

## Shear-induced microstructure and rheology of cetylpyridinium chloride/sodium salicylate micellar solutions

Dae-Geun Choi, Won-Jong Kim and Seung-Man Yang\*

Department of Chemical Engineering Korea Advanced Institute of Science and  
Technology, 373-1 Kusong-dong, Yusong-gu Taejeon 305-701, Korea

(Received November 15, 2000)

### Abstract

In this article, we considered shear-induced microstructure and rheological behavior of micellar solutions of cationic surfactant, cetylpyridinium chloride (CPC) in the presence of a structure-forming additive, sodium salicylate (NaSal). Shear viscosity, shear moduli and flow birefringence were measured as functions of the surfactant and additive concentrations. In the presence of NaSal, the micellar solution exhibited the non-linear rheological behavior due to the formation of supramolecular structures when the molar ratio of NaSal to CPC exceeded a certain threshold value. Flow birefringence probed the change in micelle alignment under shear flow. At low shear rates, the flow birefringence increased as the shear rate increased. On the other hand, fluctuation of flow birefringence appeared from the shear rate near the onset of shear thickening, which was caused by shear-induced coagulation or aggregation. These results were confirmed by the SEM images of *in situ* gelified micelle structure through sol-gel route.

**Keywords** : shear-induced microstructure, wormlike micelle, rheology, flow birefringence, *in situ* gelation

### 1. Introduction

Surfactants are industrially ubiquitous in both chemical and consumer domains and have provided a rapidly growing area of scientific research. They are used as detergents, cleaning agents, emulsifiers in food, pharmaceuticals, and cosmetics. Surfactant molecules in solution can self-assemble into aggregates (so-called micelles) which their immiscible parts clump together. The shape and size of micelle depend on the molecular structure of the surfactant, nature of solvent and additives, and their molar composition. Specifically, the ionic surfactant molecules form spherical micelles when their concentration exceeds the critical micelle concentration (CMC). The presence of ionic or cosurfactant additives reduces the repulsions between micelle head groups and thereby affects the structural transitions. In addition, the micellar aggregates can grow anisotropically under appropriate conditions, changing their shapes from spheres to rods or highly flexible wormlike aggregates. Such evidence provided some analogies between giant flexible cylindrical micelles and conventional polymeric solutions (Israelachvili, 1985). Meanwhile, when immersed in a mean flow, surfactant micelles show various flow-induced microstructures and flow properties of these

systems are of interest in technological processes.

Wormlike micelles are large one-dimensional aggregates observed in a number of surfactant solutions (Rao *et al.*, 1988; Kim *et al.*, 1997; Bury *et al.*, 1998). These self-assemblies of surfactant molecules are locally cylindrical and behave like a semi-flexible polymeric chain. Typically, their structural dimensions are 20-50 Å in diameter, 150-200 Å in persistence length ( $l_p$ ) and several micrometers in average linear length. Wormlike micelles have stimulated considerable theoretical and experimental interests during the last two decades because of its unique and fascinating rheological behavior (Cates and Candau, 1990; Rehage and Hoffmann, 1991). In the late 80s, attention was paid to the linear viscoelasticity. In the linear response region, these complex fluids appear to be described by a simple Maxwell model. The low-frequency mechanical properties are determined by a plateau modulus  $G_0$  and a relaxation time  $\tau_R$ . The plateau modulus characterizes the elasticity that can be stored by the network under strain whereas the relaxation time describes the relaxations occurring in a viscous dissipation process. It has been shown that the rheological properties of wormlike micelles in aqueous solutions have a remarkable resemblance to those of polymers in a good solvent (Phanton *et al.*, 1998). However, unlike ordinary polymers, micellar chains can reversibly break and recombine (Cates and Candau, 1990). They reform by addition and loss of individual amphiphiles or by the scission and

\*Corresponding author: smyang@kaist.ac.kr  
© 2000 by The Korean Society of Rheology

recombination of entire micelles.

