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Temperature sensitivity of wormlike micelles in poly(oxyethylene) surfactant solution: Importance of hydrophilic-group size

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ABSTRACT

We have studied the temperature sensitivity of the rheology of the wormlike micellar solutions formed in poly(oxyethylene) cholesteryl ether ($ChEO_m$, m = 15 and 30) upon addition of tri(ethyleneglycol) mono *n*-dodecyl ether ($C_{12}EO_3$) and monolaurin. We have found that increasing the poly(oxyethylene) chain length of $ChEO_m$ greatly reduces the temperature-sensitivity of the viscosity of the solution. In the viscous region small changes in the cosurfactant composition can subtly change the temperature sensitivity depending on the temperature range and type of cosurfactant. For, $C_{12}EO_3$, which is a poly(oxyethylene) surfactant, the temperature sensitivity is lower at lower temperatures and higher at higher temperatures if the cosurfactant mixing fraction is high and vice versa if the mixing fraction is low. For monolaurin, the temperature sensitivity increases with cosurfactant mixing fraction in the viscous region. In the $ChEO_{30}$–monolaurin system viscous solutions are not formed at any temperature that we studied. We have discussed these results in terms of the reduction of the average curvature of micellar interface with temperature due to dehydration of the poly(oxyethylene) chain and formation of branches in long micelles. We indicate the scientific and technical significance of our findings.

1. Introduction

Surfactant molecules can self-assemble in dilute aqueous solution to form aggregates greatly extended in one dimension [1–5]. Such growth can occur due to the addition of electrolytes, hydrophobic cosurfactants, polar oils or even in binary systems with increasing concentration of surfactant [6–19]. All these factors reduce the spontaneous curvature of the surfactant self-assembly and cylindrical geometry becomes more stable with respect to the more curved spherical geometry. When the contour length of such aggregates exceeds a certain length called the persistence length, their structure and dynamics resemble those of flexible polymers in solution, and are described as wormlike micelles [20,21]. Lattice statistical theories (e.g. mean-field theory) originally developed for polymer solutions have been adapted to describe the equilibria of these systems [21,22]. Similarly, application of the reptation theory of polymer solution has helped explain the dynamics of these systems, in particular the power law dependence of viscoelastic relaxation time on the length of micelles [23–25].

The mean-field theory equilibrium description mentioned above predicts an average micelle contour length that decreases exponentially with increasing temperature if there does not exist any other factor that modifies this behavior [21]. In poly(oxyethylene) surfactants, the average curvature reduction of the surfactant layer due to the dehydration of the head-group with increasing temperature is a potential mechanism favoring temperature induced micellar growth [26–28]. For micelles of short poly(oxyethylene) chain surfactants, some studies reveal that the temperature induced curvature reduction can be strong enough for the high viscosity compositions to encourage the formation of threefold junctions with local negative curvature [10,16]. This effect reduces the viscosity with increasing temperature. In the case of the lower viscosity compositions, viscosity was found to increase with temperature, indicating micellar growth. Whatever the case, it can be concluded that the reduction of the average curvature of micellar interface with temperature can overcome the thermal stabilization of micellar end-caps.

The rheological properties of wormlike micellar solution formed in water/Tween-80/$C_{14}EO_3$ system were found to be considerably temperature-sensitive [11]. The hydrophilic head-group of Tween-80 contains a large number of poly(oxyethylene) groups. However, the head-group is branched and there are no known data on similar systems to compare and conclude on the effect of head-group size variation on the temperature sensitivity of poly(oxyethylene) surfactants.

Poly(oxyethylene) cholesteryl ether ($ChEO_m$) surfactants are remarkable in that they form highly viscous micellar solutions when appropriate cosurfactants are added in aqueous or mixed solvents [13,17,29]. Recently, we reported the formation of viscoelastic wormlike micellar solutions of poly(oxyethylene) cholesteryl ether surfactant having large head-group (30 ethylene oxide

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units) [30]. This result opens up the possibility of studying the variation of temperature sensitivity of poly(oxyethylene) surfactant wormlike micelles through changing the chain length of the poly(oxyethylene) head-group over a large range.

Therefore, we have proceeded with the investigation of the temperature sensitivity of the rheology of the $ChEO_m$ (m = 15 and 30) micellar systems containing $C_{12}EO_3$ and monolaurin cosurfactant, the same surfactants studied in Ref. [30]. We report our findings in this presentation. We have performed rheological measurements on the several systems. We present the data and the analysis and discuss the results by comparing with other complementary researches.

2. Experimental

2.1. Materials

Poly(oxyethylene) cholesteryl ether (abbreviated as $ChEO_m$, m = 15 and 30) was purchased from Nihon Emulsion Co., Japan. Monolaurin (98%) was supplied by Tokyo Kasei Kogyo Co. Ltd. (Japan). Triethyleneglycol dodecyl ether ($C_{12}EO_3$) was obtained from Nikko Chemicals Co., Japan. All these chemicals were used as received. Millipore-filtered water was used to prepare all the samples.

2.2. Methods

2.2.1. Observation of micellar transformation

Different ratios of the selected surfactants were dissolved in water by mixing well using magnetic stirrer. The samples were equilibrated for long times at 15, 20, 25, 30, 35, 40 and 45 °C. They were observed between crossed polarizers. Birefringence of samples at rest and in shaken condition was carefully noted at different temperatures.

2.2.2. Rheological measurement

Samples for rheological measurements were prepared by adding the required amount of $C_{12}EO_3$ and monolaurin to measured volumes of aqueous 0.06 M $ChEO_m$ solutions. The samples were homogenized and kept in a water bath at some set temperature (15, 20, 25, 30, 35, 40, 45 °C) for at least 48 h to ensure equilibration before performing measurements. Rheological measurements were performed in a stress-controlled rheometer, AR-G2 (TA Instruments Co.), using cone-plate geometry modified with a solvent-trap to minimize evaporation and with the plate temperature controlled by a peltier unit. Frequency sweep measurements were performed in the linear viscoelastic regime of the samples, as determined previously by dynamic strain sweep measurements.

3. Results

3.1. Steady shear rheology

Steady-state shear-rate viscosity data for the aqueous 0.06 M (excluding cosurfactant) $ChEO_{30}$ and $ChEO_{15}$ systems containing various monolaurin and $C_{12}EO_3$ ratios at 25 °C were published in Ref. [30]. For ease of reference we present the most relevant results of that research in Table 1.

