

## Rheological behavior and wall slip of dilute and semidilute CPyCl/NaSal surfactant solutions

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(Received May 1, 2003; final revision received August 25, 2003)

### Abstract

In this research, experimental studies were performed to examine the rheological behavior of equimolar solutions of cetylpyridinium chloride (CPyCl) and sodium salicylate (NaSal) solutions with concentration. The surfactant solutions were prepared by dissolving 2 mM/2 mM–80 mM/80 mM of surfactant/counterion in double-distilled water. It has been observed that the zero shear viscosity shows abrupt changes at two critical values of  $C^*$  and  $C^{**}$ . These changes are caused by the switching of relaxation mechanism with concentration of CPyCl/NaSal solutions at those concentrations. The wall slip velocities of dilute and semidilute CPyCl/NaSal solutions show a dramatic increase with shear rate where the shear viscosity exhibits shear thickening behavior for dilute solutions and shear thinning behavior for semi-dilute solutions, respectively. Considering that the dramatic increase in wall slip velocity should be related to the formation of shear-induced structure (SIS) in the surfactant solution, the shear thickening behavior of semi-dilute solutions is caused by elastic instability unlike the case of dilute solutions.

**Keywords :** zero shear viscosity, wall slip, shear induced structure, elastic instability

### 1. Introduction

Surfactants have many practical applications like cosmetic industries where it is important to control the flow behavior and the viscoelastic properties of the surfactant solutions (Reif *et al.*, 2001; Hoffmann, 1994). Cationic surfactant molecules are amphiphilic that consist of a hydrophilic head group with positive charge and a lyophilic tail. In a solution state, it is well known that cationic surfactant molecules spontaneously self-assemble to form highly flexible, locally cylindrical aggregates with an average size approaching several microns. The dynamics of these systems differs from those of conventional polymers in that the wormlike micelles are continuously breaking apart and recombining. The rheological behavior of these surfactant solutions is known to follow "reaction-reptation model" (Cates, 1987) which is an extension of the reptation model of polymer relaxation to cylindrical micelles of surfactant molecules undergoing reversible scission and recombination processes.

The linear and nonlinear viscoelastic properties of surfactant solutions have been extensively studied over past few years, both theoretically (Cates, 1994; Cates and Candau, 1990) and experimentally (Hu *et al.*, 2002; Shikata *et*

*al.*, 2002; Lin *et al.*, 2002; 2001; Hoffmann, 1994; Rehage, 1994; Rehage and Hoffmann, 1991). In general, it is observed that there is a critical shear rate above which the viscosity dramatically increases for dilute concentration of surfactant solution. The cause of this shear thickening phenomenon is believed to be the flow-induced structure of surfactant solution under shear flow (Hu *et al.*, 1998a; 1998b; 2002; Rehage and Hoffman, 1982). With increasing flow intensity, the micelles undergo coalescence or tend to be stretched toward the flow direction, and as shear flow is going with time, the shear-induced structure of wormlike micelles continuously breaks down and re-forms at high shear rate (Kim and Yang, 2000). This shear-induced structure (SIS) behaves like a gel and shows strong flow birefringence in solution state (Lin *et al.*, 2001). For semidilute surfactant solutions, zero shear viscosity initially increased with concentration, reached a maximum, and then decreased (Rehage and Hoffmann, 1991; Hoffmann, 1994; Zana, 2002). Also, the shear viscosity of semi-dilute CPyCl/NaSal solutions showed almost a constant value until the critical shear rate and then shear thinning began, followed by shear thickening at higher shear rate (Kim and Sung, 2001).

In the present study, we have compared the effects of concentration on rheological properties and the formation of shear induced structure over a wide range of CPyCl solutions (from 2 mM (dilute region) to 80 mM (semi-dilute

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region)). Also, we give here a first account of a relationship between wall slip and the formation of shear-induced structure in dilute and semi-dilute CPyCl/NaSal solutions.

## 2. Experimental

### 2.1. Materials

In this study, cetylpyridinium chloride (CPyCl) and sodium salicylate (NaSal), purchased from Aldrich Chemical Co., were chosen as the cationic surfactant and the counterion, respectively. Double-distilled water was used as the solvent. The ratio of concentrations of the surfactant and counterion was 1.0 and sample concentrations (surfactant/counterion) were 2–80 mM/80 mM.