The addition of inorganic salts decreases the electrostatic interactions between monomers in the micelle, which induces micellar growth and viscosity increment. Interactions between aromatic electrolytes and cationic surfactants in aqueous medium produce viscoelastic responses at very low surfactant concentrations. These viscoelastic properties are due to the formation of long surfactant self-assemblies and the aromatic species enhance the structure formation by being situated between the cationic head groups. In this work, we examined experimentally aqueous solutions of a cationic surfactant (cetylpyridinium chloride; CPC henceforth) in the presence of strongly binding salicylic counterions (NaSal hereafter). Several studies were performed on the effects of salts and organic additives on the micellar association in aqueous CPC solutions (Rehage and Hoffmann, 1988, 1991; Cates and Candau, 1990; Berret *et al.*, 1993; Kabir-ud-Din *et al.*, 1997). Our previous study suggested the microstructural change and rheological properties of wormlike micellar solution in CTAB/NaSal system (Kim and Yang 2000 a, b). CPC molecule has a bulky benzyl group in head group with respect to CTAB molecule show a linear structure. Therefore, the CPC molecules prohibited the penetration of benzyl additives into the micelles core and induced loosely packed. In the dilute regime, the solutions behave as a real sol with a rather low viscosity. As the shear flow applied, wormlike micellar solution exhibits anomalous behavior, a dramatic increase in viscosity above a critical shear rate. Above a well-defined threshold value of the velocity gradient, a supramolecular structure can be formed from the micellar aggregates. This shear-induced structure behaves like a gel and exhibits strong flow birefringence. It has been suggested that these phenomena are associated with aggregation of micelles induced by the shear flow (Liu and Pine, 1996; Kim and Yang, 2000a and 2000b; Hu *et al.*, 1998; Humbert and Decruppe, 1998). Similar behavior of the shear-induced microstructure has been observed in particulate suspensions (Fuller, 1995; Macosko, 1994; Lee and Yang, 1998; Bender and Wagner, 1995). In the present work, we considered the rheological responses and flow-induced microstructure of dilute and semi-dilute wormlike micellar solutions by measuring flow birefringence under shear flow. In addition, we captured the flow-induced microstructure of wormlike CPC/NaSal micelles by *in situ* gelation through sol-gel reaction of an alkoxide. The SEM image of the captured microstructure was compared with rheological and rheo-optical results.

## 2. Experimental

CPC and NaSal were purchased from Aldrich. Highly de-ionized water was used as a solvent. The CPC concentration was in the range from 1 mM to 50 mM and

NaSal concentration was varied with the molar ratio,  $R = [\text{NaSal}]/[\text{CPC}]$ , changing from 0.1 to 10.0. Before measurements were taken, samples were kept for at least three days to attain equilibrium.

Flow characteristics of the CPC solutions were measured using ARES rheometer with no modification. ARES rheometer (cone-and-plate geometry with 50 mm in diameter and a cone angle of 0.04 rad) is of rotational mode which is useful at relatively low shear rates. Steady shear viscosity was measured at the shear rate in the range of 0.1–1000  $\text{s}^{-1}$  at room temperature. Dynamic oscillatory behavior of the CPC solutions was examined under 50% strain. Flow-induced birefringence of the solutions was investigated through optical alignments described by Fuller (1995). Specific optical trains were introduced in our precedent paper (Kim and Yang 2000b). Applied shear rate was varied from 0.01 to 60  $\text{s}^{-1}$ .

To capture the flow-induced microstructure, tetramethylorthosilicate (TMOS: Aldrich) in hydrochloric acid was used as a silica precursor and ammonium hydroxide as a morphology catalyst. Samples were prepared in the annulus between two coaxial cylinders as used in the optical experiment. The samples were dried for 12 hours and prepared for the scanning electron microscope.

## 3. Results and discussion

### 3.1 Rheological behavior of CPC micellar solution

Rheological properties of the CPC solution in the presence of NaSal are investigated as a function of the molar ratio  $R$  of NaSal to CPC and the result is reproduced in

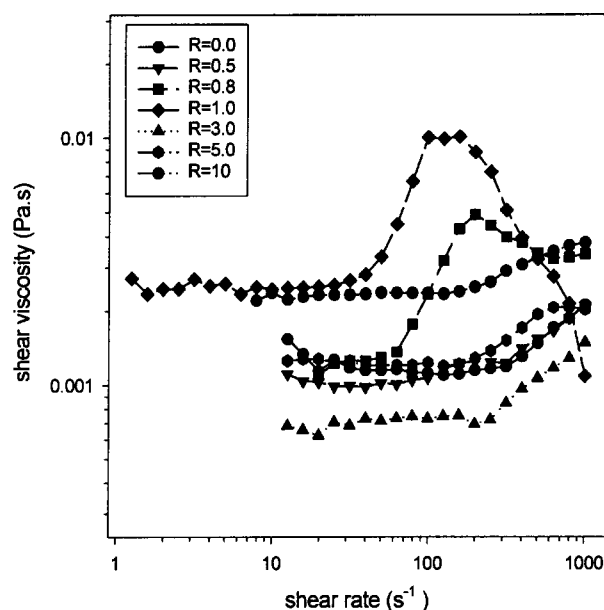


Fig. 1. Effects of the molar ratio of NaSal to CPC on the shear viscosity for 5 mM CPC solution. The molar ratio  $R$  of NaSal to CPC is varied from  $R=0$  to 10.

