Rheological Behavior of Polyoxyethylene Phytosterol-Polyoxyethylene Cholesterol/Tetraethylene Glycol Monododecyl Ether/Water Systems

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Abstract: We have studied the rheological properties of mixtures of polyoxyethylene (10 mol) phytosterol (PhyEO10) and polyoxyethylene (10 mol) cholesterol (ChEO10) mixed in different ratios along with tetraethylene glycol monododecyl ether (C12EO4) surfactants in water. Addition of C12EO4 to the aqueous solution of a mixture of (PhyEO10 + ChEO10) results in one-dimensional micellar growth and formation of viscoelastic solution of entangled wormlike micelles. Steady-shear rheological measurements show the Newtonian flow behavior at low shear-rate region and non-Newtonian flow behavior at higher shear-rate for viscous samples. The dynamic rheological data of the viscoelastic samples indicate the plateau modulus (Go) increases monotonically with C12EO4 concentration and relaxation time (τR) display a maximum at a composition corresponding to the viscosity maximum. The prepared viscoelastic sample in mixed nonionic surfactant systems has potential applications in cosmetic formulation.

Key words: polyoxyethylene phytosterol, polyoxyethylene cholesterol, zero-shear viscosity, wormlike micelle, rheology

1 INTRODUCTION

In most practical applications, mixtures of surfactants rather than individual surfactants are used. This is often because the materials used in commercial products are impure. In other cases, different types of surfactants are intentionally mixed to provide the enhanced performance of the final product. When different types of surfactants are mixed in water, several properties of the mixed system change compared to those of the single surfactant as a result of synergism. Mixtures of two nonionic surfactants with similar head group usually show an almost ideal behavior, namely, the values of the molecular interaction parameter β are small1. Here, β indicates the nature and strength of the interaction between the two different surfactant molecules forming the mixed micelles in an aqueous solution; the larger the value of β, the stronger the interaction between the two surfactants2. It has been found that the β is small and negative for polyoxyethylene alkyl ether surfactant systems.

There are several reports on the formation and rheological behavior of the viscoelastic solution of wormlike micelles in mixed nonionic surfactant systems3-8. In these systems, interfacial curvature of the aggregates can be tuned to induce the sphere-rod transition and one-dimensional micellar growth via the addition of lipophilic surfactants, such as polyoxyethylene alkyl ether or long chain monoglyceride. Sharma et al.9-12 noted the similar tendency in the mixed nonionic fluorocarbon surfactant systems. Polyoxyethylene phytosterol and polyoxyethylene cholesterol are well-known environment-friendly surfactants, and are widely used as emulsifiers, and also in pharmaceutical and cosmetic formulations. In these surfactants, the segregation tendency between the hydrophilic and the hydrophobic group is very strong compared with conventional alkyl ethoxylated surfactants, and hence, they show unique phase behavior in the presence of water and water/cosurfactant13-16. Naito et al.15 reported the formation of viscoelastic wormlike micellar solution in polyoxyethylene phytosterol (PhyEO10 and PhyEO20) surfactant systems and studied the effect of head group size of cosurfactant. Acharya et al.3,17 found that highly viscoelastic wormlike micelles can be formed in the salt-free condition when a lipo-
philic nonionic surfactant such as short hydrophilic chain polyoxyethylene alkyl ether or dodecanoyl-$N$-methylethanolamide is added to the dilute micellar solution of polyoxyethylene cholesterol surfactant. However, there is no systematic study on the micellar growth in an aqueous solution of a mixture of surfactants with similar head group. In this context, we studied the rheological behavior of viscoelastic wormlike micelles in an aqueous mixture of polyoxyethylene phytosterol and polyoxyethylene cholesterol under the presence of short-chain polyoxyethylene alkyl ether type nonionic surfactant as a cosurfactant.