We have performed steady-shear rheometry on the same systems at various temperatures. The monolaurin containing systems could not be measured at low temperatures because the cosurfactant phase separates as solid. Also, for systems containing large amount of $C_{12}EO_3$ the cloud point is below 40 °C and so there are no data. For clarity of presentation we present the data of only the most viscous systems at various temperatures (Figs. 1 and 2).

Table 1
Important rheological data from Ref. [30] (all measurements at 25 °C).

	0.06 M $ChEO_{15}$/$C_{12}EO_3$/water	0.06 M $ChEO_{30}$/$C_{12}EO_3$/water	0.06 M $ChEO_{15}$/monolaurin/water
X[a]	0.62	0.77	0.53
η_0/Pa·s	1429	1269	0.8
τ_R/s	23	20	–
G_0/Pa	47	60	–

[a] Molar ratio of cosurfactant and surfactant of the highest viscosity compositions.

The aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ (X = 0.77) is remarkable in that the plots at different temperatures almost superimpose at all shear-rates (Fig. 1a). However, at high shear-rates nonlinear effects and shear-induced structure formation complicates the understanding and so we discuss mainly the low-shear data below. The low-shear viscosity values of the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ (X = 0.77) system (Fig. 1a) and the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ (X = 0.74) system (Fig. 1b) manifest lower order of magnitude variation than those of the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ (X = 0.62) system (Fig. 1c) and the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ (X = 0.6) system (Fig. 1d). We point out that the difference between the first pair and the second is that $ChEO_{30}$ used in the first pair has a larger head-group than that of $ChEO_{15}$ in the latter. Also, the systems in Fig. 1a and c reach very high ($\sim 10^3$ Pa s) low-shear viscosities at 25 °C. For the systems in Fig. 1b and d only $\sim 10^2$ Pa s viscosity is achieved and the variation of low-shear viscosity is greater at low temperatures and lower at high temperatures whereas the opposite is observed for the systems in Fig. 1a and c. We notice that, for all systems in Fig. 1, at all temperatures, shear-thinning is observed, that is above a critical shear-rate $\dot{\gamma}_c$, the viscosity falls rapidly with increasing shear. This non-Newtonian behavior is an indication of formation of network structures of long wormlike micelles, which is also supported by the observation of shear birefringence in the samples. Shear-thinning occurs due to alignment of aggregates under flow if the deformation is faster than the time required to regain an equilibrium network structure, and with increasing network density the relaxation becomes slower; i.e. shear thinning begins at a lower shear rate. The zero-shear viscosity (η_0), an important rheological quantity, has been obtained by extrapolating the low shear plateau data. In the cases where the low shear-rate viscosity is high, beginning of shear-thinning is observed at lower shear-rates, which indicates increased structuring in the material. In Figs. 1 and 2b we notice that the low-shear viscosity first increases, reaches a maximum and then decreases as temperature is increased. Lower viscosity usually implies shorter average micellar contour length. But in our case, we argue that the decrease in viscosity at high temperature is due to micellar junction formation, supported by dynamic rheological data presented below. These junctions are labile and unlike physical cross-links in polymer gels, promote faster stress relaxation. Such branched micellar networks should also behave as non-Newtonian fluids and so shear-thinning is observed at high shear-rates (Figs. 1 and 2b). The system in Fig. 2a manifests simple rise in low-shear viscosity and decrease in critical shear-rate with increasing temperature, suggesting mainly micellar growth with temperature rise in the temperature range of investigation. Also, this system is Newtonian at low temperature.

The systems in Figs. 1 and 2 are all formed at rather high cosurfactant composition. For low cosurfactant compositions (data not presented) we did not observe any shear-thinning or shear birefringence. The significance of these results is discussed further below.

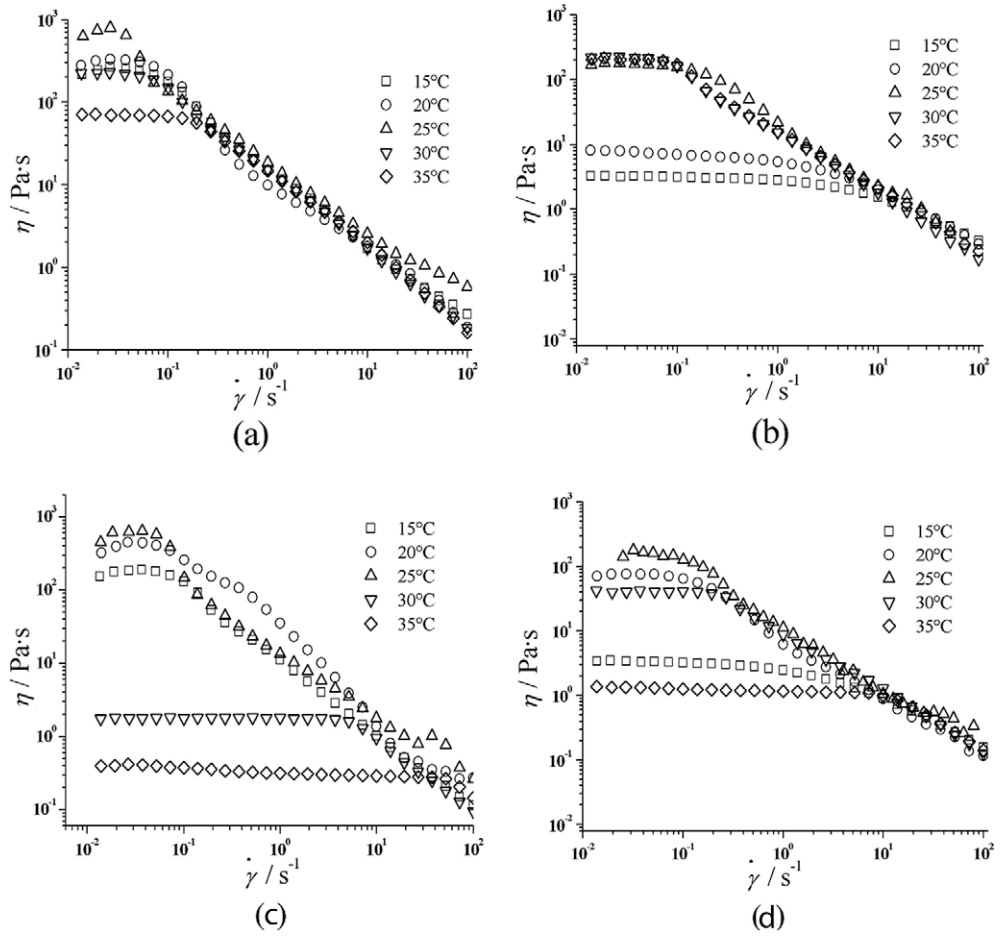

Fig. 1. Effect of temperature on the steady-shear rheology of 0.06 M (excluding cosurfactant) $ChEO_m$ (m = 15 and 30) containing different mixing fraction (X) of $C_{12}EO_3$: (a) $ChEO_{30}$–$C_{12}EO_3$, X = 0.77; (b) $ChEO_{30}$–$C_{12}EO_3$, X = 0.74; (c) $ChEO_{15}$–$C_{12}EO_3$, X = 0.62; and (d) $ChEO_{15}$–$C_{12}EO_3$, X = 0.6.