Fig. 1. The surfactant concentration is fixed at 5 mM and the molar ratio  $R$  is changed from 0.1 to 10. The results show that the micellar solution exhibits non-linear rheological behavior when the molar ratio was around unity. The CPC molecules form wormlike micelles when the molar ratio  $R$  exceeds a certain threshold value. Below the threshold molar ratio, the micelles in dilute CPC solution are spherical and the solution exhibits Newton behavior. As the molar ratio increases above 0.5, the solution is transformed from a low-viscosity Newtonian liquid to a high viscosity non-Newtonian solution. In this case, the CPC/NaSal solution displays a Newtonian plateau viscosity at low shear rates. However, as the shear rate approaches a critical value, shear thickening appears. The onset of shear thickening depends weakly on the molar ratio. It can be also noted that as the shear rate increases further, viscosity shear thins. This nonlinear rheological behavior of shear thickening followed by shear thinning occurs clearly around  $R = 1$ . Also shown is that the shear viscosity increases until the molar ratio reaches unity. Meanwhile, the shear viscosity decreases as the molar ratio exceeds the equimolar ratio. This implies that the scission of the micelle network junctions occurs at higher concentrations of NaSal owing to the hindrance effect of the excess salicylate ions. In our pervious study, CTAB/NaSal system was investigated (Kim and Yang, 2000c). As before mentioned, it is expected that CPC molecules prohibite the penetration of NaSal into the micellar core. In addition, bulky headgroups are relatively loosely packed. These effects are confirmed by comparison both of the shear viscosity responses in CPC/NaSal with in CTAB/NaSal system. At the fixed concentration (5 mM) of surfactant and additives, the magnitude of shear viscosity in CTAB/NaSal ten times larger than that in CPC/NaSal. Larger micelle aggregates are formed in CTAB than CPC because of the structural difference. Also, shear viscosity in CPC/NaSal system shows Newtonian plateau at low shear rate. It means that the micelles under low shear rate are still isotropic and no flow-induced structures are formed. However, shear viscosity in CTAB/NaSal system shows shear thinning behavior in whole the shear rates. It indicates that the wormlike micelles align to the flow direction and form the flow-induced structure. In semi-dilute region (as shown in Fig. 5), it is consistently observed.

In Fig. 2, the first normal stress difference is plotted as a function of the shear rate for various molar ratios. The normal stress difference is useful to investigate the structure evolution. As shown in Fig. 2, the normal stress difference remains constant until the shear rate approaches a certain critical value. It is interesting to note that the critical shear rate at which the normal stress difference begins to increase rapidly is identical to the onset shear rate of shear thickening. This is indicative of the flow-induced micro-

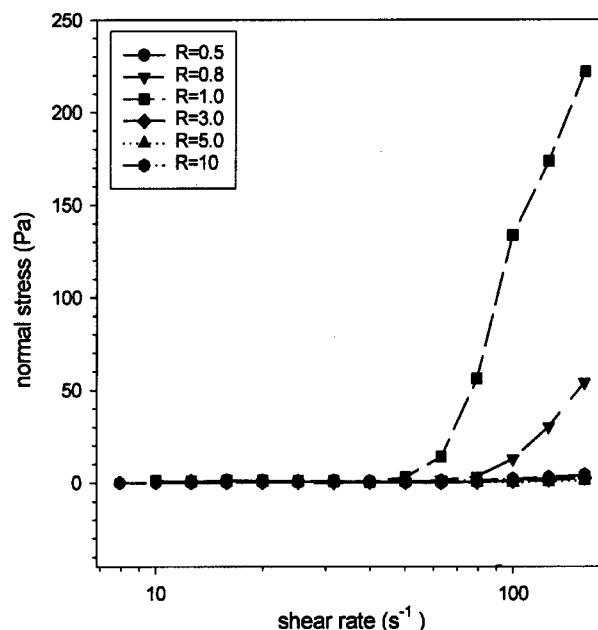
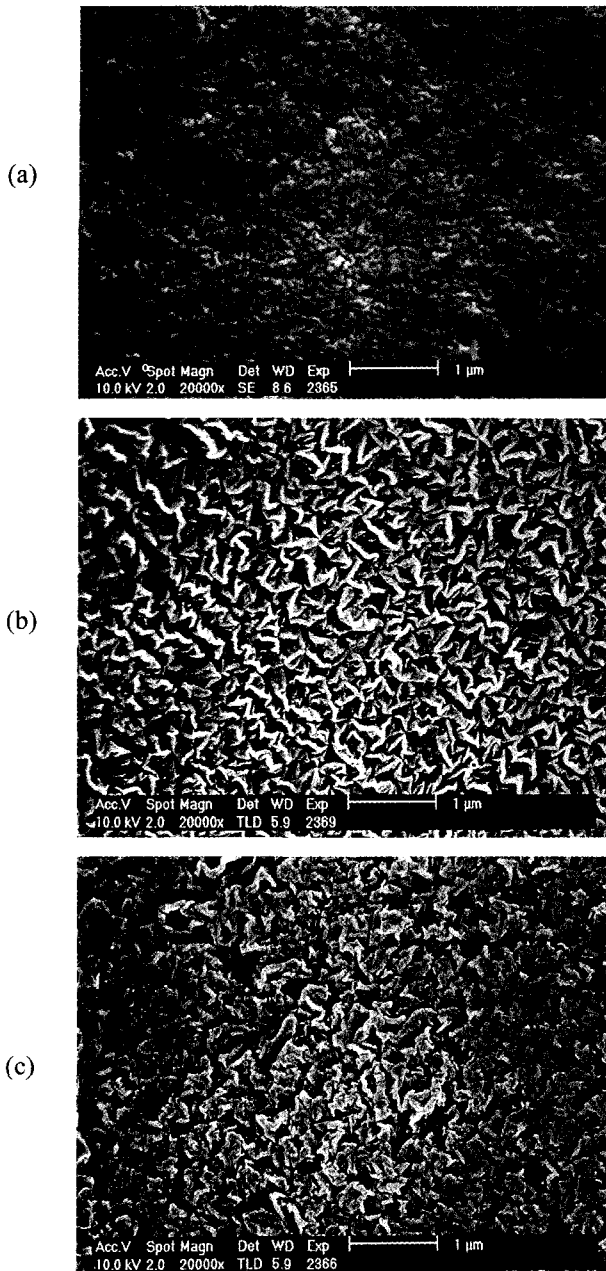