### 2.2. Rheological measurements

**Shear and complex viscosity** Shear viscosity and linear viscoelastic properties were measured using an Advanced Rheometric Expansion System (ARES, Rheometrics Co.) with the Couette cell geometry. The Couette cell had a cup diameter of 34 mm and bob diameter of 32 mm. The bob length was 33.25 mm. Temperature was controlled by a fluid bath within  $\pm 0.5$  K of the experimental temperature, 298 K (25°C).

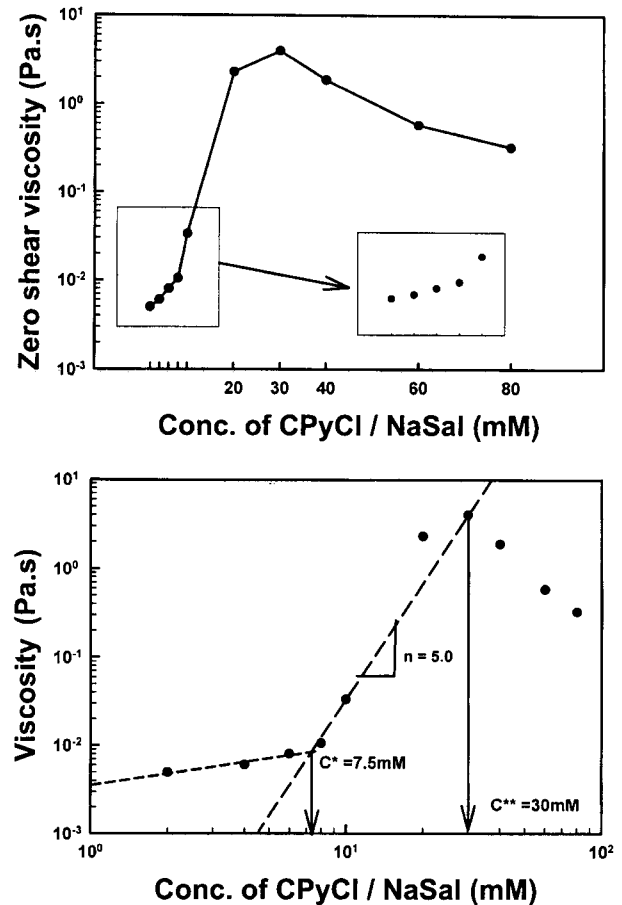
The shear viscosity of 2 mM/2 mM, 4 mM/4 mM, 6 mM/6 mM, and 8 mM/8 mM CPyCl/NaSal solutions at low shear rate region can not be detected by our rheometer (ARES), so that the zero shear viscosity of these solutions were obtained from creep measurements using a stress type rheometer (AR 2000<sup>TM</sup> from TA Instrument).

**Wall slip measurements** A stress-controlled rheometer (AR2000<sup>TM</sup>) was used with a parallel-plate geometry to obtain steady shear viscosity as a function of gap-distance. The upper plate was an acrylic plate with a diameter of 60mm and the lower plate was a constant temperature peltier with a larger diameter than the upper plate. It was assumed that the wall-slip velocity should be dependent only on shear stress and therefore the apparent shear rate should decrease as the inverse of the fixture gap distance at a constant shear stress (Yoshimura and Prudhomme, 1988; Hu *et al.*, 2002). Therefore, the wall slip velocity was obtained from the relationship between apparent shear rate and fixture gap distance. This procedure will be discussed further in wall slip measurements section.

