth is also discussed.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Worm-like micelles; Viscoelastic micelles; Sucrose surfactant; CTAB; Nonionic surfactant; Micellar growth

1. Introduction

When a hydrophilic surfactant is dissolved in water, in most of the cases, spherical or sphere-like aggregates or micelles are formed. Aqueous surfactant solutions containing small sphere-like micelles show Newtonian flow behavior. However, under certain condition (for example, adding salt or combining cationic or anionic surfactants), one-dimensional growth of micelles takes place and long flexible aggregates called worm-like or thread-like micelles are produced [1–9]. Due to entanglement of the worm-like micelles, its aqueous systems show highly viscoelastic behavior. Although the formation of worm-like micelles has been reported in aqueous nonionic surfactant solutions [10,11], highly viscoelastic solutions were mainly investigated in cationic and/or cationic–anionic surfactant systems, often in the presence of inorganic or organic salts.

Recently, it was reported that viscoelastic micellar solution of worm-like micelles are formed in the salt-free condition when lipophilic nonionic surfactant such as short hydrophobic-chain poly(oxyethylene) alkyl ether or alkanolamide is added to the dilute micellar solution of hydrophilic cationic, anionic or nonionic surfactant [12–17]. Size of the head and tail group of the lipophilic surfactant is one of the factors that affect the micellar growth and the rheological behavior of the solution [12–14,16,17]. Upon addition of lipophilic surfactant to hydrophilic one, an average cross sectional area per surfactant decreases and the packing or surfactant parameter increases. It causes the change in micellar shape from sphere to rod. The length of the rod-like micelles or the extent of the one-dimensional-micellar growth is associated with the excess free energy of the hemispherical end-caps in comparison to the curvature free energy of the cylindrical part. Any factor that reduces the interfacial curvature, for example, incorporation of...
the lipophilic nonionic surfactant, tends to increase the free energy of the end caps if the surfactants are homogenously mixed in the micelles. In this case, formation of long micelles has been found to affect the extent of the micellar growth. For sodium dodecyl sulphate, hexadecyltrimethylammonium bromide (CTAB), gemini and sucrose alkanoate surfactant systems, C12EO3 is the most efficient to increase the viscosity of the solutions [13,18,19]. If the shorter EO chain C12EO\textsubscript{n} is added, phase separation takes place before increasing viscosity. On the other hand, if longer EO or more hydrophilic surfactant is employed, the micellar growth is not sufficient to form aqueous viscoelastic solutions.

There are numerous reports on the rheological behavior of worm-like micelles in cationic surfactant-salt systems but the worm-like micelles formed in salt-free mixed surfactant systems are relatively new area and therefore demands more attention. The viscoelastic micellar solutions formed in mixed nonionic systems such as polyoxyethylene cholesteryl ethers or sucrose alkanoates are not only useful in practical applications but also suitable to test the electrostatic interactions. Much is to be studied about micellar growth and rheological behavior of nonionic worm-like micellar systems.

As mentioned above, the micellar growth in the mixed surfactant systems is sensitive to the head group size of the lipophilic nonionic surfactant such as C12EO\textsubscript{3}, which is related to their ability to modify the spontaneous interfacial curvature and also the end cap energy. Thus, careful selection of lipophilic surfactants allows one to control the viscosity and flow properties of the mixed surfactant solution, which is important in their practical applications such as cosmetic, pharmaceutical formulations etc. However, for practical applications, commercial surfactants have to be used. Distribution in the chain length of commercial surfactant may affect the rheological properties. Study on the effect of the distribution of molecular length, for example, EO chain length in polyoxyethylene alkylether would be useful not only for practical application, but also to develop a basic understanding about the micellar growth in mixed surfactant systems.