Fig. 2. First normal stress difference as a function of the shear rate for various molar ratios. The CPC concentration is fixed at 5 mM.

structure evolution at such a high shear rate.

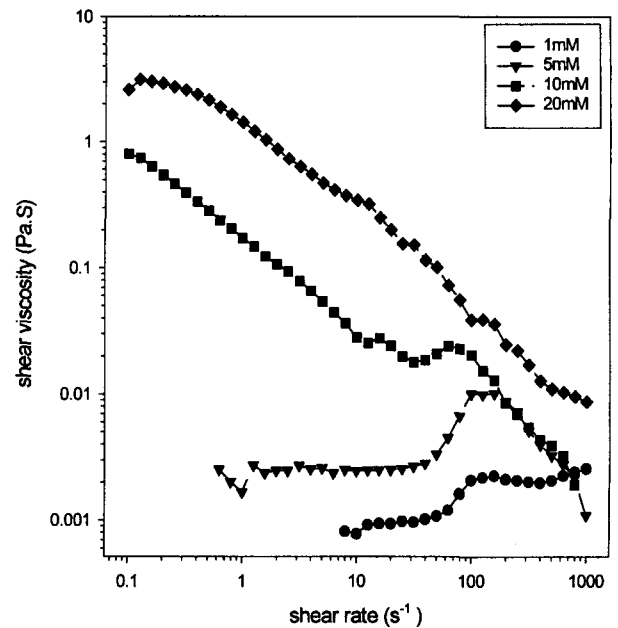
We observe the flow-induced microstructure change by *in situ* gelation of the micellar solution. In Fig. 3, SEM images of the captured microstructure of silica-micelles complex are reproduced for equimolar solution of 5 mM CPC/NaSal at various shear rates. It can be noted from Fig. 3(a) that small-scale zigzag structure is formed with no apparent flow-induced alignment at very low shear rate of  $0.07 \text{ s}^{-1}$ . It can be expected that the elongated micelles are aligned to flow direction as the shear rate increases. Indeed, as shown in Fig. 3(b), well-aligned microstructure is developed in the flow direction at  $5.27 \text{ s}^{-1}$ . When the shear rate increases further and exceeds a certain critical value, the stretched worm-like micelles are fluctuated and interlayer coagulation occurs by strong hydrodynamic interaction, as shown in Fig. 3(c). The critical shear rate for the occurrence of interlayer coagulation was shown to be near the onset shear rate of shear thickening. These SEM images well explain the rheological behavior such as sudden viscosity buildup and shear thickening above the critical shear rate.

In Fig. 4, the shear viscosity is plotted as a function of the shear rate for various surfactant concentrations. In this plot, the molar ratio of NaSal to CPC is fixed at unity. We can observe that the apparent viscosity of equimolar solution increases with the increase in CPC concentration. Also noted is that the Newtonian plateau at low shear rates does not exist as the surfactant concentration exceeds 10 mM, which separates the dilute and semi-dilute regimes. In the semi-dilute regime, viscosity behavior is observed

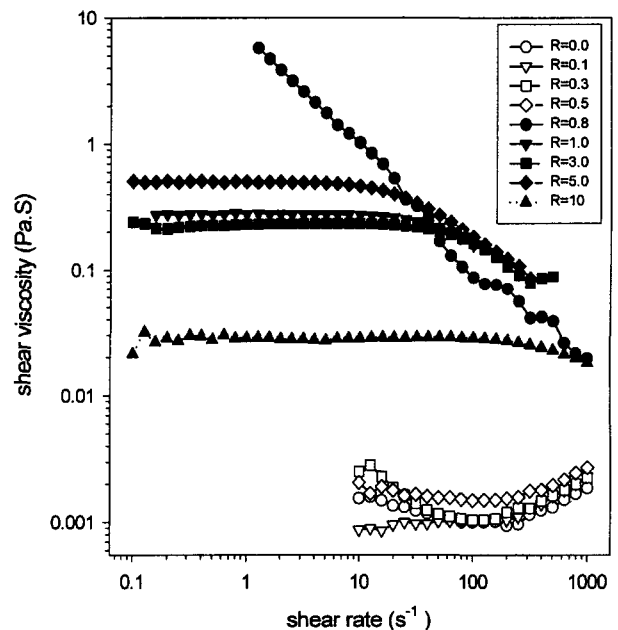


**Fig. 3.** SEM images of the captured microstructures. (a) at shear rate of  $0.074 \text{ s}^{-1}$ ; (b) at shear rate of  $5.27 \text{ s}^{-1}$ ; (c) at shear rate of  $22.58 \text{ s}^{-1}$ . The CPC concentration is 5 mM with the molar ratio fixed at unity.