## 3. Results and discussion

### 3.1. Shear viscosity and linear viscoelastic properties

Figure 1 shows the zero shear viscosity of CPyCl/NaSal solutions with concentration. In Fig. 1, it is observed that the zero shear viscosity of CPyCl/NaSal solutions begins to increase abruptly from about 7.5 mM/7.5 mM which marks the cross-over concentration,  $C^*$ , from dilute to the



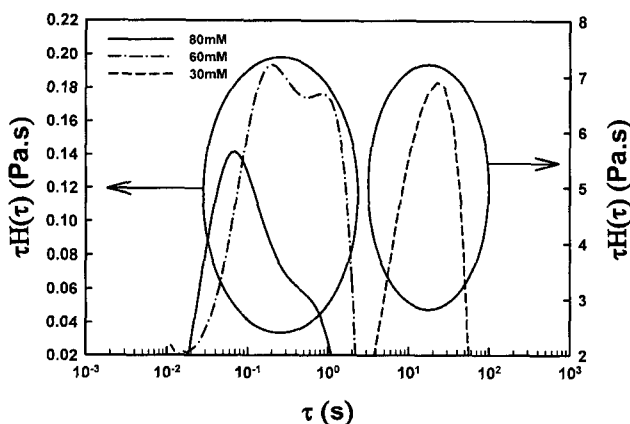
**Fig. 1.** (a) Log-log plot of zero shear viscosity for CPyCl/NaSal solutions against concentration at 25°C. The *inserted figure* is the magnification of dilute region of CPyCl/NaSal solutions. (b) CPyCl/NaSal solutions show power law behavior within the range of  $C^* < C < C^{**}$ , and power exponent of CPyCl/NaSal solutions at this range is about 5.0.

semi-dilute solutions. From this abrupt increase in zero shear viscosity, it is considered that micelles in CPyCl/NaSal solutions overlap and form an entangled network of wormy micelles from  $C^*$ . Above 30 mM/30 mM, the zero shear viscosity of CPyCl/NaSal solutions decreases with increasing the concentration of surfactant solution. We will call this critical concentration  $C^{**}$ . Hoffmann (1994) has suggested that the viscosity of surfactant solutions can be represented by a power law of the form  $\eta \propto (C/C^*)^x$  in which the power exponent ( $x$ ) varies from  $x = 1.3$  to 8.5. He has also suggested that the rheological behavior of surfactant solutions which have a high exponent (close to 8.5) is probably governed by the pure reptation mechanism while the rheological behavior of surfactant solutions which have a low exponent (close to 1.3) is probably governed by a purely kinetic, diffusion controlled process. From Fig. 1, we obtain that the power exponent of CPyCl/NaSal solutions in  $C^* < C < C^{**}$  region is about 5.0, and this exponent value is close to the slope of  $4.5 \pm 0.5$  which is

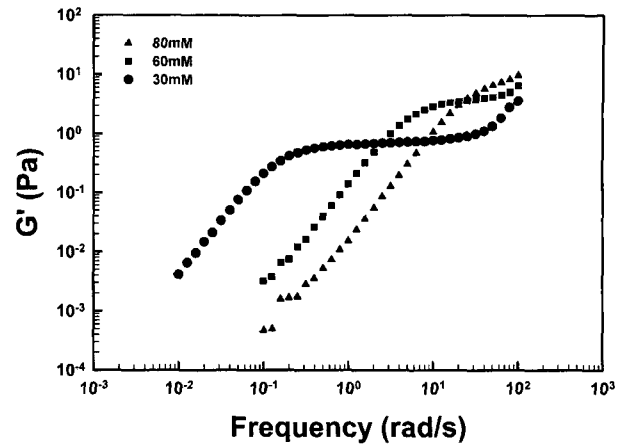
expected for a large polymer molecule which does not change its size with concentration (Hoffmann, 1994). Therefore, it is postulated that the rheological behavior of CPyCl/NaSal solutions in semi-dilute region ( $C^* < C < C^{**}$ ) is governed by the pure reptation mechanism. However, it is found that the power exponent of CPyCl/NaSal solutions shows a negative value above  $C^{**}$ . In surfactant solutions, zero shear viscosity and self-diffusion coefficient can be expressed as a function of concentration (Cate and Candau, 1990), and these two parameters are correlated as follows: zero shear viscosity increases with increasing concentration of surfactant solution in semi-dilute region while self diffusion coefficient decreases with concentration in this region. Recently, Narayanan *et al.* (1998) reported that self-diffusion coefficient was found to be increasing with concentration of cationic surfactant solution above the critical concentration in semi-dilute region. In that case, the concentration dependence of the zero shear viscosity cannot be described by the reptation model for linear worms above the critical concentration of cationic surfactant solution in semi-dilute region (Lequeux, 1992). Therefore, the phenomenon, the decrease in zero shear viscosity with increasing concentration above  $C^{**}$  in semi-dilute region, is an indication that CPyCl/NaSal system can undergo a switch of the relaxation mechanism when the concentration is increased.