3.2. Dynamic rheology

To study the viscoelastic properties of the wormlike micellar solutions in the above systems, oscillatory shear measurements have been performed. Fig. 3 shows the variation of the elastic or storage modulus (G') and the viscous or loss modulus (G'') with oscillation frequency at different temperatures for the aqueous 0.06 M $ChEO_m$ solutions containing $C_{12}EO_3$ with those $C_{12}EO_3$ concentrations that form highly viscous solutions. In the aqueous 0.06 M $ChEO_{15}$ solutions containing monolaurin, viscoelasticity is indicated in dynamic measurements only at high temperatures for the most viscous compositions. Such small quantity of data is

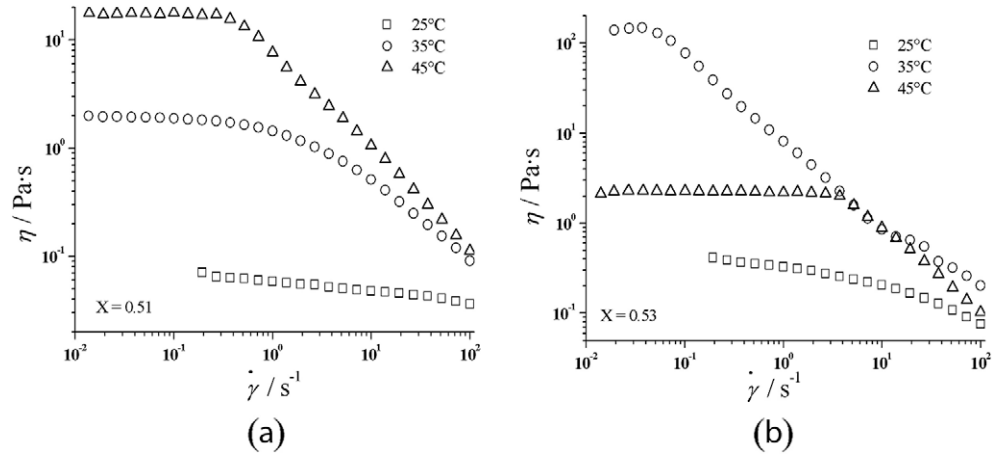

Fig. 2. Effect of temperature on the steady-shear rheology of 0.06 M (excluding cosurfactant) $ChEO_{15}$ containing different mixing fraction (X) of monolaurin: (a) X = 0.51 and (b) X = 0.53.

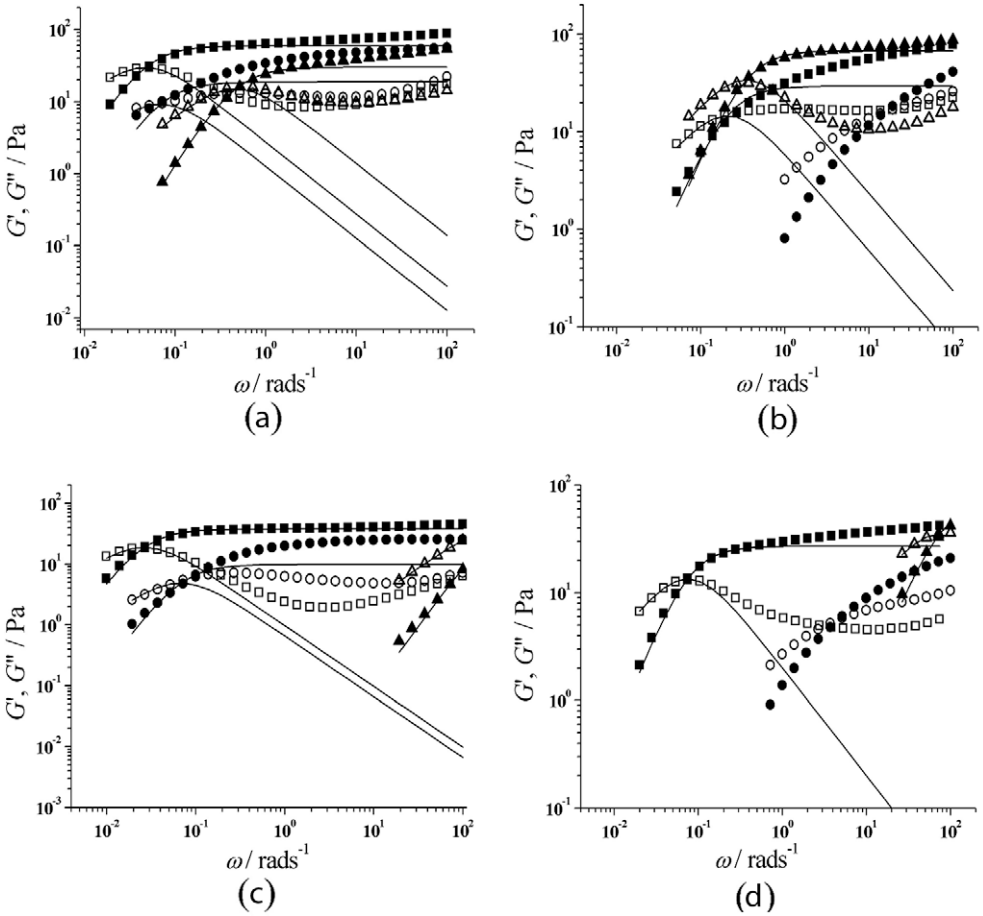

Fig. 3. Effect of temperature on the dynamic rheology of 0.06 M (excluding cosurfactant) $ChEO_m$ (m = 15 and 30) containing different mixing fraction (X) of $C_{12}EO_3$: (a) $ChEO_{30}$–$C_{12}EO_3$, X = 0.77; (b) $ChEO_{30}$–$C_{12}EO_3$, X = 0.74; (c) $ChEO_{15}$–$C_{12}EO_3$, X = 0.62; and (d) $ChEO_{15}$–$C_{12}EO_3$, X = 0.6. Legends: filled symbols G', open symbols G'' – 15 °C, ●○; 25 °C, ■□; and 35 °C, ▲△. The lines are the best fit to the Maxwell model.

not much useful for comparison and so we do not graphically present them here. In the aqueous 0.06 M $ChEO_{30}$ solutions containing monolaurin, all compositions are fluid at all temperatures. Therefore, we did not perform dynamic rheometry for this system.

