The Study of Salt Induced Viscoelastic Wormlike Micelles in Aqueous Systems of Mixed Anionic/Nonionic Surfactants

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Abstract

Formation of viscoelastic wormlike micelles in aqueous systems of mixed amino acid based anionic and nonionic surfactants in presence of salt is presented. N-dodecylglutamic acid (LAD) upon neutralization with L-Lysine in 1:2 mole ratio forms globular type of micelles above critical micelle concentration and the solution follows Newtonian fluid like behavior at 25°C. The addition of tri(oxyethylene) n-monotetradecyl ether ($C_{14}EO_3$) to the semi-dilute aqueous solution of the LAD-Lysine-2 induces one dimensional micellar growth and viscosity of solution increases. After a certain concentration of $C_{14}EO_3$ micelles get entangled and form a rigid network of wormlike micelles and viscosity increases by several orders of magnitude. The wormlike micellar solutions show a viscoelastic character and can be described the Maxwell mechanical model with a single stress relaxation. Rheological measurements have shown that zero shear viscosity (η_o) increases with the $C_{14}EO_3$ concentration gradually at first sharpl, and then finally decreases before phase separation.

Keywords: nonionic surfactant, wormlike micelles, rheology, viscoelastic solutions.

Introduction

Surfactants when added in water self assemble into a variety of microstructures like spherical, cylindrical and reverse micelles above critical micelle concentration (CMC), and at high concentrations variety of lyotropic mesophases are formed.[1] These microstructures have strong influence on the rheological properties. Under a certain conditions of temperature or the presence of counter-ions, one dimensional micellar growth takes place forming a long flexible aggregate

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called wormlike micelle.[2-6] Above an overlapping concentration, the wormlike micelles get entangled with each other to form a transient network, which in turn exhibit viscoelastic properties and is very much similar to those observed in solutions of flexible polymers.[7] However, wormlike micelles are in dynamic equilibrium with their monomers and the micellar chains can break and recombine.[8] These micelles are practically important because of their peculiar properties and potential industrial applications like food emulsion, cosmetics, paints, pharmaceuticals, adhesives and many household products.[9,10] Therefore, wormlike micelles have been studied with an interest since few decades. The knowledge of structure and dynamics of the wormlike micelles is of the essence for the optimization of its practical applications.

In the case of charged micelles, micellar growth occurs as a consequence of the reduction of repulsion between the surfactant head and groups. Inorganic or organic salts, strongly binding counter ions or cosurfactants induce sphere-to-wormlike transition in the nanostructure in ionic surfactants[11-13] or in mixed ionic/nonionic surfactant systems.[14-16] Similarly, wormlike micelles have been reported in several sets of mixed cationic and anionic surfactants systems.[17-19] Anionic surfactants are biodegradable and less toxic compared to the cationic ones. It had reported that the formation of wormlike micelles produced by anionic surfactants could offer many advantages over their cationic counterparts in many applications like cosmetics, toiletry and pharmaceutical products.[20] Amino acid based anionic surfactants both natural and synthetic types have been the subjects of many studies, mostly due to their huge potential applications in cosmetic and household products because of their mildness to the skin.

The paper at hand reports the formation of wormlike micelles in the dilute aqueous systems of mixed amino acid based anionic/nonionic surfactant systems.

Experimental Methods

The anionic surfactant LAD with 99.9 % pure was received from Ajinomoto Co., Inc. Japan. The nonionic surfactant tri(oxyethylene) *n*-monotetradecyl ether, ($C_{14}EO_3$) was from Nikko Chemicals Co., Ltd. Japan. The LAD was neutralized by L-Lysine in the molar ratio of 1:2. For the sake of clarity we have represented the neutralized products as LAD-Lysine-2. All the surfactants were used as received without further purifications. Millilpore filter water was used. The molecular structure of the LAD is shown in Scheme 1.

For the study of phase behavior, sealed ampoules containing required amount of reagents were mixed at higher temperature and homogenized with a vortex mixer and by repeated centrifugation. After proper mixing, the samples were kept in a thermostated water bath at 25°C for several days to ensure equilibrium. The

equilibrium phases were identified by visual observations through normal and crossed polarizer.
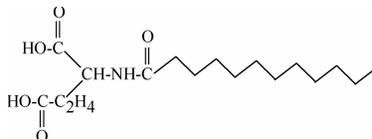
Scheme 1: Molecular Structure of N-dodecylglutamic acid (LAD).

