

## ARTICLE

# Rheological Behavior of Aqueous Solutions of Cationic Guar in Presence of Oppositely Charged Surfactant

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The cationic guar (CG) is synthesized and the rheological behavior of aqueous solutions of CG in the presence of sodium dodecyl sulfate (SDS) is studied in detail. The steady viscosity measurements show that the zero shear viscosity enhancement can be almost 3 orders of magnitude as the concentration of SDS increases from 0 to 0.043%. The gel-like formation is observed as the concentration of SDS is greater than 0.016%. The oscillatory rheological measurements of CG solutions in the presence of SDS show that the crossover modulus is almost independent of the concentration of SDS whereas the apparent relaxation time increases swiftly upon increasing the concentration of SDS. The experimental results indicate that the strength rather than the number of the cross-links is greatly affected by SDS molecules. The mechanism concerning the effect of SDS upon the rheology of CG solutions can be coined by the two-stage model. Before the formation of cross-links at the critical concentration, the electrostatic interaction between SDS and cationic site of CG chains plays a key role and the SDS molecules bind to CG chains through the electrostatic interaction. After the formation of cross-links at the concentration greater than the critical concentration, the cooperative hydrophobic interaction become dominant and SDS molecules bind to the cross-links through the hydrophobic interaction. The rheological behavior of aqueous solutions of CG in the presence of SDS is chiefly determined by the micelle-like cross-links between CG chains. In fact, the flow activation energy of CG solution, obtained from the temperature dependence of the apparent relaxation time, falls in the range of transferring a hydrophobic tail of SDS from the micelle to an aqueous environment.

**Key words:** Cationic guar, Sodium dodecyl sulfate, Rheological behavior, Relaxation time, Zero-shear viscosity

## I. INTRODUCTION

Guar gum is a natural non-ionic polysaccharide produced from the seeds of two annual leguminous plants, *Cyamopsis tetragonolobus* and *psoraleoides*. The guar gum macromolecule is a chain of (1→4)-linked  $\beta$ -D-mannopyranose units with  $\alpha$ -D-galactopyranose units connected to the mannose backbone through (1→6) glycosidic linkages. The poly-mannose chain is randomly substituted with galactose units at a mannose-to-galactose ratio of 1.8–1.0. Guar has been used widely as an effective food additive, gelling, thickening agent in various fields such as food, mining, paper, textile, ceramic, paint, cosmetic, pharmaceutical and explosives [1, 2], mainly because of its ability to produce a highly viscous solution even at low concentration. The high viscosity of guar solution arises due to the high molec-

ular weight of guar (up to 2 million) and the presence of extensive intermolecular association (hyperentanglement) through hydrogen bonding [3–5]. However, guar gum does not form “truly molecular” solution. Under normal condition, aqueous solutions of guar gum contain a small fraction of undissolved colloidal aggregates and only a combination of high temperatures and pressures during the solution preparation stage results in a complete (or nearly complete) dissolution and hydration of the guar gum [6]. The less good solubility of guar gum in water limits its more wide applications. In attempt to eliminate this problem and broaden its applications in numerous industries, guar gum has been modified into various water-soluble derivatives by using reactive functional groups to substitute free hydroxyl groups along the macromolecular backbone of its chains. For example, the treatments of guar with ethylene oxide, propylene oxide and chloroacetic acid in an alkaline medium result in the formation of hydroxyethyl guar, hydroxypropyl guar, and carboxymethyl guar, respectively [7–9]. In particular, faster and better solubility in water as well as multifunctional characteristics can be obtained

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for this biomacromolecule by the introduction of ionic substituents.

In this work, the cationic guar (CG) is synthesized and the rheological behaviors of CG solution in the presence of the oppositely charged surfactant sodium dodecyl sulfate (SDS) are measured. It is well known that in solution of a rigid polyelectrolyte such as cationic cellulose in the presence of the oppositely charged surfactant, the strong interaction between polymer and surfactant can lead to a large increase in solution viscosity, or even a gel-like behavior [10–15]. For example, when an anionic surfactant, such as SDS, sodium dodecylbenzenesulfonate (SDBS), or sodium bis(ethylhexyl) sulfosuccinate (AOT), is added into a cationic cellulose solution, a great increase in apparent viscosity occurs. In fact, the formation of strong, clear aqueous gels has been observed at quite low levels of polymer (about 1%) with the surfactant at about one-tenth of this concentration. On the other hand, in solutions of a flexible polyelectrolyte based on repeated vinyl chemistry structure units, the addition of an oppositely charged surfactant into the solutions always results in a single phase at low and high surfactant concentration, whereas a phase separation at intermediate levels of surfactant concentration [16]. Gel-like behavior has not been observed during the whole process. However, for semi-rigid polyelectrolytes such as CG, the mechanism concerning the effect of the oppositely charged surfactants upon the rheological behavior of its semi-dilute solution, to our knowledge, has not yet been reported in detail.