In the systems of Fig. 3, liquid-like behavior ($G' < G''$) is observed in the low-frequency region, but both G' and G'' increase with ω and viscoelastic behavior ($G' > G''$) is observed in the high-frequency region. The cross-over occurs at the longest relaxation time, the terminal relaxation time τ_R, of the system.

The η_0 values for the Newtonian systems of low viscosity have been obtained by extrapolating the viscosity to zero-shear rate. For viscoelastic systems following Maxwellian behavior at low-shear frequency, η_0 values were estimated from the following relation involving the plateau modulus (G_0) and the terminal relaxation time (τ_R):

$$\eta_0 = G_0\tau_R \tag{1}$$

Alternately, the following relationship allows one to estimate η_0 by extrapolating the complex viscosity values ($|\eta^*|$) to zero shear frequency:

$$|\eta^*| = \frac{(G'^2 + G''^2)^{1/2}}{\omega} = \frac{\eta_0}{\sqrt{1+\omega^2\tau_R^2}} \tag{2}$$

The values of viscoelastic samples obtained from the estimated values of G_0 and τ_R are only approximate values.

The viscoelastic behavior of the entangled micelles is described by the Cates model [23–25], which considers two processes of stress relaxation – reptation or the reptile-like motion of the micelle along a tube and the reversible scission of micelles – taking place on two time scales, namely, the reptation time τ_{rep} and the breaking time τ_b. The viscoelastic behavior of such a system at low shear frequency often follows the Maxwell model of viscoelastic fluids with a single relaxation time τ_R given by $(\tau_b \cdot \tau_{rep})^{1/2}$ and plateau modulus (G_0) described by the following equations [31]:

$$G'(\omega) = \frac{\omega^2\tau_R^2}{1+\omega^2\tau_R^2}G_0 \tag{3}$$

$$G''(\omega) = \frac{\omega\tau_R}{1+\omega^2\tau_R^2}G_0 \tag{4}$$

The Maxwell material is characterized by a clear maximum in the G'' curve, a plateau in the G' curve at high frequency, and a cross-over of the two curves at the G'' maximum. The τ_R obtained from experiment is well approximated by the relaxation time appearing in the model. In cases where the maximum in G'' and the plateau in G' are not clear, we did not try to fit to Maxwell model (data for 15 °C in Fig. 3b and d). The systems in Fig. 3b and d are the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ (X = 0.74) and the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ (X = 0.6), respectively. Since the cosurfactant content is comparatively lower in these systems than the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ (X = 0.77) in Fig. 3a and the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ (X = 0.62) in Fig. 3c, at low temperatures the average interfacial curvature is expected to be high for the systems in Fig. 3b and d, and so, shorter micelles should abound, giving low relaxation times (0.07 s in the former and 0.44 s in the latter) and

stronger deviation from the Maxwell model. Such deviations are not observed for the systems in Fig. 3a and c, which in fact have rather low cross-over frequency at low temperatures, indicating higher relaxation time on account of the rather slow reptation of large micelles. This high relaxation time correlates well with the high low-shear viscosity of the same systems (Fig. 1a and c). Also, at high frequencies, in each system in Fig. 3, the G' and the G'' plots make positive deviation from the prediction of Maxwell model. This type of upturn is usually attributed to stress relaxation by local motions or small length-scale motions in the system. Due to this upturn at high frequencies, it is not easy to get an idea of the elasticity of the systems directly from the data. Fitting to the Maxwell data gives an estimate of the lower bound of the possible plateau modulus values. In the data presented in Fig. 3 we notice that for each system, the cross-over frequency shifts from high to low value and again rises as temperature is gradually increased. This corresponds well with the shift of steady-rate zero-shear viscosity with temperature for the same systems (Fig. 1). This suggests some structural change with temperature rise, which allows faster stress relaxation in the high temperature domain. Consideration of both the relaxation times and the plateau modulus indicates that this change is due to increased micellar branching. Also, the variation of the cross-over frequency with temperature for the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) in Fig. 3a and for the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.74$) in Fig. 3b is order of magnitude lower than that for the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$) in Fig. 3c and the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.6$) in Fig. 3d. Again, this corresponds well with the variation of the steady low-shear viscosity with temperature of these systems shown in Fig. 1 and can be attributed to the difference in the head-group sizes of $ChEO_{15}$ and $ChEO_{30}$. Discussions of these results are presented below.

4. Discussion

4.1. Effect of hydrophilic surfactant head-group size

In Fig. 4 we present the summary of the zero-shear viscosity data of the several systems at different temperatures. The order of magnitude rise in the viscosity at certain X value (cosurfactant composition) is indication of the formation of long micelles, supported by shear-thinning, flow birefringence and isotropy at rest, which are characteristics not shared by surfactant liquid crystals and sponge phase. The value of X at which viscosity dramatically rises, if such rise is present, shifts to lower value upon increase in the temperature (Fig. 4). It is evident from Fig. 4 that the viscosity in the 0.06 M aqueous $ChEO_{30}$ systems is much less sensitive to temperature variation than that in the 0.06 M aqueous $ChEO_{15}$ systems. In the 0.06 M aqueous $ChEO_{30}$ solutions containing monolaurin there is no indication of long micelle formation at any temperature. In fact the plots of the system are approximately flat and almost superimposed (Fig. 4d). However, this fact, coupled with the result that the viscosity rises in the 0.06 M aqueous $ChEO_{15}$ solution containing monolaurin at certain X value and the shift of this value with temperature (Fig. 4c) is indirect support of the fact that the $ChEO_{30}$ systems are less temperature sensitive