This argument can be confirmed by inspecting the relaxation spectrum of CPyCl/NaSal solution with concentration. Fig. 2 shows the weighted relaxation spectra ( $\tau \cdot H(\tau)$ :  $H(\tau)$  is the relaxation spectrum) with relaxation time ( $\tau$ ) for low (30 mM/30 mM) and high (60 mM/60 mM and 80 mM/80 mM) concentrations of CPyCl/NaSal in semi-dilute region. The weighted relaxation spectra were obtained from the storage modulus data shown in Fig. 3. Given the experimental data on  $G'$  and  $G''$ ,

$$G'(\omega) = \int_{-\infty}^{\infty} [H(\tau)\omega^2\tau^2/(1+\omega^2\tau^2)]d(\ln \tau) \quad (1)$$



**Fig. 2.** Weighted relaxation spectrum  $\tau H(\tau)$  as a function of the relaxation time  $\tau$  for the 30 mM/30 mM, 60 mM/60 mM, and 80 mM/80 mM CPyCl/NaSal solutions at 25°C.



**Fig. 3.** The storage modulus  $G'$  and loss modulus  $G''$  as a function of the angular frequency  $\omega$  for the 30 mM/30 mM, 60 mM/60 mM, and 80 mM/80 mM CPyCl/NaSal solutions at 25°C.

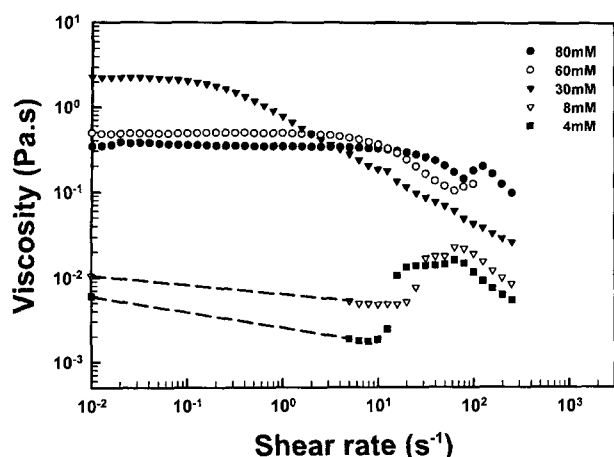
$$G''(\omega) = \int_{-\infty}^{\infty} [H(\tau)\omega\tau/(1+\omega^2\tau^2)]d(\ln \tau) \quad (2)$$

the relaxation spectrum ( $H(\tau)$ ) can be determined using the Tschoegle approximation as follows (Tschoegle, 1989):

$$H(\tau) = G' \left[ d \log G' / d \log \omega - \frac{1}{2} (d \log G' / d \log \omega)^2 - (1/4.606) d^2 \log G' / d (\log \omega)^2 \right]_{1/\omega = \tau/\sqrt{2}} \quad (3)$$

where  $\omega$  is frequency and  $\tau$  is relaxation time. From Fig. 2, it is observed that there is a single relaxation time at about 20 sec for low concentration CPyCl/NaSal solution in semi-dilute region. For highly concentrated solutions in semi-dilute region, we can observe two separate peaks which might correspond to the two main processes causing stress relaxation. Rehage (1994) has suggested that one extreme value of two different peaks describes the average breaking time and the other one the reptation property of the rodlike micelles. From the results of zero shear viscosity and relaxation spectrum with concentration of the solutions, we can anticipate that rheological behavior of low and high concentration CPyCl/NaSal solutions in semi-dilute region is governed by the reptation model and another mechanism, respectively.