Samples for rheological measurements were homogenized and kept in water bath at specified temperature for at least 24 hrs to ensure equilibration before performing measurements. The rheological measurements were performed on an AR-G2 stress-controlled rheometer using cone-plate geometries with Peltier-based temperature controller. A sample cover was used to minimize the change in sample composition by evaporation during the measurement. Frequency sweep measurements were performed in the linear viscoelastic regime of the samples.

Results and Discussion

Phase behavior

The LAD does not form any self-assembled structures in water at 25 °C due to its higher Krafft temperature (58°C). There appears only solid and liquid phase at normal room temperature. However, when it is neutralized by L-Lysine in 1:2 mole ratios, the Krafft temperature is reduced and it forms micellar solution at room temperature.

The partial ternary phase diagram of LAD-Lysine-2/water/$C_{14}EO_3$ systems at 25 °C in the dilute region is shown in Fig. 1. The shaded area in the phase diagram represents the viscous region. In the LAD-Lysine-2/water binary system, isotropic solution is formed over wide range of surfactant concentrations at 25°C. At high surfactant concentrations (>40 wt%) the isotropic discontinuous cubic (I_1) phase is observed. A large head-group of the surfactant molecule favors small and discrete aggregates of positive curvature. When the volume fraction of the surfactant increases, the number density of the micelles increases instead of micellar elongation and at higher concentrations repulsive intermicellar interaction comes into play, which induces micelle ordering to cubic phase.

The extended W_m domain in the ternary phase diagram shows that the micellar solution of LAD-Lysine-2 can solubilize a significant amount of $C_{14}EO_3$. Upon successive addition of $C_{14}EO_3$, at higher concentrations of LAD-Lysine-2 (>20 wt%) viscosity increases gradually at first and then sharply till phase separation. However, highly viscous region was not observed below 20 wt% of the LAD-Lysine-2. The samples in the highly viscous regions are isotropic at rest, but

are birefringent when applied a shear, which is a typical behavior of wormlike micelles indicating the formation of wormlike micelles. Further increasing concentration results phase separation giving different phases depending on the mixing fraction of the surfactant LAD. As for example, two liquid phases are observed below the 20 wt% LAD and at higher concentrations, lamellar liquid crystal separates out from the isotropic solution. At higher surfactant concentrations, ~40 wt% line, hexagonal phase is observed. The structures of liquid crystal phases are confirmed by small-angle X-ray scattering (SAXS).
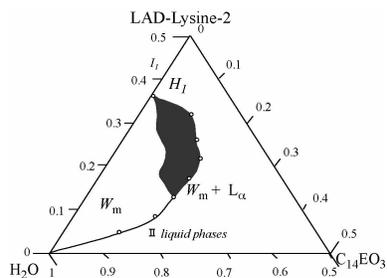
Figure 1: Phase diagram of the LAD-Lysine-2/water/$C_{14}EO_3$ system in dilute region at 25 °C. W_m is the micellar phase. The H_1, L_α, and I_1 is the hexagonal, lamellar and discrete cubic phases, respectively. The shaded area shows highly viscous region of wormlike micelles (Ref. 19).

Rheological behavior

Figure 2 shows the steady shear-rate ($\dot{\gamma}$) – viscosity (η) curves for 10 wt% LAD-Lysine-2 + $C_{14}EO_3$ system at different mixing fraction of $C_{14}EO_3$, expressed in wt% of $C_{14}EO_3$ in total surfactant in the presence of 1M NaCl at 25°C. At lower concentrations of the $C_{14}EO_3$, η is very small close to that of pure solvent and independent of $\dot{\gamma}$, i.e., Newtonian flow behavior is observed throughout the measured $\dot{\gamma}$. However, as the concentration of the $C_{14}EO_3$ is increased, η increases and the shear thinning which is a typical behavior of wormlike micelles is observed. At 8.5% $C_{14}EO_3$, the behavior is still Newtonian over wide range of shear rate, but shear thinning occurs at $\dot{\gamma} \geq 100$ s^{-1}. With further increasing concentration, the critical shear rate, $\dot{\gamma}_c$ shifts gradually to the lower values and also the viscosity in the plateau region (low-$\dot{\gamma}$ region) increases. This phenomenon highlights that the system is getting more structured. The observed rheological behavior is typical of network structure formed by wormlike micelles. When network structure is deformed by applying a shear, shear thinning occurs due to alignment of aggregates under flow if the deformation is faster than the time required to regain equilibrium network structure, and with increasing network density the relaxation becomes slower, i.e., shear thinning begins at lower shear rate.