2 EXPERIMENTAL

2.1 Material and sample preparation

Polyoxyethylene (10 mol) phytosterol (abbreviated as PhyEO$_{10}$) was kindly supplied from Cosmos Technical Centre, Co., Ltd., Japan. Similarly, polyoxyethylene (10 mol) cholesterol (designated as ChEO$_{10}$) was purchased from Nihon Emulsion Co., Japan. The schematic molecular structures of PhyEO$_{10}$ and ChEO$_{10}$ are shown in Scheme 1. Tetraethylene glycol monododecyl ether (C$_{12}$EO$_{4}$) was purchased from Nikko Chemicals Co., Ltd., Japan. All the chemicals were used as received. Millipore water was used throughout the experiment. First, 0.06M solutions of PhyEO$_{10}$ and ChEO$_{10}$ were prepared separately. After equilibration for 24 h at room temperature, mixtures of the two solutions (PhyEO$_{10}$ and ChEO$_{10}$) at various ratios were prepared keeping the total surfactant concentration fixed at 0.06M. The samples were prepared by adding required amount of C$_{12}$EO$_{4}$ to a weighted amount of 0.06M (PhyEO$_{10}$ + ChEO$_{10}$) solution.

2.2 Rheological measurements

Samples were homogenized and kept in a water bath at 25°C for at least 24 h to ensure equilibration before performing measurements. The rheological measurements were performed in a stress-controlled rheometer, AR-G2 (TA Instruments, UK) using cone-plate geometries (diameter of 60 mm with cone angle of 2° 1’ 9” for low-viscosity sample and diameter 40 mm with cone angle of 2° 0’ 4” for high-viscosity sample) with the plate temperature controlled by a Peltier unit. A sample cover was used to minimize the change in sample composition by evaporation during the measurement. Frequency sweep measurements ($\omega = 100$ rad.s$^{-1}$ to 0.01 rad.s$^{-1}$) were performed in the linear viscoelastic regime of the samples, as determined previously by dynamic strain sweep measurements.

3 RESULTS AND DISCUSSION

3.1 Steady-shear rheological behavior

In the water/PhyEO$_{10}$ and water/ChEO$_{10}$ binary systems, the micellar (W$_m$) phase appears up to ~14 wt% and ~30 wt% of surfactant at 25°C, respectively. It has been found that micellar solution of 0.06M PhyEO$_{10}$ behaves as viscoelastic fluid while 0.06M ChEO$_{10}$ solution forms spherical micelles.$^{5,14,16}$ In order to obtain the information about the structural change of micelles in the surfactant mixture,

![Scheme 1 Schematic Molecular Structures of PhyEO$_{10}$ (a) and ChEO$_{10}$ (b).](image)

![Fig. 1 Steady Shear-rate ($\dot{\gamma}$) versus Viscosity ($\eta$) Curves for [0.06M (PhyEO$_{10}$+ChEO$_{10}$)+C$_{12}$EO$_{4}$] Systems at Various Mixing Fraction of C$_{12}$EO$_{4}$ in Total Surfactant, X with R=50/50.](image)
steady-shear rheological measurements were carried out on 0.06M (PhyEO$_{10}$ + ChEO$_{10}$) + C$_{12}$EO$_{4}$ solutions at various $R$ (PhyEO$_{10}$ to ChEO$_{10}$ weight ratios).