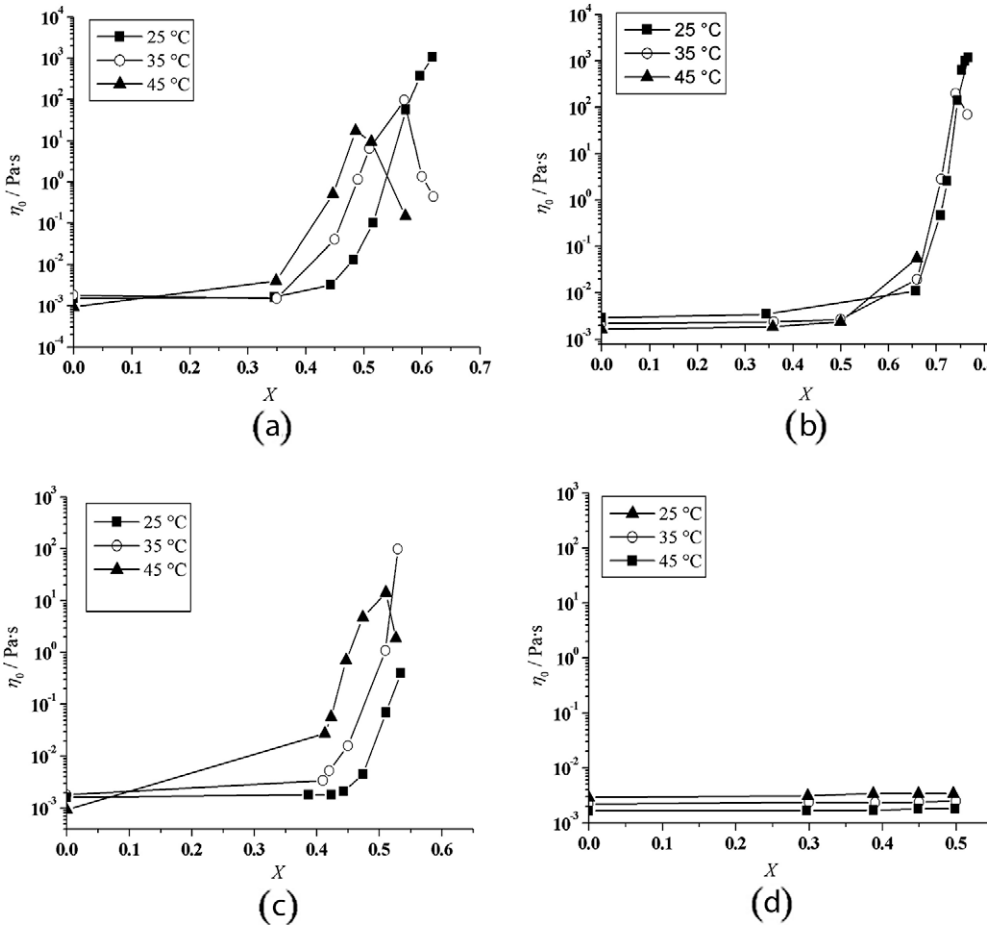

Fig. 4. Variation of zero-shear viscosity with temperature and cosurfactant mixing fraction (X) for the 0.06 M (excluding cosurfactant) $ChEO_m$ systems: (a) $ChEO_{15}$–$C_{12}EO_3$, (b) $ChEO_{30}$–$C_{12}EO_3$, (c) $ChEO_{15}$–monolaurin, and (d) $ChEO_{30}$–monolaurin. Lines are meant to be guide for the eye only.

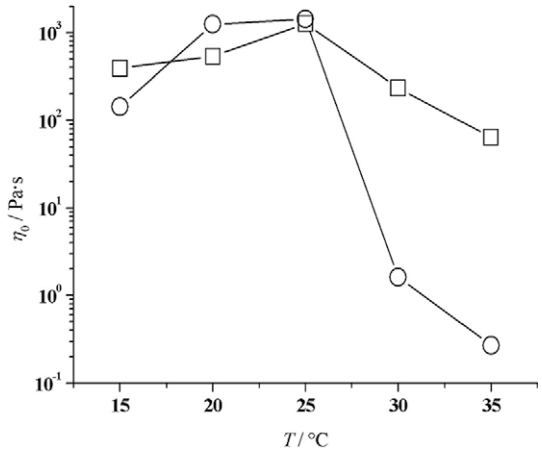

Fig. 5. Variation of the zero-shear viscosity of the most viscous aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$) (○) and the most viscous aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) (□) with temperature. Lines are meant to be guide for the eye only.

than the $ChEO_{15}$ systems. Thus, increase of the POE chain length of surfactant can reduce the temperature sensitivity of the viscosity of wormlike micellar solutions.

To bring the point in focus, we separately present the zero-shear viscosity data of the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$) and the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) in Fig. 5. These are the most highly viscous solutions, with the same order of magnitude zero-shear viscosity ($\sim 10^3$ Pa s) at 25 °C, found in the two systems. The cosurfactant mole fractions are different, but since highly viscous solutions are formed in either systems in such a small composition regime that this mismatch is unavoidable. Both plots rise and following a maximum, fall as temperature is increased. Clearly, for the first system, in the temperature range studied, the maximum viscosity obtained is more than 3 orders of magnitude higher than the minimum viscosity obtained. In the latter system the difference is less than 2 orders of magnitude. We also present the terminal relaxation time of the same systems in Fig. 6a. The order of magnitude differences in the variation of the relaxation times of the two systems are similar to those for the zero-shear data (Fig. 6a).

Referring to Fig. 5, it should be mentioned that a truly temperature-insensitive system would yield a horizontal viscosity–temperature plot. The aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) comes closer to reaching this ideal, compared to the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$). In case of the commonly studied ionic wormlike systems, only monotonic decrease of viscosity with increasing temperature has been observed [5,21]. In ionic systems, the translational entropy contribution of the micellar end-caps favors shorter micelles with greater net end-cap density and overcomes the end-cap energy as the temperature is raised. In POE surfactants the effect of temperature on the surfactant spontaneous curvature is dominant over the usual entropy/energy balance [32]. From our results in Fig. 5 we notice that temperature sensitivity of the micellar growth, which is determined by the interfacial curvature, can be tuned by changing the POE chain length. Thus the importance of using very long chain POE surfactant like $ChEO_{30}$ to form wormlike micelle is clear. We discuss this point further below.