In this paper, we discuss the formation of viscoelastic worm-like micellar solutions and their rheological behavior in the two different mixed surfactant systems—one consisting of ionic surfactant, CTAB, and another consisting of nonionic surfactant, sucrose hexadecanoate (P1695) of comparable alkyl chain length, in presence of mixed C12EO\textsubscript{n} with average EO number of 3. The phase behavior of CTAB/C12EO\textsubscript{3}/water and P1695/C12EO\textsubscript{3}/water systems, and formation of highly viscoelastic regions in the dilute micellar region has been recently reported [13,19]. The phase diagrams of each of these ternary systems are shown in Fig. 1. With successive addition of C12EO\textsubscript{3} to the micellar solution of CTAB, highly viscoelastic micellar solution is formed above a critical concentration of C12EO\textsubscript{3}. In the P1695 system, viscosity increases even with small amount of C12EO\textsubscript{3}. Starting from binary CTAB– and P1695–water systems, we added C12EO\textsubscript{n} mixtures with average EO number of 3, hereafter represented by C12EO\textsubscript{3}, and carried out rheological measurement to follow the structural evolution in the system with increasing concentration of C12EO\textsubscript{3} at a fixed concentration of CTAB or P1695, along the direction of arrow in the respective phase diagrams (Fig. 1). The effect of the dispersion of the EO chain length on the rheological behavior of the CTAB systems will be discussed first, and then behavior of the nonionic P1695 system will be discussed and compared with the CTAB system.

2. Experimental

2.1. Materials

P1695 (monoester content>93.6%) was obtained from Mitsubishi Chemical Co. (Japan). The molecular structure of P1695 is shown in Scheme 1. Polyoxyethylene dodecyl ethers were purchased from Nikko Chemicals Co. (Japan) and

![Scheme 1. Schematic molecular structure of sucrose hexadecanoate, P1695.](image-url)
CTAB was the product of Tokyo Kasei Kogyo. All chemicals were used as received without further purification. For the preparation of the samples Millipore-MilliQ water was applied.

2.2. Rheological measurements

In order to obtain the samples for the rheological measurements stock solutions of sucrose alkanolate (5 wt%, ~0.086 M) and CTAB (5.5 wt%, 0.15 M) were prepared. The desired amount of C12EO5 was added to a weighed amount of the stock solution. The average EO number was achieved by taking equimolar combinations of C12EO2 + C12EO3, C12EO1 + C12EO4, C12EO3 + C12EO1 and a mixture of C12EO5 + C12EO0 at a molar ratio of 1:3. These mixtures will be denoted hereafter by C12EO12, C12EO11, C12EO10 and C12EO9, respectively. The composition of the sample is expressed in the mole fraction of C12EO0 in total surfactant, X. The prepared samples were slightly heated up and mixed thoroughly. To assure equilibration all samples were kept in a thermostated water bath at desired temperature for at least 24 h in case of the liquid-like sample, and for at least 48 h in case of the viscoelastic samples. As the Kraft temperature of the P1695 was found to be around room temperature the equilibration and all the measurements of P1695–C12EO5 systems were performed at 30 °C to avoid precipitation. For the aqueous CTAB–C12EO5 systems, however, 25 °C was maintained.

All rheological measurements were carried out using an ARES rheometer (Rheometric Scientific). Depending on the viscosity of the samples, three different geometries were used. Liquid-like samples were investigated using Couette geometry with a cup diameter of 34 mm, a bob diameter of 32 mm and a bob length of 33.3 mm. For the sample of intermediate and high viscosity, cone-and-plate sensors of 25 and 50 mm in diameter, both having a cone angle of 0.04 rad, were used. To avoid the evaporation of the sample during the measurement a device was installed. Oscillatory sweep measurements were performed in the viscoelastic regime (at a strain of 10%) as determined by the viscoelastic regime (at a strain of 10%) as determined by the viscoelastic regime (at a strain of 10%) as determined by the measurement was carried out up to a shear rate of γ = 0.583. At higher mixing fractions, a phase separation takes place.

Stress (σ)–γ plot (inset of Fig. 2) for a sample (X = 0.432) near viscosity maximum shows a linear increase in the shear rate range. With increasing mixing fraction of C12EO5, up to X > 0.50, the minimum shear rate at which shear thinning begins shifts to lower values, and also the zero shear viscosity (η0), which can be obtained by extrapolating the viscosity—shear rate curve to zero shear rate, increases sharply. It indicates the progressive formation of micellar network with increasing X.

At compositions X > 0.50, Newtonian behavior is extended toward higher shear rate values indicating an abrupt change in the microstructure of the aggregates. The steady shear rate measurement was carried out up to X = 0.583. At higher mixing fractions, a phase separation takes place.