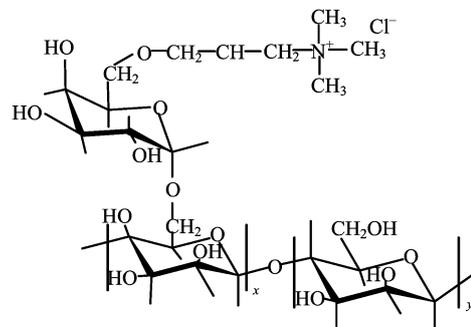
## II. EXPERIMENTS

### A. Materials

Guar gums of  $M_W=1.8 \times 10^6$  was a gift sample by Production Engineering Research Institute of Daqing Oil Field. Sodium dodecyl sulfate (SDS) with the purity greater than 99.9% was obtained from Second Chemical Company (Xuzhou, China) and used as received without any further purification. 3-chloride-2-hydroxypropyl N,N,N-trimethylammonium chloride, A.R. of sodium hydroxide and acetic acid were procured from Shanghai Chemical Reagent Company.

### B. Methods

Cationic guar was obtained by grafting hydroxypropyl trimethylammonium chloride groups both on mannose and galactose units according to Chowdhary's method [17]: Guar gum was first added to 85% isopropyl alcohol solution. Then, 3-chloride-2-hydroxypropyl-N,N,N-trimethylammonium chloride was added over a 15 min period and the mixture was stirred for an additional 15 min. 50% NaOH solution was added over a 15 min and the mixture was stirred for an additional 15 min. Thereafter, the mixture was heated to 65 °C and held at this temperature for 3 h.



Scheme 1 Chemical structure of the cationic guar.

The mixture was cooled to about room temperature and neutralized to a pH of about 7 by the addition of glacial acetic acid. The reactor was purged with  $N_2$  in all the procedures. The mixture was filtered and the filtered solids was washed successively with 50% isopropyl alcohol aqueous solution, 85% isopropyl alcohol aqueous solution, 100% isopropyl alcohol, and acetone. The charges are believed to be randomly distributed along the chains (Scheme 1). The degree of cationic substitution, determined by nitrogen analysis according to Kjeldahl analysis [18], was found to be 13.8%.

All samples were individually prepared by mixing appropriate aqueous stock solutions of polymer and surfactant at different ratios to achieve the desired final composition. The solutions were homogenized by stirring for 1 day and further centrifugated for 30 min at 3500 r/min in order to remove eventual bubbles resulting from stirring. Note that the aqueous solutions investigated with or without surfactant were in all cases perfectly homogeneous and transparent for the concentration employed.

Oscillatory shear and steady shear measurements were performed using a TA AR-G2 rheometer, depending on the viscosity of the sample, using the cone plate system (diameter of 35 mm, angle of 2°) or the system of coaxial cylinders (stator inner radius of 15 mm, rotor inner radius of 14 mm) cylinder immersed height of 42 mm). To avoid the effect of solvent evaporation, a specially constructed vapor lock filled with the solvent was used. The sample was equilibrated for at least 20 min at certain temperature prior to conducting measurements. The storage modulus  $G'$  and the loss modulus  $G''$  were measured over the frequency range  $10^{-3}$ –100 rad/s. The values of the stress amplitude were checked in order to ensure that all measurements were performed within the linear viscoelastic region, where the dynamic storage moduli were independent of applied stress.