At lower temperatures, the viscosity rises with temperature in the systems in Fig. 5. There is a corresponding rise in the relaxation times as seen in Fig. 6a. Since relaxation time is an indication of linear micellar growth, the viscosity increase in the low temperature range can be attributed to mainly the increase in average micelle contour length due to curvature reduction with temperature. As we have mentioned in Section 1, for POE surfactant wormlike micelles, the drop that follows the rise of the zero-shear viscosity with temperature rise, as observed in our data is explained by the predominance of the formation of threefold junctions with rise in temperature. These junctions have lower local curvature, and are favored by higher temperature in POE surfactants. These junctions are quite fluid, and can slide along the micellar contour. This motion provides a very fast stress relaxation mechanism. Thus although the branched micelles formed by such junctions have higher network density, the relaxation time is quite low. Therefore, the viscosity of branched micellar network is also low. Cates' model has been extended to branched micelles, and it has been demonstrated that all the results concerning the rheology of linear micelles can be applied to branched micelles, if instead of the average micellar contour length L by L_c is used throughout, where L_c represents the harmonic mean between the average distance from one point along the micelle to the first cross-link and the average distance from that point to the first end-cap, or equivalently, the ratio of the total length over the concentration of end-caps plus twice that of junctions [33]. In this definition, we notice that the junction density contributes more toward reducing L_c than the end-cap density. Now from Fig. 6a we see that the relaxation times go through a maximum as temperature is raised both for the

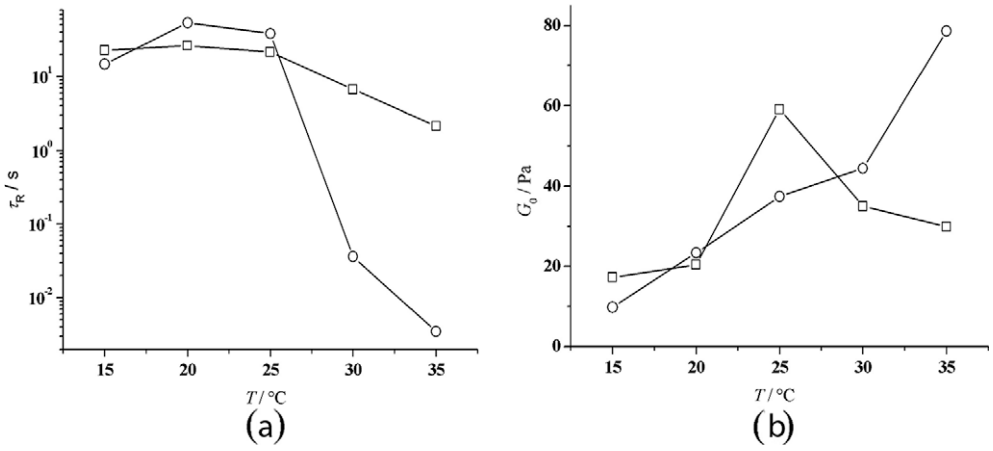

Fig. 6. Variation of the relaxation time (a) and plateau modulus (b) of the most viscous aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$) (○) the most viscous aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) (□) with temperature. Lines are meant to be guide for the eye only.

aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$) and for the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$), although for the latter the maximum, occurring at 20 °C, is not strongly peaked. This reflects that L_c, as defined above, passes through a maximum value in either system. The relaxation times at 15 °C in the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ at $X = 0.62$ (~15 s) is smaller than that in the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ at $X = 0.77$ (~23 s). Therefore, at this temperature, we may assume slightly higher end-cap density in the former system compared to the latter which is justified by the smaller net content of the hydrophobic $C_{12}EO_3$ in the former system compared to the latter. If the ratio of the hydrophilic surfactant, which in this case is $ChEO_m$, compared to the hydrophobic cosurfactant is large, the hydrophilic molecules can be accommodated in the high curvature end-caps by increasing their density [32]. As temperature is raised, the end-cap density decreases and produces a rise in the relaxation time. Thus, at the low temperature zone, the relaxation time of the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ at $X = 0.62$ increases faster than that of the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ at $X = 0.77$, reflecting again the greater temperature sensitivity of the interfacial curvature of shorter POE chain surfactants (Fig. 6a). However, at intermediate temperatures, junction formation becomes predominant and the relaxation time drops. The sharper fall of the relaxation time following the maximum in the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$) as compared to the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) indicates that in the former system stronger temperature induced curvature reduction favors greater formation of low local-curvature junctions in the high temperature regime, which reduces L_c more strongly, compared to the latter system (Fig. 6a). Of course, formation of shorter micelles with greater end-cap density and lower entanglement density would reduce the relaxation time, but would also reduce the elastic modulus. Increase in the junction density of entangled network can increase the elasticity of the system. We have found, as shown in Fig. 6b, the modulus increases with temperature for the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$), but for the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) system it passes through a maximum and then does not change appreciably as temperature is raised. This kind of decrease in the elastic modulus with decrease in micellar interfacial curvature has been observed in other systems [34,35]. The explanation invoked is the formation of saturated, multi-connected network without any entanglement, whose elasticity would be lower than the elasticity of a network containing both entanglements and junctions. The fact that the modulus does not change appreciably after a sharp fall, as can be seen in Fig. 6b, provides confidence in assuming that in the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$), saturated network forms at high temperature. Thus, from considerations of the dynamic rheology results in Fig. 6, the fall in viscosity of the same systems (Fig. 5) with temperature rise can be ascribed to increase in micellar junction density due to curvature reduction. The alternative assumption of increasing end-cap density due to the formation of shorter micelles can be rejected because end-caps are not favored by reduced curvature and decrease in micelle contour length cannot increase the elastic modulus.

We ascribe the origin of the difference between the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$) and the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) systems mainly to the difference in the size of the POE chains. NMR investigation of dodecyl oligoethylene oxide surfactant solutions indicate that the water of hydration of POE chains decreases mainly from the innermost ethylene oxide groups at increasing temperatures [28]. This implies less reduction of the curvature, and therefore less micellar growth, for the surfactant of longer POE chain upon increasing temperature, since at any temperature a longer chain will retain more water than a shorter chain. This is experimentally verified by recent investigations on alkyl POE surfactants, in agreement with molecular thermodynamic models [27,36]. Thus, we can assume that with temperature rise the dehydration of POE chains of $ChEO_{15}$ causes greater curvature reduction compared to $ChEO_{30}$.

It would be interesting to compare our results with the viscosity-variation behavior of aqueous mixtures of a surfactant and a hydrophobically modified (HM) water-soluble polymer [37]. In such systems, mixed micelles formed by surfactant molecules and the hydrophobic side-groups of the polymer molecules act as reinforcing cross-links between polymer chains. This type of cross-link increases the viscosity of the system, similar to physically cross-linked polymer gels. If in this type of system, the physical cross-links are strong enough to persist in sufficient numbers at high temperatures, then it is possible that an increase in the system volume with temperature might increase the viscosity up to a certain temperature, above which excessive break-down of cross-links would decrease the viscosity. Such a mechanism would result in a system with a viscosity maximum, like our systems. We have not utilized HM-polymers in our study, but it seems to be a very good idea to attempt to develop another temperature-insensitive high viscosity systems with a different self-assembly structure.

We focused on the difference between the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ and the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ systems for different X values. Of course, at $X = 0.77$, the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ is phase separated and therefore comparison cannot be made. The viscosity of the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ at $X = 0.62$ is not very high at any temperature, indicating poor micellar growth (Fig. 4b). Therefore, appropriate comparison cannot be made with the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ at $X = 0.62$. So, we chose the most viscous systems for detailed comparison.