shear thinning in whole shear rate ranges. Therefore, the semi-dilute micellar solution of CPC/NaSal behaves like entangled polymer solutions. In Fig. 5, the shear viscosity is plotted as a function of the shear rate for 50 mM of CPC solution. In this case, the molar ratio of NaSal to CPC is varied from 0.0 to 10.0. As the molar ratio  $R$  increases from zero, the shear viscosity at low shear rates increases and appears to pass a maximum when molar ratio  $R$  approaches 0.8. However, when increasingly more excess



**Fig. 4.** Viscosity as a function of the shear rate for various CPC concentrations with the molar ratio  $R$  fixed at unity.



**Fig. 5.** Effects of the molar ratio of NaSal to CPC on the shear viscosity for 50 mM CPC solution.

salicylic ions are present, the shear viscosity decreases. Therefore, when the molar ratio is located away from unity, Newtonian plateau is observed again.

It has been shown that the dynamic rheological response of semi-dilute micellar solution follows a Maxwell model with a single relaxation time. This is especially true when the structure-enhancing benzyl additive is present at equimolar content. According to Maxwell model, the stor-

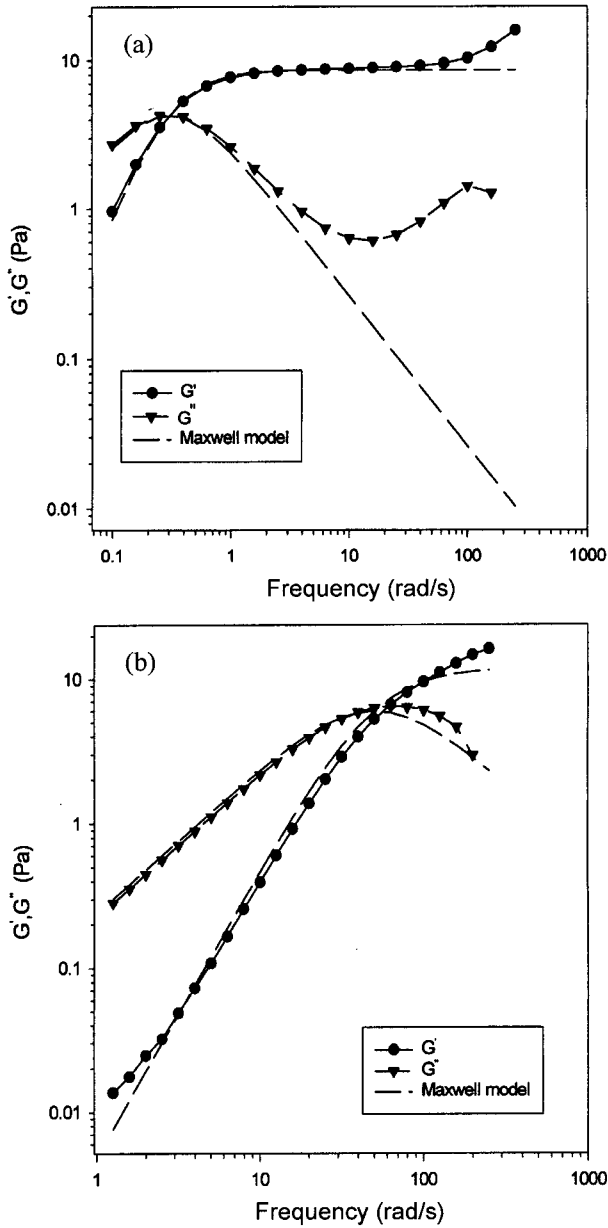


Fig. 6. Dynamic shear moduli versus the applied frequency for 50 mM CPC solution at 50% strain. (a) for  $R = 0.8$ ; (b) for  $R = 3.0$ .