Stress (σ)–γ plot (inset of Fig. 2) for a sample (X = 0.432) near viscosity maximum shows a linear increase in the shear rate range. With increasing mixing fraction of C12EO5, up to X > 0.50, the minimum shear rate at which shear thinning begins shifts to lower values, and also the zero shear viscosity (η0), which can be obtained by extrapolating the viscosity—shear rate curve to zero shear rate, increases sharply. It indicates the progressive formation of micellar network with increasing X.

At compositions X > 0.50, Newtonian behavior is extended toward higher shear rate values indicating an abrupt change in the microstructure of the aggregates. The steady shear rate measurement was carried out up to X = 0.583. At higher mixing fractions, a phase separation takes place.

Stress (σ)–γ plot (inset of Fig. 2) for a sample (X = 0.432) near viscosity maximum shows a linear increase in the shear rate range. With increasing mixing fraction of C12EO5, up to X > 0.50, the minimum shear rate at which shear thinning begins shifts to lower values, and also the zero shear viscosity (η0), which can be obtained by extrapolating the viscosity—shear rate curve to zero shear rate, increases sharply. It indicates the progressive formation of micellar network with increasing X. The Newtonian behavior is extended toward higher shear rate values indicating an abrupt change in the microstructure of the aggregates. The steady shear rate measurement was carried out up to X = 0.583. At higher mixing fractions, a phase separation takes place.

Stress (σ)–γ plot (inset of Fig. 2) for a sample (X = 0.432) near viscosity maximum shows a linear increase in the shear rate range. With increasing mixing fraction of C12EO5, up to X > 0.50, the minimum shear rate at which shear thinning begins shifts to lower values, and also the zero shear viscosity (η0), which can be obtained by extrapolating the viscosity—shear rate curve to zero shear rate, increases sharply. It indicates the progressive formation of micellar network with increasing X. The Newtonian behavior is extended toward higher shear rate values indicating an abrupt change in the microstructure of the aggregates. The steady shear rate measurement was carried out up to X = 0.583. At higher mixing fractions, a phase separation takes place.
in comparison to the timescale of the scission, the viscoelastic micellar solutions behave as a Maxwell-fluid with single relaxation time, and variation of the elastic or storage modulus \( G'(\omega) \) and the viscous or loss modulus \( G''(\omega) \) as a function of oscillatory shear frequency \( \omega \) is described by following relations:

\[
G' = \frac{\omega \tau_g}{1 + (\omega \tau_g)} G_0 \tag{1}
\]

\[
G'' = \frac{\omega \tau_g}{1 + (\omega \tau_g)} G_0 \tag{2}
\]

where \( G_0 \) is called shear (plateau) modulus. The relaxation time, \( \tau_g \), can be estimated as \( (\omega \tau_g)^{-1} \) where \( \omega \) is the cross-over frequency, that is, the shear frequency at which \( G' = G'' \). Shear modulus and relaxation time give zero-shear viscosity according to relation:

\[
\eta_0 = \frac{G_0 \tau_g}{\omega}
\]

(3)

At low \( \omega \), and \( \omega \tau_g \ll 1 \), \( G' \) and \( G'' \) show different scaling behavior \( (G' \propto \omega^2 \text{ whereas } G'' \propto \omega) \), with \( G' > G'' \). For \( \omega \tau_g \gg 1 \), that is, \( \omega \gg \omega_c \), \( G'' \) approaches a constant limiting plateau value, \( G''_\infty \). \( G''_\infty \) is defined plateau of \( G'' \) in the high frequency region \( (G''_\text{max}) \) and \( G_0 \), according to relation [23]:

\[
\frac{G''_\text{max}}{G_0} \approx \frac{L}{h^3}
\]

(4)

The entanglement length or the average distance between entanglement points along contours of the worm-like micelles can be estimated from the mesh size \( L \) using the relation:

\[
L \approx \frac{2.43}{\eta_f} \]

(5)

where \( L_p \) is the persistence length of worm-like micelle. The plateau modulus allows one to obtain the mesh size of the network at temperature \( T \) using the relation [24,25]:

\[
G_0 \approx \frac{k_B T}{L^3}
\]

(6)

where \( k_B \) is Boltzmann constant. At a particular temperature, \( G_0 \) is the measure of the degree of entanglements. It should be noted that these relations are based on the polymer dynamics, and therefore, they are best applicable to nonionic systems.