Figure 4 shows the shear viscosity with shear rate for the various concentration of CPyCl/NaSal solutions at 25°C. The shear viscosities of 2–8 mM CPyCl/NaSal solutions slightly decrease (very weak shear thinning behavior) until about 20  $s^{-1}$ . Above 20  $s^{-1}$ , it is observed that the shear viscosity of these dilute solutions abruptly increases by about 2.1–2.7 fold. The shear-thickening phenomenon of these solutions at high shear rate is a strong evidence of the formation of a gel-like structure called “shear induced structure (SIS)” (Larson, 1999). Similar rheological behavior was reported for CPyCl/NaSal system with different sur-



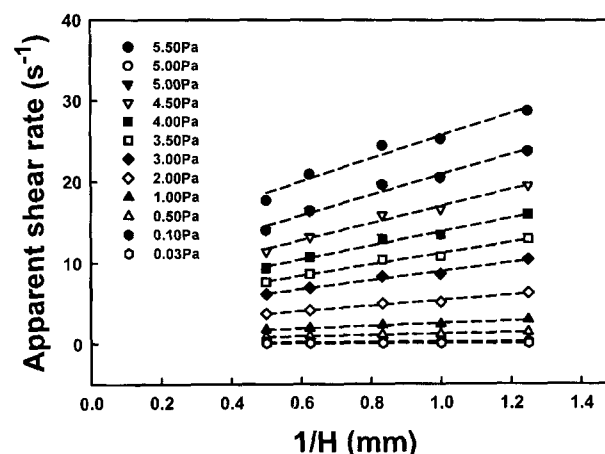
**Fig. 4.** Apparent shear viscosity vs. apparent shear rate for various concentration CPyCl/NaSal solutions at 25°C. Note the shear viscosity of 4 mM/4 mM and 8 mM/8 mM CPyCl/NaSal solutions at low shear rate region (dot line in figure) can not be detected by ARES, so that zero shear viscosity of these solutions were obtained from creep measurements. Also, dot line in figure represents simple straight connection between zero shear viscosity obtained from creep measurements using stress type rheometer (TA 2000) and shear viscosity which could be measured using ARES.

factant/concentration ratio from the present study by Hu *et al.* (1998a; 1998b), for TTAA/NaSal system by Boltenhagen (1997) and for CTAB/NaSal system by Liu and Pine (1996).

In the case of cetyltrimethylammonium chloride with added sodium salicylate (CTAC/NaSal), wormy micelles are formed when the ratio of the molarity of NaSal to that of CTAC exceeds 0.20 (Larson, 1999). Therefore, we also expect that wormy micelles should be easily formed in our equimolar system. In Fig. 4, the shear viscosity of 60 mM/60 mM CPyCl/NaSal solution shows almost constant value until 4 s<sup>-1</sup> followed by shear thinning behavior while it increases somewhat at higher shear rate (about 60 s<sup>-1</sup>). Similarly, the shear viscosity of 80 mM/80 mM CPyCl/NaSal solutions is almost constant until about 10 s<sup>-1</sup> above which shear thinning begins followed by shear thickening at about 70 s<sup>-1</sup>. For the semi-concentrated CPyCl/NaSal solutions, the cause of shear thinning behavior is reported to be caused by the formation of SIS under shear flow (Lin *et al.*, 2001).

### 3.2. Wall slip measurements

When there is slip between fluid and the solid boundaries of parallel plates the actual (true) shear rate that fluid experiences is not the same as the apparent shear rate determined by the rotational speed and gap distance. These two shear rates are related as follows assuming that wall slip velocity does not depend on gap distance at constant shear



**Fig. 5.** The determination of the wall slip velocity and the true shear rate for differing shear stress using the Mooney analysis. The slope of each curve is the twice the slip velocity and the intercept is the true shear rate.

stress (Yoshimura and Prud'homme, 1988):

$$\dot{\gamma}_{app} = \dot{\gamma}_{true} + \frac{2V_s}{h} \quad (4)$$

where  $\dot{\gamma}_{app}$  is apparent shear rate,  $\dot{\gamma}_{true}$  is true shear rate,  $V_s$  is wall slip velocity, and  $h$  is the gap distance between plates. According to Eqn. (4) the intercept of the plot of apparent shear rate vs. inverse of the gap is the true wall shear rate and the slope is twice the slip velocity for the assumed wall shear stress.

Figure 5 shows the plot of apparent shear rate vs. the inverse of gap distance at different shear stresses. In Fig. 5, it is found that the apparent shear rate is not constant for differing  $h$ , and therefore we can confirm that there is wall slip indeed. It is also found that the relationship between  $\dot{\gamma}_{app}$  and  $1/h$  is linear at constant stresses from 0.03 to 5.5 Pa indicating that we can apply Eqn. (4) to our system to determine wall slip velocities. Figure 6 shows the wall slip velocities of CPyCl/NaSal solutions at various concentrations.