age and loss moduli,  $G'$  and  $G''$ , are given by

$$G' = \frac{G_0 \omega^2 \lambda_R^2}{1 + \omega^2 \lambda_R^2}, \quad G'' = \frac{G_0 \omega \lambda_R}{1 + \omega^2 \lambda_R^2} \quad (1)$$

in which  $G_0$  denotes a plateau modulus, which is a measure of the average length between entanglement points in a network, and  $\omega$  and  $\lambda_R$  are the frequency of oscillatory shear flow and the relaxation time, respectively. At high frequencies,  $G'$  approaches  $G_0$  and the system behaves like an elastic material. At low frequencies,  $G'$  becomes proportional to  $\omega^2$  whereas  $G''$  proportional to  $\omega$  which

implies that the system behaves like a simple liquid. In Fig. 6(a), the storage and loss moduli of 50 mM CPC solution are plotted versus the frequency with the molar ratio  $R$  fixed at 0.8. Also included for illustrative purpose are the storage and loss moduli predicted from Maxwell model with a single relaxation time. When highly elongated micelles are entangled in the presence of sodium salicylate, the rheological response of CPC/NaSal solution is quite similar to that of a concentrated polymer solution. In this case, the moduli in Fig. 6(a) are close to those predicted from Maxwell model with a single-relaxation time. Meanwhile, when excess salicylic ions are present, the surfactant solution behaves like a dilute polymer solution. As the concentration of anionic salicylic ions increases, the surface charges are neutralized, so that the surface charge area per head group decreases. Consequently, the micelles begin to grow and the relaxation time increases until the molar ratio reaches the optimal value for the structure formation (around 0.8 for 50 mM CPC solution). When, the concentration of NaSal increases above the optimal value, the relaxation time begins to decrease. This can be explained by the fact that excess salicylic ions accelerate the kinetics of breakage and recombination of the CPC/NaSal micelles or their interconnection, thus allowing more rapid relaxation of the long micelles, see Kim and Yang (2000c). In Fig. 6(b), storage and loss moduli are shown at the molar ratio 10.0. Indeed, our result shows that the relaxation time ( $\lambda_R$ ) changes from 3.3 s at  $R = 0.8$  to 0.02 s at  $R = 3.0$ .

### 3.2 Rheo-optical response of CPC micellar solution

Flow birefringence and other optical intensity were measured to investigate the change in micelle alignment under a shear flow. Surfactant solutions in the dilute regime respond quickly to the inception of flow, and are restored to the initial state after the cessation of flow. However, as the surfactant concentration increases, the wormlike micelles aligned to the flow direction are restored with long relaxation times to the random and isotropic configuration after flow stops. In semi-dilute surfactant solutions, it is difficult to measure flow birefringence and orientation angle because the fully entangled structure induces linear and nonlinear responses with long relaxation times. Since the rheo-optical system has been described in the literature (Fuller, 1995), only the intensity analysis was briefly outlined here. The optical intensity measured for flow birefringence can be expressed in terms of harmonic oscillations with frequency,  $n\omega$  for signal analysis. The decoupled amplitude functions  $I_{dc}$ ,  $I_{1\omega}$  and  $I_{2\omega}$  of zeroth, first, and second harmonics together with the calibration constants,  $J_0$ ,  $J_1$  and  $J_2$ , determine the orientation angle,  $\chi$ , and the retardance,  $\delta$ , via Jones' calculus. The results are

$$I_{dc} = \frac{1}{2} [1 - J_0 \sin(2\chi) \sin \delta] \quad (2)$$

$$I_{1\omega} = J_1 \cos(2\chi) \sin \delta \quad (3)$$

$$I_{2\omega} = -J_2 \sin(2\chi) \sin \delta. \quad (4)$$

Couette geometry was used to measure the flow birefringence in the vorticity direction ( $\Delta n$ ). The flow birefringence is given by  $\Delta n = \lambda \delta / 2\pi d$  for a light signal of wavelength,  $\lambda$ . The ratio of Bessel functions,  $J_1(A)$  and  $J_2(A)$ , was given as  $J_1/J_2 = 1.214$ , which was very close to the theoretical value of 1.2.

Fig. 7 shows the measured intensity  $I_{1\omega}$  scaled by  $I_{dc}$  as a function of the elapsed time at various shear rates for the *dilute* regime. In this case, the CPC concentration is 5 mM with the molar ratio fixed at unity. Steady shear flow was applied for a period of 30s at 25°C. The magnitude of normalized intensity  $I_{1\omega}/I_{dc}$  increases with the elapsed time after flow inception, which implies that the micelles align to flow direction. As the shear rate increases above  $3.78 \text{ s}^{-1}$ , the optical intensity become stronger under the imposed shear flow, indicating flow-induced alignment of the wormlike micelles. This is consistent with the SEM image of Fig. 3(b). As the shear rate increases above  $5.27 \text{ s}^{-1}$ , the intensity begins to fluctuate and the onset of fluctuation occurs at earlier times with the increase in shear rate. It is worth reminding that the onset of shear thickening occurs at shear rate between  $20 \text{ s}^{-1}$  and  $30 \text{ s}^{-1}$ . Indeed, the intensity fluctuates very strongly when the shear rate reaches  $22.58 \text{ s}^{-1}$  due to the shear-induced interlayer coagulation of wormlike micelles. Evidently, this intensity fluctuation is caused by the coagulated structure that is reproduced in