Figure 1 shows shear-rate ($\gamma$) versus viscosity ($\eta$) curves for 0.06M (PhyEO$_{10}$ + ChEO$_{10}$) + C$_{12}$EO$_{4}$ systems at various mixing fraction of C$_{12}$EO$_{4}$, expressed in mole fraction of C$_{12}$EO$_{4}$ in total surfactant, $X$ with $R=50/50$ at 25°C. The $\eta$ of surfactant mixture without addition of C$_{12}$EO$_{4}$ is very low and almost independent of $\gamma$, although very weak shear thinning is observed at higher $\gamma$. At $X=0.292$, the Newtonian behavior is limited at low $\gamma$, but shear thinning occurs at large deformation ($\gamma \approx 10$ s$^{-1}$), which is typical for wormlike micellar solution aligned under shear.$^{18}$ The micellar growth induced by C$_{12}$EO$_{4}$ will be discussed in the next section. With further increasing $X$ up to $X=0.453$, the wormlike micelles become entangled into a transient network, thereby enhancing the viscoelasticity of the fluid. However, upon further addition of C$_{12}$EO$_{4}$ at $X=0.491$ and 0.608$, the viscosity decreases indicating the structural transition. This behavior can be attributed to micellar branching which causes the formation of slipping points that allow fast relaxation process.$^{19,20}$ Steady-shear measurements on 0.06M (PhyEO$_{10}$ + ChEO$_{10}$) + C$_{12}$EO$_{4}$ systems with $R=100/0, 80/20, 20/80, 0/100$ show a similar trend of shear-rate versus viscosity curves, although a relatively higher viscosity value is observed with increasing PhyEO$_{10}$ content in the surfactant mixture. The additional branching of the alkyl chain in the lipophilic moiety of the phytosterol surfactant, which in turn reduces the interfacial curvature of the aggregate in the mixed system to a greater extent, seems to be a possible reason for the enhanced micellar growth.

3.2 Zero-shear viscosity

The variation of zero-shear viscosity ($\eta_0$) as a function of the mixing fraction of C$_{12}$EO$_{4}$ in total surfactant, $X$ at different $R$ for 0.06M (PhyEO$_{10}$ + ChEO$_{10}$) + C$_{12}$EO$_{4}$ systems is presented in Fig. 2.

The $\eta_0$ values for the Newtonian systems have been estimated by extrapolating the viscosity data points to zero shear-rate. For viscoelastic samples, $\eta_0$ can be calculated from oscillatory shear measurement (see eq. 3). As can be seen in the figure, above a certain value of $X$, $\eta_0$ increases steeply, achieves the maximum, and then declines for all $R$. The increase in $\eta_0$ with increasing $X$ suggests the formation of wormlike micelles due to decrease in the surfactant layer curvature with the incorporation of C$_{12}$EO$_{4}$ into the plicated layer of the surfactant aggregate. As $X$ is increased further, wormlike micelles start to form a transient network that exhibit viscoelastic properties. With further addition of $X$, $\eta_0$ passes through a maximum and then decreases, which indicates a structural change, probably the formation of micellar joints as explained above. The trend of $\eta_0$ versus $X$ curves for all $R$ is essentially similar but the viscosity maximum gradually shifts to a lower value of $X$ with increasing $R$. The shifting of $\eta_0$ versus $X$ curves toward the left side reveals that the enhanced micellar growth takes place at lower concentration of C$_{12}$EO$_{4}$ due to higher PhyEO$_{10}$ content in the surfactant mixture. At higher concentration of C$_{12}$EO$_{4}$ (i.e., $X>0.48$), $\eta_0$ is nearly same until the phase separation for all $R$.

3.3 Dynamic rheological behavior

Viscoelastic wormlike micellar solutions are formed in the vicinity of the maximum-viscosity region. Viscoelastic properties of such solutions were investigated by dynamic frequency sweep measurements. Under oscillatory shear, the viscoelastic micellar solutions usually behave as a Maxwell fluid with a single relaxation time, and the elastic or storage modulus $G'(\omega)$ and the viscous or loss modulus $G''(\omega)$ obey the following relations as a function of the oscillatory shear frequency ($\omega$):

$$G'(\omega) = \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} G'_0$$

$$G''(\omega) = \frac{\omega \tau}{1 + \omega^2 \tau^2} G'_0$$

where $G'_0$ and $\tau_0$ are the shear (plateau) modulus and the relaxation time respectively. At high-$\omega$, $G'$ tends to attain a constant value equal to $G'_0$. The relaxation time, $\tau_0$ may be estimated from the $G''$ - $G''_0$ crossover frequency, that is, $\tau_0 = 1/\omega_0$ when $G'' = G''_0$. The zero-shear viscosity ($\eta_0$) can be calculated using following relation:

$$\eta_0 = G'_0 \tau_0$$

Figure 3a shows the representative plots of elastic mod-
ulus ($G'$) and viscous modulus ($G''$) as a function of oscillatory shear frequency ($\omega$) for 0.06M (PhyEO10+ChEO10)+C12EO4 with $R = 50/50$ at $X = 0.344$, 0.409, and 0.549. At low-$\omega$, the sample exhibits liquid-like behavior ($G'' > G'$), but both $G'$ and $G''$ increase with $\omega$, and solid-like behavior ($G' > G''$) is attained at high-$\omega$. The arrows highlight the intersection point of $G'$ and $G''$.