Fig. 3(a) shows the oscillatory-shear rate behavior of the viscoelastic samples of the CTAB–C12EO4 and C12EO6 systems at compositions corresponding the maximum viscosity region. The oscillatory shear behavior at low frequency region can be described by the Maxwell behavior. Fig. 3(b) shows the Cole–Cole plot for different CTAB–C12EO4 systems. As can be seen from Fig. 3(a) and (b), with increasing \( X \) up to \( X \sim 0.50 \), the system approaches closer to the Maxwellian behavior with a well defined plateau of \( G' \) in the high-\( \omega \) region, and the \( \omega_0 \) shifts to low frequency which means that \( \tau_g \) increases. At \( X = 0.525 \), the \( \omega_0 \) shifts back to a higher frequency values which corresponds to a sharp decrease in \( \tau_g \) and the oscillatory-shear behavior shows increasing deviation from Maxwellian behavior again as can be seen from the Cole–Cole plot.

The rheological parameters \( G_0 \) and \( \tau_g \) may be obtained by fitting of the oscillatory shear data to the Maxwell equations (Eqs. (1) and (2)). As can be seen from Fig. 3, \( G' \) at high-\( \omega \) region \( (G'_0) \) does not always attain a perfect plateau if there are additional fast relaxation processes, but it is often higher than the \( G_0 \) value obtained by fitting the low-frequency data points to Maxwell model. Therefore, the values of \( G_0 \) estimated from Maxwell equations should be considered as the lower limit for the shear modulus. The values of \( G_0 \) and \( \tau_g \) obtained from Maxwell fit are plotted as a function of \( X \) and shown in Fig. 7. The increase in these parameters up to \( X \sim 0.50 \) (viscosity-maximum) may be taken as the evidence of the one-dimensional micellar growth, and consequently, an increase in the degree of the entanglement of the worm-like micelles. Further increase in \( X \) results in a nearly constant \( G_0 \) but a sharp decrease in \( \tau_g \), which means that the network of worm-like micelles remains roughly unchanged, but some structural change occurs that allows a fast stress relaxation. One of the possibilities...
is that after the saturation of micellar growth, further addition of C\textsubscript{12}EO\textsubscript{3}\(\textsubscript{0.055}\) to the system results in the connection of the worm-like micelles with each other, forming a saddle-shaped joint that can slip along its length, thereby allowing a faster and easier way of stress relaxation \([4,26]\).

If we assume similar degree of branching at the viscosity-maxima, then the decreasing \(\tau\) with increasing EO chain length dispersion could be due to shorter micellar length if we assume similar degree of branching at the viscosity-maxima.

### 3.2. Rheological behavior of aqueous P1695--C\textsubscript{12}EO\textsubscript{3} systems

Fig. 5 shows the results of steady-shear rate sweep tests of P1695--C\textsubscript{12}EO\textsubscript{3}\(\textsubscript{0.27}\) systems at 30 °C for different values of \(X\). General pattern of the steady shear rate--viscosity curve is similar to that of the CTAB system described previously, but shear-thinning in the P1695 system is observed at comparatively lower value of \(X\) (\(X=0.055\)). At \(X=0.153\), the system attains a maximum \(\eta\) and forms a well-developed network. This concentration is significantly lower than the corresponding values for the CTAB systems. Stress plateau is observed at high shear rate (Fig. 5 inset) in P1695 systems of high viscosity, indicating shear banding. At \(X=0.40\), phase separation takes place in the P1695 system.

Viscoelastic solutions are formed at compositions around the viscosity-maximum. The results of oscillatory-shear measurements at two different compositions, \(X=0.153\) and 0.267, are shown in Fig. 6(a). In the figure, the corresponding Maxwell fit to the data points are shown by solid line. At high molar ratio \(C\textsubscript{12}EO\textsubscript{3}\textsubscript{0.67}\), \(X>0.27\), no \(G^\prime\)'--\(G^\prime\) cross-over (that is, \(G^\prime\prime\) > \(G^\prime\))
Fig. 6. (a) Oscillatory shear behavior of aqueous P1695–C12EO¯3(1+5) systems. $G'$ (open symbols), $G''$ (filled symbols). (b) Cole–Cole plots of the system at different values of $X$: 0.106 (A), 0.153 (B), 0.184 (C), 0.213 (D) and 0.267 (E). (c) Variation of $G_0$ and $\tau_R$ for the P1695–C12EO3 systems as a function of $X$.