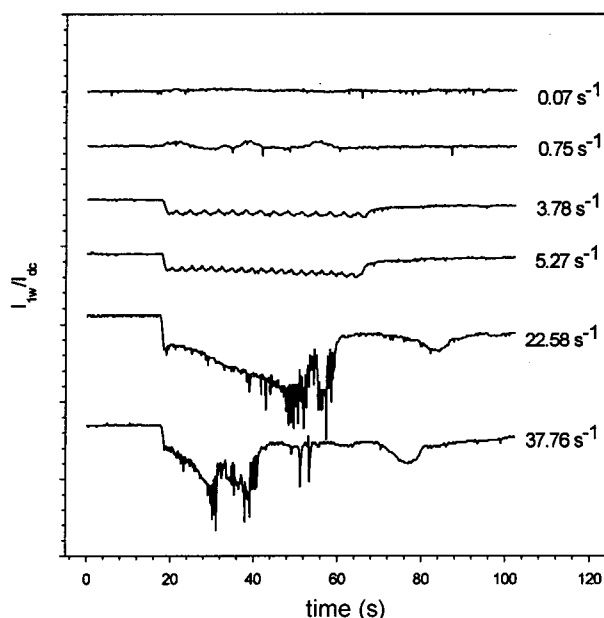


Fig. 7. Normalized optical intensity as a function of the elapsed time at various shear rates. The CPC concentration is 5 mM with the molar ratio fixed at unity.

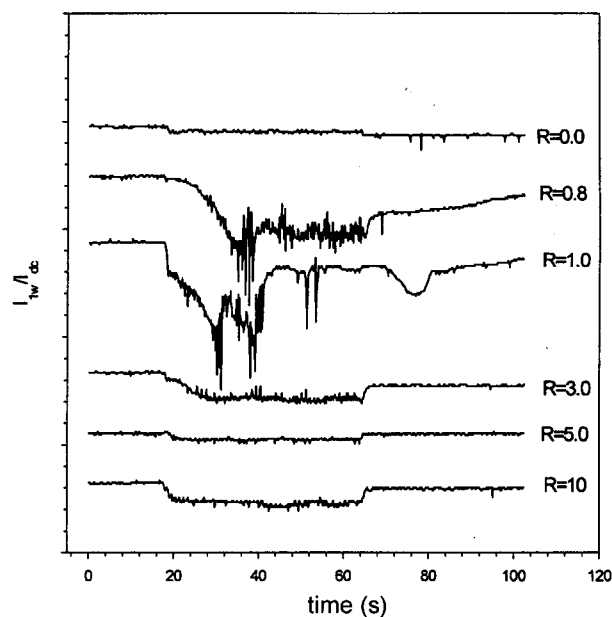


Fig. 8. Normalized optical intensity as a function of the elapsed time for various molar ratios at shear rate of  $37.76 \text{ s}^{-1}$ . The CPC concentration is fixed at 5 mM.

the SEM image of Fig. 3(c). Thus, the shear-induced coagulation is responsible for the onset of shear thickening.

In Fig. 8, the normalized intensity  $I_{1\omega}/I_{dc}$  is illustrated as a function of the elapsed time after inception of a shear flow with shear rate of  $37.76 \text{ s}^{-1}$  for various molar ratios. In this plot, the CPC concentration is fixed at 5 mM. As expected from the previous rheological responses, the intensity fluctuates the most strongly when the molar ratio is around unity, which is the most effective for the structure formation. However, at higher molar ratios, the intensity fluctuation becomes weak due to the scission of micelle junctions by the presence of excess NaSal. In Fig. 9, the shear-rate dependence of flow birefringence is shown for 5 mM CPC solution for various molar ratios. The flow birefringence is related not only to the orientation of anisotropic micelles toward the flow direction but also to the flow-enhanced coagulation of wormlike micelle. Thus, flow birefringence is the strongest at the equimolar ratio near unity.

Although the rheo-optical responses in the *semi-dilute* regime are not reproduced here, the results are summarized as follows. As the surfactant concentration increases, the onset shear rate of the sudden rise in the birefringence was reduced. Around the optimum molar ratio, the micellar solution in the semi-dilute regime is highly viscoelastic owing to the entangled chains and a sudden increase in flow birefringence is observed at relatively low shear rates. However, flow birefringence decreases as the shear rate increases. When the surfactant concentration is as high as 50 mM with the molar ratio around, any reproducible flow birefringence cannot be obtained due to very strong

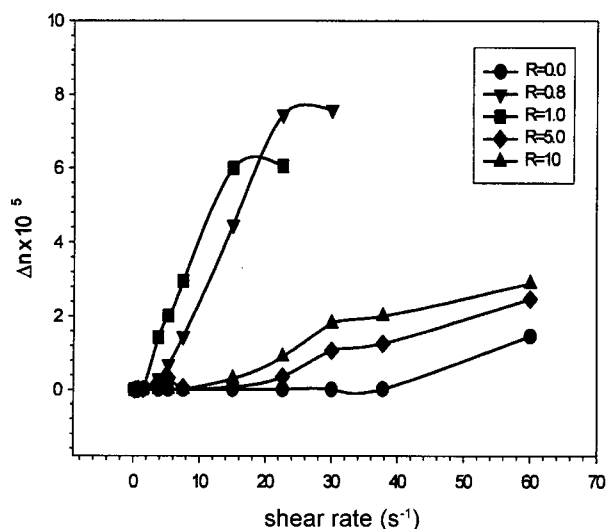


Fig. 9. Steady flow birefringence as a function of the shear rate for 5 mM CPC solution with various molar ratios.

intensity fluctuations caused by shear-induced coagulation.