Successive increase in the surfactant concentration above 10.2%, decreases viscosity and a slightly higher deformation rate is required to induce shear thinning indicating microstructural structural transformation in the network structure. One of the possibilities is that the system becomes less structured, i.e., micellar length decreases and network structure is gradually lost. This point will be discussed in the dynamic rheological section performed for the same set of samples under the identical conditions.

Figure 3 shows the zero –shear viscosity (η_0) versus wt% of $C_{14}EO_3$ with and without salt systems at 25 °C. In absence of salt, with increasing $C_{14}EO_3$ concentration the viscosity increases almost in a linear fashion above 5 wt% $C_{14}EO_3$ until phase separation. The maximum η_0 observed prior to phase separation is ~ 0.3 Pa.s. The viscosity growth with increasing $C_{14}EO_3$ concentration can be taken as a strong evidence of anionic micellar growth induced by the nonionic cosurfactant. However, these elongated micelles could not entangle with each other to form a rigid network of wormlike micelles.
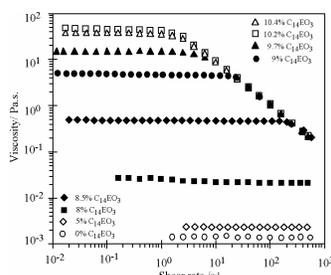
Figure 2: Viscosity versus shear rate of the LAD-Lysine-2/water/$C_{14}EO_3$ system along 10 wt% LAD-Lysine-2 line at different mixing fraction of the $C_{14}EO_3$ in the presence of 1M NaCl at 25 °C.

A dramatic change in the steady shear rheological behavior is observed when 1 M NaCl is incorporated in the system as shown in Fig. 3. The η_0 of the salt added system is much higher than that without salt. Until 5 wt% of $C_{14}EO_3$, there is no difference in the steady shear rheology and the viscosities of both systems are identical. Above this concentration, there is a sharp increase in the viscosity of the salt added system. With further increasing concentration, the viscosity reaches to a maximum value and then decreases prior to phase separation. The viscosity decay after the maximum is caused due to some microstructure changes in the network structure of wormlike micelles. Thus, the salt effectively increases the viscosity of the system and in the salt added system a lower amount of cosurfactant is needed to induce micellar growth.

Viscoelastic properties of the wormlike micelles were investigated by oscillatory-shear (frequency sweep) measurements. Frequency sweep measurements were carried out as a function of $C_{14}EO_3$ concentrations at a fixed mixing ratio of LAD-Lysine-2 and the results are presented in Fig. 4. The dynamic rheology data

shows the variation of elastic modulus (G'), and viscous modulus (G'') as a function of oscillation frequency (ω). As can be seen from the Fig. 4, at high ω, the sample exhibits elastic behavior (G' shows a plateau value and dominates over the G''), whereas at lower-ω, the sample shows a viscous behavior (G'' exceeds G'). Thus, the samples show the viscoelastic behavior, which is attributed to the entanglement of the wormlike micelles to form a transient network. In the low-ω regions, the data points of G' and G'' fits well to the following Maxwell's mechanical model of viscoelastic material described elsewhere.[21]
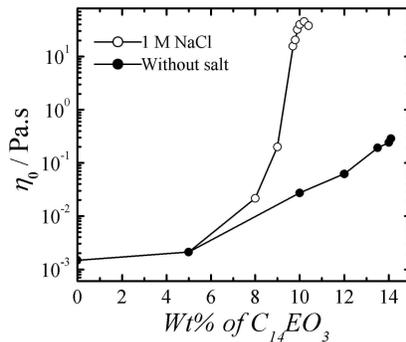
Figure 3: Zero-shear viscosity versus wt% of $C_{14}EO_3$ for different salt systems. In all the systems salt concentration is fixed to 1 M. The composition of LAD-Lysine-2 is fixed to 10 wt% at 25°C. Zero-shear viscosity date without salt is also included for comparison.
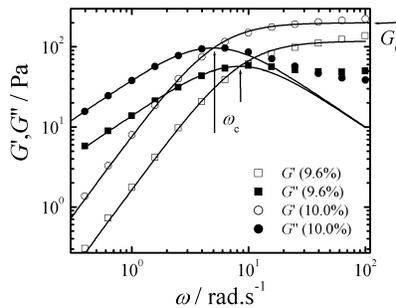
Figure 4: Elastic modulus, G' (open symbols) and viscous modulus, G" (closed symbols) versus oscillatory shear frequency (ω) at different concentrations of $C_{14}EO_3$ expressed in wt%, for the 10 wt%LAD-Lysine-2/water/ $C_{14}EO_3$ system in the presence of 1 M NaCl at 25°C. The solid lines are the Maxwell model fit.