4.2. Effect of the cosurfactant fraction and type

In Fig. 7 we present the viscosity–temperature plot of the aqueous 0.06 M $ChEO_m$ solution containing $C_{12}EO_3$ for X values that form highly viscous solutions. The maxima in the viscosity–temperature plot is a general feature in these systems, implying predominantly growth in micellar contour length followed by mainly branching and later perhaps saturation by branch points, all due to average curvature reduction with increasing temperature. Before the maximum is reached contour length increase is the main contribution, whereas following the maximum increased branching is the dominant process. In Fig. 7a we notice that for the lower $C_{12}EO_3$ concentration ($X = 0.6$) viscosity rise in the low temperature region is sharper (the slope of the low temperature branch of the plot is steeper) and viscosity fall in the high temperature region is weaker (the high temperature branch, following the maximum of the plot, is less steep) than those for the higher cosurfactant composition ($X = 0.62$). This behavior is seen with the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ also (Fig. 7b). It appears that for the higher cosurfactant compositions in either system, the average interfacial curvature is sufficiently reduced at any temperature so that there is always some tendency of formation of low local-curvature junction points. Such coexistence of junctions and end-caps, that is branched and cylindrical micelles has been observed by cryo-TEM in nonionic surfactant systems even at 18 °C [38]. Increase in temperature reduces the average interfacial curvature of the micellar interface and therefore allows for both elongation of the cylindrical body of the micelles (which has lower curvature than that of end-caps) as well as increase in the density

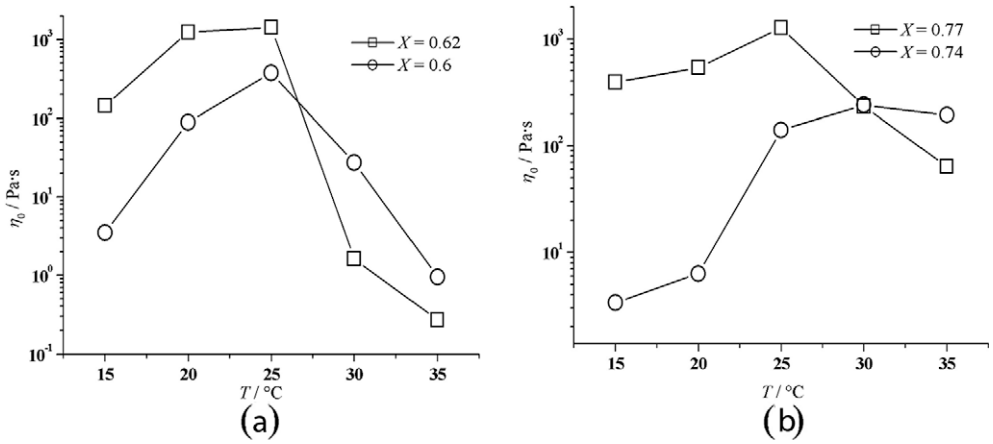

Fig. 7. Comparison of the variation of the zero-shear viscosity with temperature 0.06 M (excluding cosurfactant) solution of $ChEO_m$ for different mixing fraction (X) of cosurfactant: (a) $ChEO_{15}$–$C_{12}EO_3$ and (b) $ChEO_{30}$–$C_{12}EO_3$.

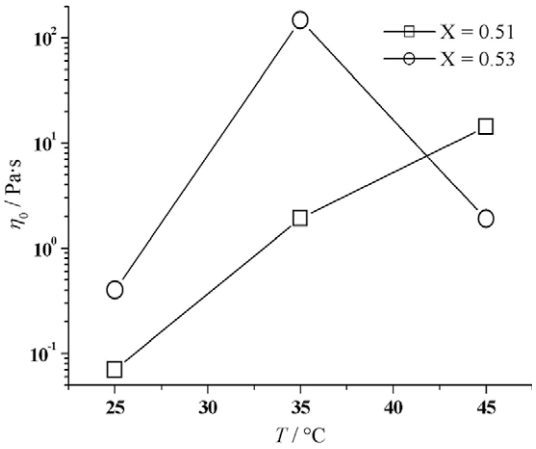

Fig. 8. Variation of zero-shear viscosity of 0.06 M (excluding cosurfactant) $ChEO_{15}$ solution containing monolaurin systems for different mixing fractions (X) with temperature.

of the low local-curvature junction points [39]. In other words, temperature rise favors both micellar growth and branching, although branching becomes significant for the lower cosurfactant compositions (higher average curvature) only at rather high temperatures (Fig. 7). Whereas micellar growth favors increase in viscosity, branching lowers the viscosity due to the faster relaxation process of the sliding movement of the fluid junctions. Thus, with temperature rise, the increase in the junction density of the lower average curvature systems in Fig. 7 compensates somewhat for the micellar growth induced viscosity rise in the lower temperature zone and results in rather flat viscosity–temperature plots. Since at higher temperature, lower average curvature allows for more low local-curvature junctions, following the temperature at which branching becomes predominant, junction density increases more rapidly for the same high cosurfactant content systems in Fig. 7 and the viscosity falls much more sharply due to the faster relaxation processes of the sliding movement of junctions. The relaxation times in Fig. 9a can be seen to behave in manner quite similar to the viscosity of the same systems in Fig 7. This is understandable, since the relaxation time reflects the magnitude of L_c, a quantity which is decreased due to increase in both end-cap density and junction density of a system [33]. Thus, we can explain the slow rise in the relaxation times in the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ system ($X = 0.77$) and the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ system ($X = 0.62$) at low temperatures due to decrease in end-cap density and increase in junction density, two effects which oppose each other toward increasing L_c. At high temperature, junction formation becomes predominant and L_c falls, thereby reducing the relaxation time. In