is observed over entire range of $\omega$ studied. The Cole–Cole plot of the P1695–C12EO3 systems are shown in Fig. 6(b). The Maxwellian behavior is observed over wide range of composition. Fig. 6(c) shows the plot of $G_0$ and $\tau_R$, as obtained from the Maxwell fit, as a function of $X$. The $\tau_R$ shows a trend similar to that observed in the CTAB–C12EO3 system (Fig. 7), that is, it increases up to its maximum value at $X$ corresponding to viscosity maximum, followed by a decrease. However, $G_0$ keeps up an increasing trend. This trend suggests that even after the maximum viscosity, interconnected network continues to form. Estimation of mesh size of the network using Eq. (6) at a composition corresponding to maximum viscosity gives a mesh size of $\xi \sim 58$ nm which seems to a reasonable value for worm-like micellar network. Estimation of $l_p$ from $\xi$ requires the value of $l_p$ (see Eq. (5)) which is not available for the present nonionic system. Typical values of $l_p$ for worm-like micelles in cationic surfactant of comparable alkyl chain length and salt systems ranges from 15–46 nm [27]. The lowest value for $G''_{\text{min}}/G_0$ for the P1695–C12EO3 system is 0.087. If we assume $l_p = 100$ nm, which lies within the range of typical values of $l_p$ reported for worm-like micellar systems, the maximum contour length $L$ for the present system may be estimated (Eq. (4)) to be $\sim 1$ µm.

$G_0$–$l_p$ and $G''_{\text{min}}$ of different P1695 systems are shown in Fig. 7(a). The growth rate of zero-shear viscosity for different P1695 systems is nearly similar in the rapid micellar growth regime (Figs. 4 and 8). It can be seen that the growth rate of $\eta_0$ as a function of $X$ in the rapid micellar growth regime is nearly similar in the P1695 and CTAB systems (Figs. 8(a)). In the P1695 system the effect of the dispersion of the EO chain on the zero-shear viscosity is pronounced only at compositions corresponding to the maximum viscosity region ($X \sim 0.15$).

Fig. 8. (a) Variation of zero-shear viscosity ($\eta_0$) of different P1695–C12EO3 systems as a function of $X$. (b) Variation of $\eta_0$, $G_0$ and $\tau_R$ in the mixed surfactant systems at compositions corresponding to the viscosity maxima.
Viscoelastic solutions are formed with C12EO0(0+4) in P1695 solution. Note that C12EO6 does not form viscoelastic solution in CTAB system, but shows phase separation at low mixing fraction.

To obtain the information on the effect of the EO chain dispersion on the microstructure of the viscoelastic system at maximum-viscosity region, a plot of n0, G0 and Gη for different systems are shown in Fig. 8(b). Variation of the rheological parameters in the P1695 system with EO chain dispersion show the trend essentially similar to that observed in the CTAB system (Fig. 4b). Nearly constant G0 in all EO dispersions implies that there is no significant effect of EO chain dispersion on the network density or mesh size.

4. Discussion

The rheological measurements in the CTAB–C12EO3 and P1695–C12EO3 as well as P1695–C12EO6 systems show that the micellar growth in the mixed surfactant system is affected by the dispersion of the EO chain length. On the basis of these results, it is reasonable to expect that, although the average EO chain length is 3 in the C12EO3 mixture, the short and long EO chain molecules are not distributed homogeneously in the aggregates. This type of inhomogeneity in the distribution of amphiphilic molecules in the aggregates of mixed surfactant is associated with the inhomogeneity in the interfacial curvature in the aggregate.