Figure 6 shows the wall slip velocity and the true shear viscosity for differing concentration of surfactants. When the surfactant solution is dilute (Fig. 6 (a), 8 mM), the wall slip does not occur when the true shear rate is less than 7 s<sup>-1</sup>. The viscosity is almost the same at a very low value in this case. But when the shear rate has a slightly larger value the slip velocity increases almost vertically and the true viscosity also increases abruptly. It appears that the data obtained here does not seem to be the true value even after the wall-slip correction since it has multiple values. From the viscosity data we can confirm that the surfactant solution becomes a gel phase. On the other hand, for semi-dilute solutions, the increasing patterns of wall slip velocity and viscosity are smooth with increase in true shear rate. Here, we define the critical shear rate for the sudden

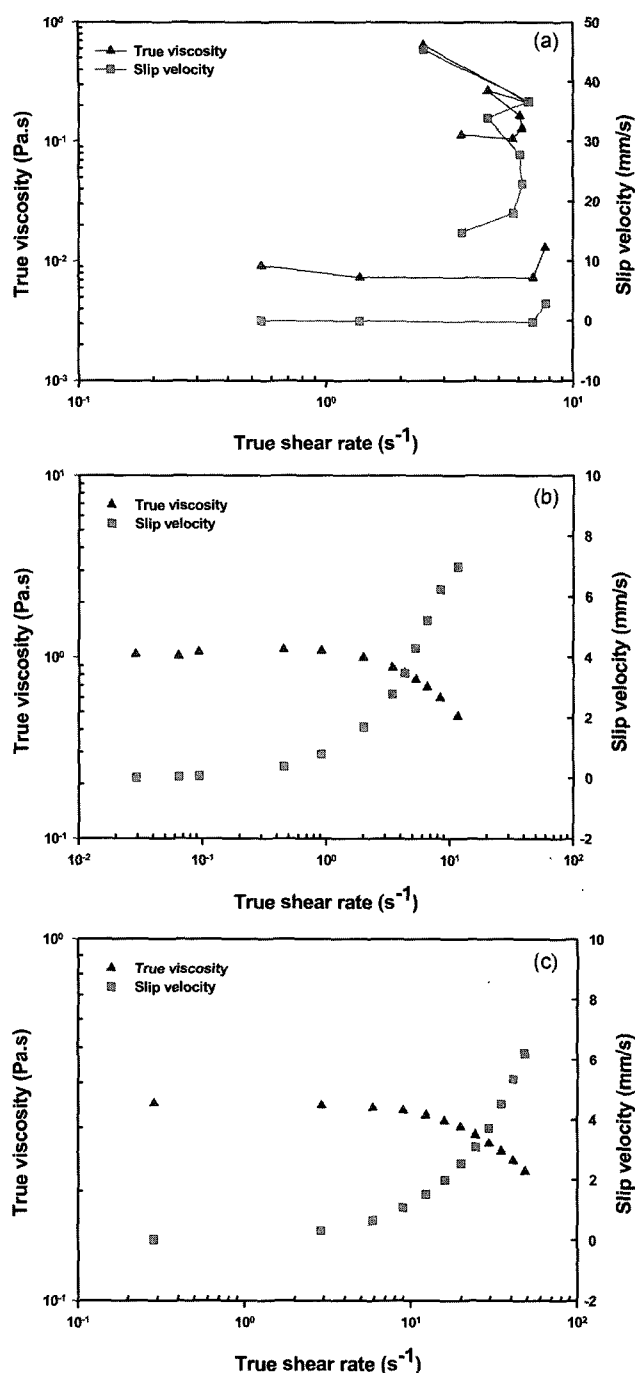


Fig. 6. True viscosity and wall slip velocity after the wall slip correction. (a) 8 mM (b) 60 mM (c) 80 mM.