The solid lines in the Fig. 4 represent the Maxwell model fit to the experimental data points (symbols). There is deviation of the G'' from the Maxwell model mainly in the higher-ω region. This deviation corresponds to the fact that wormlike micelles are in dynamic equilibrium and there is a rapid breaking and recombination process.

As can be seen in Fig. 4, with increasing the concentration of $C_{14}EO_3$, the frequency at which the G' and G'' meet (ω_c) shifts towards lower frequency and attains a smallest value at a composition corresponding to the viscosity maximum. With further increasing concentration of $C_{14}EO_3$, the ω_c was finally shifted towards the higher-ω region and thus poorer viscoelastic behavior (data not shown).

The rheological parameters G_0 and τ_R were determined from the Maxwell model fit to the experimental data. Figure 5 shows the variation of G_0 and τ_R with the $C_{14}EO_3$ concentration at 25 °C. The G_0 and τ_R increase with increasing $C_{14}EO_3$ and show a maximum at composition corresponding to the viscosity maximum (Fig. 3) and then decreases. The increasing G_0 indicates that the network density of entangled wormlike micelles increases with $C_{14}EO_3$ concentration. On the other hand, increasing τ_R indicates that the system is getting more structure and it takes longer time to gain original equilibrium condition if wormlike micelles are deformed by applying some stress. Therefore, the viscosity increases with increasing concentration of the $C_{14}EO_3$ until maximum position in η_0-curve can be attributed to the one-dimensional micellar growth and the increased density in the network structure. The decreasing trend of the rheological parameters after the attainment of the maximum values with further increasing $C_{14}EO_3$ concentration implies some structural changes occurred in the wormlike micelles and that allows a faster stress relaxation.[16] The decrease in the value of G_0 simply indicates the decrease in the network density of micelles, which is possible only when micellar breaking takes place. Thus, the viscosity decreases after the maximum (Fig. 3) is due to decrease in the rigidity of the network structures, i.e., micellar breaking.
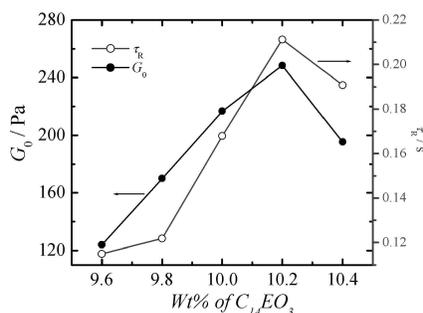
Figure 5: Variation of the plateau modulus (G_0) and relaxation time (τ_R) as a function of the $C_{14}EO_3$ concentration for 10 wt% LAD-Lysine2/water/$C_{14}EO_3$ in the presence of 1 M NaCl at 25°C.

Conclusions

Amino acid based anionic surfactant, LAD when neutralized by L-Lysine forms micellar solution over a wider range of concentrations at 25°C. At higher concentrations, the micellar solution transforms into discontinuous cubic phase. Addition of lipophilic nonionic surfactant ($C_{14}EO_3$) to the dilute solution of the

LAD-Lysine-2 favors the one dimensional micellar growth leading to the formation of wormlike micelles in the presence of salt, which are entangled between them forming a transient network of viscoelastic solution. In addition to the screening effect of the salts, the decrease in the effective cross sectional area of the surfactant by cosurfactant is responsible for the micellar elongation. The viscosity decrease after the maximum with the $C_{14}EO_3$ can be attributed to the breaking of micelles. Dynamic shear rheological measurements have shown that the wormlike micellar solutions fit the single relaxation Maxwell model. The present study can be a guideline to the microstructure control and, hence, the rheological properties of viscoelastic wormlike micelles in the mixed anionic/nonionic surfactant systems.

Acknowledgement

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