## III. RESULTS AND DISCUSSION

Figure 1 shows the viscosity as a function of shear rate for aqueous CG solution in the presence of SDS

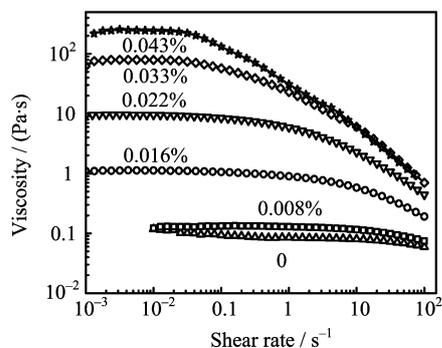


FIG. 1 The viscosity as a function of shear rate for aqueous CG solutions in the presence of various concentrations of SDS at 25 °C. The concentration of CG is 0.6%.

at 25 °C. The CG concentration is kept to be 0.6%, which is above the overlap concentration  $C^*=0.15\%$  for CG in the pure water. From Fig.1 it can be seen that the viscosity of CG solution increases significantly upon addition of SDS in solution. In particular, a viscosity enhancement is observed to be almost 3 orders of magnitude as SDS increases from 0 to 0.043%. To further demonstrate the effects of SDS molecules upon the viscosity of CG solution, we plot in Fig.2 the zero-shear viscosity  $\eta_0$  as a function of the SDS concentration for aqueous CG solutions at 25 °C. From Fig.2 it can be seen that the zero-shear viscosity of CG solution increases swiftly as the concentration of SDS in solution is greater than the critical concentration  $C_s$ . The reasonable interpretation is that SDS molecules bind to CG chains through the electrostatic interaction. When the number of SDS molecules binding to CG chains is sufficient, *i.e.* the concentration of SDS in solution is greater than  $C_s$ , the CG chains begin to associate together through the hydrophobic interaction. This leads to the formation of cross-links between CG chains in solution. The viscosity of CG solution, therefore, increases significantly as the concentration of SDS is greater than  $C_s$ .

From Fig.1 it can also be seen that the viscosity of CG solution in the presence of SDS is nearly independent of the shear rate (Newtonian behavior) at low shear rates but markedly shear-thinning at high shear rates. Furthermore, the higher the SDS concentration, the more shear thinning the solution becomes. The onset of such shear-thinning can be referred to as the formation of the new structure related to SDS molecules, or more precisely, to the cross-links of SDS molecules. The shear rate at which shear-thinning occurs can be considered as the relaxation time of the network structure under shear. The observation that shear thinning occurs at lower shear rates indicates an increase of this relaxation time with increasing SDS concentration. As presented by Chronakis *et al.* [19], the long relaxation time could be ascribed to the strong association of the polymer-surfactant complexes and may also be related to the

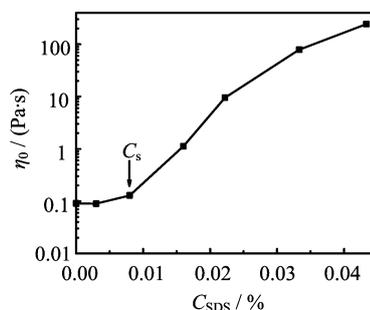


FIG. 2 The zero-shear viscosity as a function of SDS concentration for aqueous CG solutions at 25 °C.

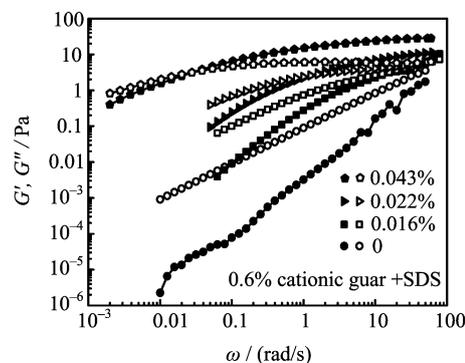


FIG. 3 Frequency dependencies of the storage modulus  $G'$  (filled symbols) and the loss modulus  $G''$  (open symbols) for aqueous CG solutions in the presence of SDS with various concentrations at 25 °C.

slow dissociation of associated complex domain. Therefore, the addition of SDS to CG solution may increase either the cross-link density or the lifetime of cross-links. To obtain the detailed information concerning the mechanism of SDS upon the rheology of CG solution, the oscillatory rheological measurements of CG solution in the presence of SDS are carried out in this work.