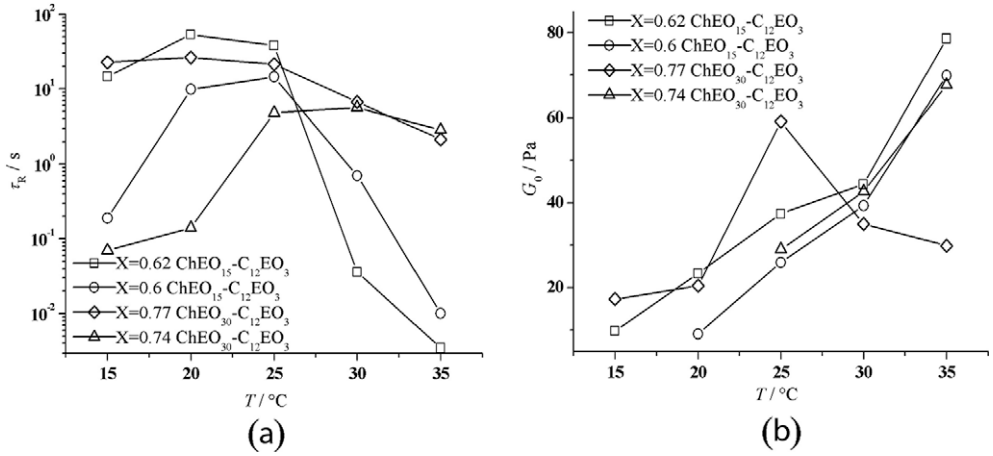

Fig. 9. Variation of the terminal relaxation times and the plateau modulus of 0.06 M (excluding cosurfactant) $ChEO_m$ ($m = 15$ and 30) solution for different mixing fractions (X): (a) relaxation time and (b) plateau modulus.

the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.74$) and aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.6$) systems, which have higher average interfacial curvature due to lower cosurfactant ratios, low local-curvature junction formation is less probable than in the low average interfacial curvature aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) and the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$), respectively. In fact the relaxation times at 15 °C for the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ at $X = 0.6$ (~0.44 s) and the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ at $X = 0.74$ (~0.07 s) is much lower than, respectively, the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ at $X = 0.62$ (~15 s) and the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ at $X = 0.77$ (~23 s), indicating much larger end-cap density in the first two systems (Fig. 9a). Temperature rise reduces the average interfacial curvature and the end-cap density decreases, giving sharp rise in the relaxation time. Thus, L_c and therefore relaxation time rise faster in the low temperature region and falls slower in the high temperature zone in the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.74$) and in the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.6$) than in the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) and in the aqueous 0.06 M $ChEO_{15}$ solution containing $C_{12}EO_3$ ($X = 0.62$), respectively (Fig. 9a). The plateau modulus presented in Fig. 9b reflects the entanglement density of the measured system, which depends on the net surfactant volume fraction. Since the total surfactant content in our systems are differs from one to another, we do not make any direct comparison. However, we point out the fact that except for the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$), all the systems in Fig. 9b manifest an increase in the modulus with temperature rise, even in the temperature zone where relaxation times fall for the same systems (Fig. 9a). This can be only explained by the increase in the low local-curvature junction points due to decrease in the average interfacial curvature with increasing temperature. Also as discussed in the previous section, the sharp fall in the modulus at high temperature in the aqueous 0.06 M $ChEO_{30}$ solution containing $C_{12}EO_3$ ($X = 0.77$) can be explained as the formation of saturated network having low elasticity, again due to the decrease in average interfacial curvature. Thus, the sole concept of the reduction of the average interfacial curvature with temperature can consistently explain all the observations and the dynamic rheological data supports and complements the steady shear-rate data nicely as well as providing valuable insights into the structural changes induced by temperature.

In the 0.06 M aqueous $ChEO_{15}$ solution containing monolaurin (Fig. 8), the trend seems to be different. In fact, for $X = 0.53$ the viscosity passes through a high value (~10^2 Pa s) maximum followed by a drop upon increasing temperature. Dynamic measurements, for which we did not present data, reveals that the drop in zero-shear viscosity corresponds with drop in relaxation time and increasing plateau modulus, implying predominant micellar branching with increasing temperature. For $X = 0.51$, the monotonous but slow rise of viscosity with temperature corresponds with similar monotonous rise in relaxation time and modulus, implying linear micellar growth dominating over branching. The data obtained starts from 25 °C. At this temperature the maximum viscosity achieved is not very high, implying low micellar growth and greater average interfacial curvature. Thus, there is expected to be little tendency for low local-curvature junction formation at low temperatures. Since monolaurin does not have POE head-group, $ChEO_{15}$ is the only component expected to contribute to temperature induced curvature reduction in this system. Since the POE chain of $ChEO_{15}$ is quite large, if its fraction is higher in the solution, the amount of water of hydration will also be higher. Therefore, with increasing temperature, the net water of hydration removed from the POE layer will be less for that solution which contains the larger ratio of $ChEO_{15}$. Thus, the reduction of average interfacial curvature upon increasing temperature should be less for the higher $ChEO_{15}$ fraction, i.e. the lower monolaurin fraction system. This would imply higher temperature sensitivity for the higher monolaurin composition system, which is actually observed (Fig. 8).

As mentioned above, in the 0.06 M aqueous $ChEO_{30}$ solutions containing monolaurin, micellar growth is not observed at any temperature. So, we cannot effectively compare this system with the aqueous 0.06 M $ChEO_{30}$ solutions containing $C_{12}EO_3$.

We note that the problem of clouding at high temperature in POE surfactants may be avoided by using ionic surfactants. Therefore, our future efforts will be towards the development of temperature insensitive worm-like micelles using ionic surfactants. Also, we are contemplating on the theoretical grounds on the behavior of the relaxation time upon temperature change.

5. Conclusion

We report the first indication of the possibility of making wormlike micelle solution possessing low sensitivity toward temperature-induced changes in rheological properties. We have found that for wormlike micelles formed from long POE chain cholesteryl ether surfactants with addition of appropriate cosurfactants, the temperature sensitivity of the viscosity and relaxation time of the solutions can be reduced if the POE chain length is increased. Due to dehydration of the POE chains with increasing temperature, the curvature of the micellar interface decreases and micelles become progressively longer and ultimately branched through junction formation. As a result, the viscosity passes through a maximum at some temperature. The extent of the variation of viscosity in different temperature zones may also be changed by changing the cosurfactant content. Subtle changes can occur due to changes in cosurfactant mixing ratio and type. Since the changes of the rheological properties with temperature can be explained by the transformation of micelles from cylindrical to branched, which is ultimately determined by a sensitive interplay of end-cap and junction densities, our results intimate the potential of more fruitful research toward fine-tuning these quantities.

The implication of temperature-insensitive wormlike micelles for the industry is clear. We can name shampoos, detergents, etc. as a few examples. On the scientific side, the development of temperature-insensitive wormlike micellar solutions would require changes in the theoretical approach to such systems. Since rheological data can be easily obtained and temperature is an important thermodynamic parameter that can be efficiently tuned without making internal changes in a system, any theoretical derivation can be quickly tested. A well-developed analogy between the solution behavior of POE surfactant micelles and microemulsion and that of dipolar fluids composed of magnetic colloidal nano-particles imply that such progress can benefit the whole of colloid science in general [40].

Acknowledgments

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