Solid lines in Fig. 3a show the Maxwellian fitting to the data points. The rheological behavior at low-$\omega$ region can be described by the Maxwell model but at high-$\omega$ region, experimental data show significant deviation from the Maxwell model showing an upturn in the viscous modulus $G''$. This deviation arises from the transition of the relaxation mode from “slower” reptation to “faster” Rouse modes. Maxwellian oscillatory rheological behavior of viscous solutions, such as that shown in Fig. 3, can be related to the transient network formed by the entanglement of very long and flexible wormlike micelles.

As it can be seen from Fig. 3a, with increasing $X$, the $G'$ - $G''$ crossover frequency shifts to the left and attains the smallest value at $X = 0.409$ which corresponds to a longest relaxation time for a given system. With a further increase in $X$, the $G'$ - $G''$ crossover frequency moves to the right with a shorter relaxation time and shows a weak viscoelastic property. We obtained similar results on dynamic measurements for the rest $R$. Figure 3b allows one to compare the dynamic rheological behavior near the viscosity maximum for all $R$. With decreasing $R$, the $G'$ - $G''$ crossover frequency shifts to a higher value continuously with a shorter relaxation time due to low PhyEO10 content in the surfactant mixture.

The Cole-Cole plots for 0.06M (PhyEO10+ChEO10)+C12EO4 system with $R = 50/50$ at different $X$ are presented in Fig. 4. The experimental data points closely follow Maxwell model with a semicircular behavior in the Cole-Cole plot at lower $X$.

The Plateau modulus, $G_0$ and relaxation time, $\tau_\alpha$ are estimated by fitting of the experimental data, especially the
data in low-frequency region, to the Maxwell equations. Figure 5 shows the variation of $G_\ast$ and $\tau_\ast$ as a function of $X$ at different $R$ values. The value of $G_\ast$ is related to the number of entanglements between wormlike micelles and $\tau_\ast$ given by the Maxwell equation reflects the length of wormlike micelles.

It can be seen that the continuous increase of $G_\ast$ with increasing $X$ corresponds to the increase in the network density of the wormlike micelles for all $R$. On the other hand, $\tau_\ast$ increases initially along with increasing $G_\ast$ and $X$, which may be associated with the micellar growth. With further increase in $X$, $\tau_\ast$ decreases indicating a structural change in the network that allows a faster mechanism of stress relaxation. The breaking of the micelles is not possible because the monotonic increase in $G_\ast$ clearly indicates that network density increases with $X$. These results are in accordance with the formation of micellar joints or branching, because sliding of the branching point along the micellar length can provide a fast stress relaxation. The longer relaxation time obtained toward lower $X$ values with increasing $R$ corresponds to the higher extent of micellar growth. This fact is well supported by the increase of network density or $G_\ast$ with increasing $R$.

4 CONCLUSIONS

Addition of C$_{12}$EO$_4$ to the aqueous solution of a mixture of PhyEO$_{10}$ and ChEO$_{10}$ induces one-dimensional micellar growth, and results in the formation of viscoelastic solution composed of entangled wormlike micelles at a certain mixing fraction of C$_{12}$EO$_4$. The viscosity increases more steeply for the surfactant mixture with higher PhyEO$_{10}$ content. This is attributed to the additional branching of alkyl chain in the lipophilic moiety of PhyEO$_{10}$, because it acts to reduce the micellar surface curvature and facilitates the micellar growth. We believe that the present viscoelastic sample prepared from environment-friendly and low-toxic surfactant mixtures would be extremely useful in cosmetic formulation.

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References