It is already known that in a system that can be described by a single Maxwell model (a spring and a dash pot in a series),  $G'$  and  $G''$  can be written as [20]

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

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

where  $G_\infty$  represents the plateau value of  $G'$  at high frequencies,  $\tau$  is the specific relaxation time, and  $\omega$  is the angular frequency. Figure 3 shows the frequency dependence of  $G'$  and  $G''$  for CG solutions in the presence of SDS with various concentrations at 25 °C. The concentration of CG is fixed to be 0.6%. It can be seen that the CG solution in the presence of SDS exhibit a viscoelastic behavior, with  $G'' > G'$  (viscous behavior) at low frequencies and  $G' > G''$  at higher frequencies where the elastic response dominates. From Fig.3 it can be

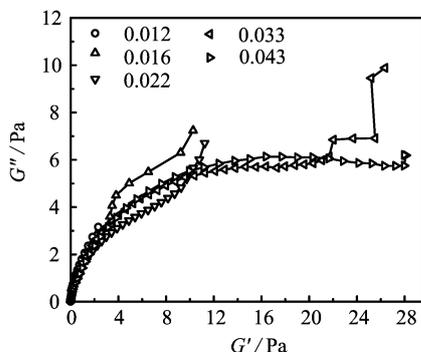


FIG. 4 Cole-cole plots of aqueous CG solutions in the presence of SDS with various concentrations at 25 °C.

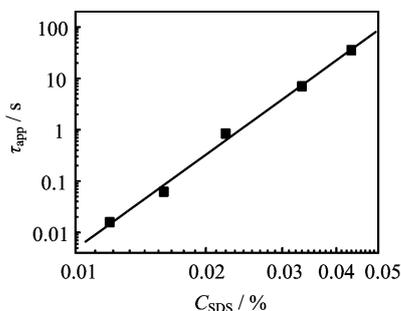


FIG. 5 The apparent relaxation time  $\tau_{app}$  of aqueous CG solutions in the presence of SDS with various concentrations at 25 °C.

seen that the limiting slopes of 2 or 1 cannot be reached respectively, for  $\lg G'$  and  $\lg G''$  when plotted against  $\lg \omega$  as indicated by Eq.(1) and Eq.(2). In particular,  $G'$  and  $G''$  cannot be indicated as a cole-cole plots as shown in Fig.4. On such a occasion, the apparent relaxation time  $\tau_{app}$  corresponding to the frequency of intersection  $\omega_c$  where  $G'$  equals  $G''$

$$\tau_{app} = 1/\omega_c \quad (3)$$

should be used to characterize the mechanical spectra [21]. The result is shown in Fig.5. From Fig.5 it can be seen that  $\tau_{app}$  increases swiftly upon increasing the concentration of SDS in solution. The reasonable interpretation is that the hydrophobic interactions or the strength of the cross-links is enhanced due to the binding of SDS molecules to the cross-links.

It is already known that  $G_c$  corresponding to either  $G'$  or  $G''$  at the frequency where  $G'$  equals  $G''$  can be applied to indicate changes in the number of cross-links [22]. From Fig.6 it can be seen that  $G_c$  is almost independent of the concentration of SDS, indicating the number of the cross-links is less changed by the addition of SDS. In our experiment, the degree of cationic substitution of CG is about 13.8%. The concentration of CG is fixed to be 0.6%. The cationic substitution of CG is 2.5 mmol/L approximately. The maximum of SDS, as applied in our experiment, is 0.043%, or

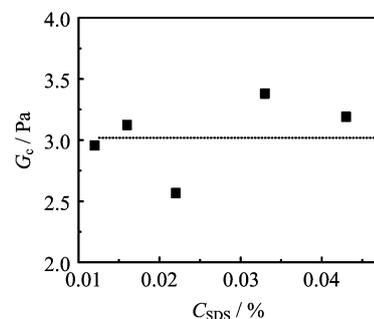
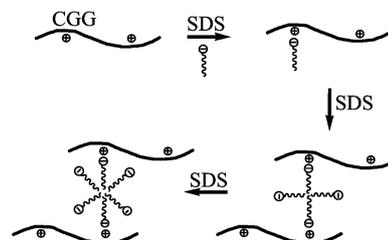


FIG. 6 The parameter  $G_c$  of aqueous solutions of CG in the presence of SDS with various concentrations at 25 °C.



Scheme 2 The mechanism of SDS upon the rheological behavior of cationic guar solution.