increase in wall slip velocity as the cross over shear rate shown in Fig. 7. We also define the critical shear rate for the sudden change in the viscosity similarly. For 60 mM/60 mM, and 80 mM/80 mM of CPyCl/NaSal solutions, wall slip velocities abruptly increase at about 2 and 10  $\text{sec}^{-1}$  at which the viscosity of the solutions begins to show shear thinning behavior. It is believed that the abrupt increase in the wall slip velocity is a strong indication that shear

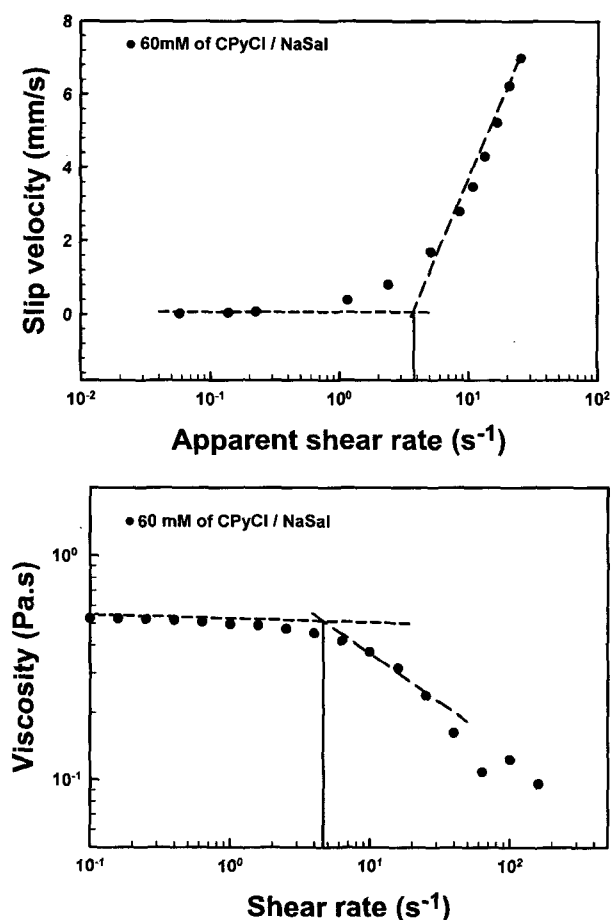


Fig. 7. Determination of the critical shear rate for the sudden increase in wall slip velocity (above) and the critical shear rate for the sudden change in viscosity (lower).

induced structure (SIS) is formed in the solution because the SIS is basically a gel phase with very large viscosity. This may be confirmed by other independent experiments such as the rheo-optic measurement or flow visualization.

The shear thickening phenomena observed in semi-dilute solutions should be caused by the elastic instability. Since the viscosity of gel phase is very large, the inertial effect should be small and therefore the shear thickening is caused by the formation of secondary flow. We can conclude that the strong shear flow imposed on the elastic gel becomes unstable. This can be also confirmed by other independent experiments such as the rheo-optic measurement or flow visualization. We may estimate the viscoelastic properties of gel phase formed in the high shear flow from the analysis of the elastic instability characteristics.

#### 4. Summary

In this research, experimental studies were performed to examine the rheological behavior of equimolar solutions of cetylpyridinium chloride (CPyCl) and sodium salicylate

(NaSal) solutions with concentration. It has been observed that the zero shear viscosity shows abrupt changes at two critical values of  $C^*$  and  $C^{**}$ . The rheological behavior of dilute ( $C < C^*$ ) and semi dilute solutions ( $C > C^{**}$ ) has been found to be qualitatively different. The cause of the difference is originated from the differences in the relaxation mechanism for the linear viscoelastic behavior. We have observed shear thickening phenomena for dilute and semi-dilute solutions. In the case of dilute solutions, the shear thickening is originated from the formation of shear induced state for the high shear flow. On the other hand, the shear thickening of semidilute solutions is caused by the elastic instability of gel phase that has been already formed before the incipience of the shear thickening phenomena. Therefore the rheological behavior of dilute and semidilute solutions is qualitatively different. For better understanding of their rheological behavior more studies are needed. It has been found that the wall slip is correction is very important in measuring the rheological properties of surfactant solutions.

### Acknowledgement

This study was supported by research grants from the Korea Science and Engineering Foundation (Project No. 2000-6-308-01-2).

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