When the packing constraints of amphiphiles in the mixed surfactant system, for example, CTAB + C12EO system, favor the formation of cylindrical aggregate, homogeneous distribution of the amphiphilic molecules in the aggregate would mean that in the end caps the amphiphiles are forced to pack into hemispherical caps with a headgroup area (ads) determined by the packing parameter \( \bar{v} = \frac{\bar{a}}{\bar{L}} \geq 1/3 \) [28]. Since \( \bar{v}/\bar{a} \geq 1/3 \) for rodlike aggregates, we get \( \bar{a}_{ads} \geq \bar{a}_{r} \), which is energetically unfavorable. The unfavorable end-energy of cylindrical micelles may be eliminated if the two ends join, thereby inducing one-dimensional growth. The frustration of the end-caps can be minimized significantly, however, if the amphiphiles with bigger head group are preferably accommodated in the end caps, and the decrease in the curvature free energy. This type of partial segregation of surfactant and cosurfactant molecules inside an aggregate with inhomogeneous curvature has been believed to be responsible for the stabilization of the aggregates [29,30]. The consequence of the partial segregation is that the micellar ends are more stable than they would be with homogeneous mixing of the amphiphiles, and a higher concentration of nonionic amphiphile is required to achieve a similar extent of micellar growth in the mixed surfactant systems.

A qualitative explanation for the observed effect of dispersion of the EO chain length on the viscosity based on the partial segregation is provided. When a mixture of C12EO6 is used instead of pure C12EO in the CTAB system, the amphiphiles of long-EO are preferably incorporated in the end-caps over those with short-EO chain. This would enhance the stability of the end-caps, and consequently, reduce the extent of micellar growth at a value of X. For a value of X above the viscosity-maximum, however, the number of micellar free end progressively decreases due to formation of micellar joints, and consequently the effect of dispersion of the viscosity is lost. It is interesting to note that the micellar growth in the CTAB–C12EO6 system is more favorable than that in the CTAB–C12EO0 system even though the degree of dispersion of the EO chain, that is, the difference between the number of EO chain between the individual C12EO3 amphiphiles, is same. The difference in the micellar growth may be attributed to the higher contribution of the C12EO6 in the stability of the end-cap. In the CTAB–C12EO0 system, no micellar growth is observed and a phase separation occurs with the formation of lamellar-like aggregate. It is possible that with C12EO8, which has a large head group area, the highly curved part is stabilized, and therefore, the C12EO8 (decanol) present in the system promotes the formation of disc-like micelle (lamellar-like structure) because of the low energy cost of the formation of the curved rim of the aggregate, although the area of the curved region has increased. This assumption is still to be confirmed experimentally.

Since nonionic P1695 has an alkyl chain length comparable to that of CTAB but has a smaller 3, the aggregates of nonionic P1695 system at a value of X is expected to be more susceptible to one-dimensional micellar growth than the aggregates of the CTAB systems. In fact, even in surfactant-water binary system, the viscosity of P1695 system is higher by one order than that of CTAB, which corresponds to a greater extent of micellar growth in the aqueous P1695 system upon adding C12EO3 to the P1695 solution. The lower extent of the effect of the dispersion of EO chain length in comparison to the corresponding CTAB system is probably due to lower degree of the segregation of the amphiphiles in the nonionic P1695 system, as compared with the ionic CTAB system. The fact that the P1695–C12EO0 system form a worm-like micelle whereas CTAB–C12EO0 systems undergo a phase separation is due to lower degree of segregation of the amphiphiles, and consequently, a high free energy cost for the formation of highly curved interface in the aggregates of P1695–C12EO0 systems.

In the present study, only the effect of bimodal distribution of EO chain has been considered. In real practice, commercial surfactants consist of more than two components with Gaussian or Schultz-like distribution of chain length. Moreover, the distribution of alkyl chain is another factor that is likely to affect the micellar growth because such a distribution would affect the packing constraint in the micellar core and consequently end cap energy. These points will be addressed in a separate paper.

5. Conclusion

Formation of viscoelastic solution of worm-like micelles upon addition of lipophilic C12EO3 to CTAB and P1695 aqueous solutions has been recently reported. The present study shows that the viscoelastic solutions can be formed by using the C12EO3 mixture with an average EO chain of 3. However, as the dispersion of the EO-chain length increases, the extent of micellar growth and the maximum viscosity that can be achieved...
is reduced, especially in the cationic system, which is attributed to the increased stabilization of the micellar end caps by long EO chain.

Acknowledgement

DPA is thankful to Japan Society for the Promotion of Science (JSPS) for financial support.

References