1.49 mmol/L. This suggests the number of cationic substitution is excessive. As a result, the number of cross-links will increase by successive addition of SDS into solution. However, the experimental result contradicts with our expectation completely. A possible interpretation is that the cooperative hydrophobic interaction between SDS molecules is stronger than the electrostatic interaction between SDS and cationic substitution of CG on the condition that the cross-links of CG chains through the aggregation of SDS molecules in solution have formed. The mechanism of SDS upon the rheological behavior of CG solution, therefore, can be indicated in Scheme 2. With the initial addition of SDS into solution, the SDS molecules bind to the cationic sites of CG chains through the electrostatic interaction. When the concentration of SDS in solution is greater than  $C_s$ , the micellar cross-links due to the aggregation of SDS through the cooperative hydrophobic interaction begin to form. With the further addition of SDS into solution, the SDS molecules bind to the cross-links through the cooperative hydrophobic interaction rather than bind to the cationic sites of CG chains through electrostatic interaction. As a result, the relaxation time increases swiftly whereas the number of the cross-links keeps almost the same with the addition of SDS molecules into solution.

Figure 7 shows the steady viscosity as a function of shear rate for CG solution in the presence of SDS at various temperatures ranging from 25 °C to 55 °C. The concentration of CG is fixed to be 0.6% whereas the con-

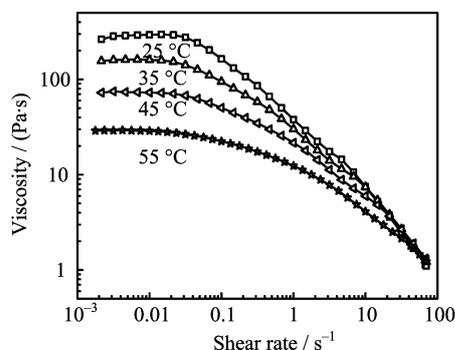


FIG. 7 The steady viscosity as a function of shear rate for aqueous CG solutions in the presence of SDS at various temperatures. The concentration of CG and SDS are 0.6% and 0.043%, respectively.

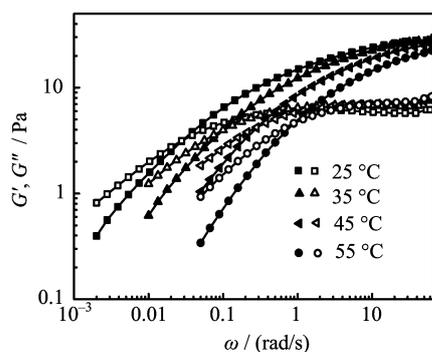


FIG. 8 Frequency dependence of  $G'$  (filled symbols) and  $G''$  (open symbols) for aqueous CG solutions in the presence of SDS at various temperatures. The concentration of CG and SDS are 0.6% and 0.043%, respectively.

centration of SDS is 0.043%. It can be seen that the viscosity decreases upon increasing temperature whereas the departure from the plateau is shifted to higher shear rate. The observation that the shear thinning shifts to higher shear rate indicates that the relaxation time of CG solution in the presence of SDS decreases at higher temperature. Figure 8 shows the frequency dependence of  $G'$  and  $G''$  for CG solution in the presence of SDS at various temperatures ranging from 25 °C to 55 °C. The concentrations of CG and SDS are 0.6% and 0.043%, respectively. It can be seen that, in the whole frequency range used in this study, the storage modulus  $G'$  decreases upon increasing the temperature. In particular, the value of  $G''$  is almost the same as the frequency is greater than 0.1 rad/s. The parameter  $G_c$  corresponding to either  $G'$  or  $G''$  at the frequency where  $G'$  equals  $G''$  for CG solutions in the presence of SDS at different temperatures, is shown in Fig.9. It can be seen that  $G_c$  is almost the same in the temperature range investigated, indicating the cross-link number between CG chains is almost independent of the temperature. On the other hand, the parameter  $\omega_c$ , as indicated in Fig.8, increases upon increasing temperature. As a result, the

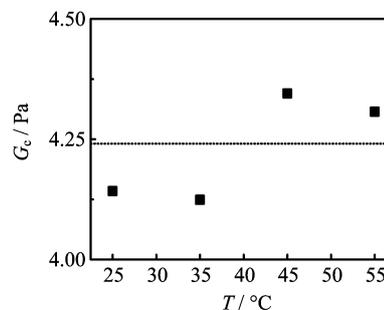


FIG. 9 The parameter  $G_c$  of aqueous CG solutions in the presence of SDS at various temperatures. The concentration of CG and SDS are 0.6% and 0.043%, respectively.