#### 4. Summary

The rheological behavior of CPC/NaSal solution depends strongly on the CPC concentration and their molar ratio  $R$ . In the *dilute* regime, the micellar solutions exhibit a Newtonian plateau at low shear rates. However, as the shear rate increases above a certain critical value, the shear thickening occurs around  $R = 1.0$  due to the shear-induced aggregation caused by strong hydrodynamic interaction. In the *semi-dilute* regime, the entangled micelles stretch and align toward the imposed shear flow and viscosity shear thins continuously when the molar ratio is around unity. In this case, a Newtonian plateau is not observed at low shear rates. However, when the molar ratio is either far away from unity, a Newtonian plateau develops at low shear rates, and subsequently viscosity shear thins. The optical results are consistent with the rheological responses. The intensity fluctuation appears at the shear rate near the onset of shear thickening, which caused by shear-induced coagulation or aggregation. The SEM images of the *in situ* gelified micelles through sol-gel route show the well-aligned microstructure in the flow direction in the shear thinning regime and the interlayer coagulated structure in the shear thickening regime.

#### References

Bender, J. W. and N. J. Wagner, 1995, Optical measurement of the contribution of colloidal forces to the rheology of con-

centrated suspensions, *J. Coll. Int. Sci.* **172**, 171.

Berret, J-F., J. Appell and G. Porte, 1993, Linear rheology of entangled wormlike micelles, *Langmuir* **9**, 2851.

Bury, R., P. Favoritu and C. Treiner, 1998, Specific interactions between salicylate derivatives and cetylpyridinium chloride, *Colloids and Surface A: Physicochem. Eng. Aspects* **139**, 99.

Cates, M. E. and S. J. Candau, 1990, Statics and dynamics of worm-like surfactant micelles, *J. Phys. Condens. Matter* **2**, 6869.

Fuller, G. G., 1995, Optical rheometry of complex fluids, Oxford Univ. press, New York.

Hu, Y. T., P. Boltenhagen and D. J. Pine, 1998, Shear thickening in low-concentration solutions of wormlike micelles. I. Direct visualization of transient behavior and phase transitions, *J. Rheology* **42**, 1185.

Humbert, C. and J. P. Decruppe, 1998, Stress optical coefficient of viscoelastic solutions of CTAB and KBr, *Colloid Polymer Sci.* **276**, 160.

Israelachvili, J. N., 1985, Intermolecular and surface forces, 2nd ed., Academic press, New York.

Kabir-ud-Din, D. Bansal and S. Kumar, 1997, Synergistic effect of salts and organic additives on the micellar association of cetylpyridinium chloride, *Langmuir* **13**, 5071.

Kim, W.-J., S.-M. Yang and M. Kim, 1997, Additive effects on the microstructure evolution in CTAB solution and its rheological properties, *J. Colloid Interface Sci.* **194**, 108.

Kim, W.-J. and S.-M. Yang, 2000a, Flow-induced silica structure during in situ gelation of wormy micellar solutions, *Langmuir* **16**, 4761.

Kim, W.-J. and S.-M. Yang, 2000b, Microstructure and rheological response of aqueous CTAB solutions in the presence of benzyl additives, *Langmuir* **16** 6084.

Kim, W.-J. and S.-M. Yang, 2000c, Effects of sodium salicylate on the microstructure of an aqueous micellar solution and its rheological responses, *J. Colloid Interface Sci.* **231**, in press.

Lee, J.-D. and S.-M. Yang, 1998, Rheo-optical behaviors and stability of a silica particle suspension coated with silane coupling agents, *J. Colloid Interface Sci.* **205**, 397.

Liu, C. H. and D. J. Pine, 1996, Shear-induced gelation and fracture in micellar solutions, *Physical Review Letters* **77**, 2121.

Macosko, C. W., 1994, Rheology: principles, measurements, and applications, VCH Publishers, New York.

Phanton, A., C. Schott and D. Quamada, 1998, Rheological behavior of flexible elongated micelles, *Colloids and Surface A: Physicochem. Eng. Aspects* **145**, 37.

Rao, D. R. K., C. Manohar, B. S. Valanlikar and R. M. Iyer, 1988, Micellar chain model for the origin of the viscoelasticity in dilute surfactant solutions, *J. Phys. Chem.* **91**, 3286.

Rehage, H. and H. Hoffmann, 1991, Viscoelastic surfactant solutions: model system for rheological research, *Mol. Phys.* **74**, 933.

Rehage, H. and H. Hoffmann, 1988, Rheological properties of viscoelastic surfactant systems, *J. Phys. Chem.* **92**, 4712.