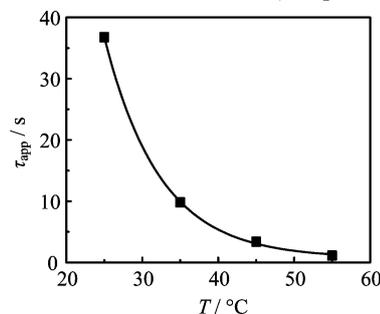


FIG. 10 The relaxation time  $\tau_{app}$  of aqueous CG solutions in the presence of SDS at various temperatures. The concentration of CG and SDS are 0.6% and 0.043%, respectively.

relaxation time  $\tau_{app}$  should decrease upon increasing temperature. Figure 10 shows the relaxation time  $\tau_{app}$  of CG solution in the presence of SDS at various temperatures. The concentration of CG and SDS is 0.6% and 0.043%, respectively. It can be seen that  $\tau_{app}$  decreases swiftly upon increasing the temperature. Figure 11 shows  $\ln \tau_{app}$  of CG solution in the presence of SDS at various temperatures. The concentration of CG is kept to be 0.6% whereas the concentration of SDS is 0.022%, 0.033%, and 0.043%, respectively. It can be seen that the linear relationship exists between  $\ln \tau_{app}$  and  $1/T$ , indicating the temperature dependence of  $\tau_{app}$  may follow the *Arrhenius* behavior

$$\tau_{app} \propto e^{E_m/kT} \quad (4)$$

where  $E_m$  is the flow activation energy and  $R$  is the gas constant. The parameter  $E_m$  can be determined from the slopes of the lines.  $E_m$  are 61.89, 70.9, and 94.3 kJ/mol, when concentration of SDS are 0.022%, 0.033%, and 0.043%. It can be seen that  $E_m$  increases significantly upon increasing the concentration of SDS. This interprets why the relaxation time or the strength of the cross-links between CG chains increases upon increasing the concentration of SDS. In particular, the value of  $E_m$  falls in a range of that transferring a hydrophobic tail of SDS from the micelle to an aqueous environment [21]. This suggests that the rheology of CG solution in the presence of SDS is mainly determined by

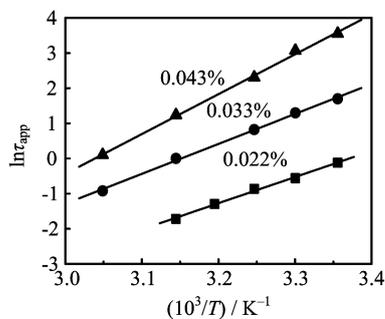


FIG. 11 The parameter  $\ln \tau_{\text{app}}$  of aqueous CG solutions in the presence of SDS at various temperatures. The concentration of CG is kept to be 0.6% whereas the concentration of SDS is 0.022, 0.033 and 0.043%, respectively.

the micellar-like cross-links between CG chains.

#### IV. CONCLUSION

Rheological measurement has been carried out on aqueous solutions of cationic guar (CG) in the presence of sodium dodecyl sulfate (SDS) at different temperatures. Results show that the viscosity of CG solution increases significantly by adding SDS into solution. The zero shear viscosity enhancement can be almost 3 orders of magnitude as the concentration of SDS increases from 0 to 0.043%. The oscillatory rheological measurements of CG solution in the presence of SDS show that the crossover modulus  $G_c$  is almost independent of the concentration of SDS. This implies that the number of the cross-links of CG chains no long increases with increasing the concentration of SDS after the formation of cross-links of CG chains at  $C_s$ . On the other hand, the apparent relaxation time  $\tau_{\text{app}}$  obtained from  $\tau_{\text{app}}=1/\omega_c$ , increases swiftly upon increasing the concentration of SDS. This indicates that the strength of the cross-links increases upon progressive addition of SDS in solution. The mechanism concerning the effect of SDS upon the rheology of CG solutions, therefore, can be coined by the two stage model. Before the formation of cross-links at the critical concentration  $C_s$ , the electrostatic interaction between SDS and cationic site of CG chains plays a key role and the SDS molecules bind to CG chains through the electrostatic interaction. After the formation of cross-links at the concentration greater than  $C_s$ , the cooperative hydrophobic interaction become dominant and SDS molecules bind to the cross-links through the hydrophobic interaction. The rheological behavior of aqueous solutions of CG in the

presence of SDS is chiefly determined by the micelle-like cross-links between CG chains. This results show that the flow activation energy  $E_m$  of CG solution, obtained from the temperature dependence of  $\tau_{\text{app}}$ , falls in the range of transferring a hydrophobic tail of SDS from the micelle to an aqueous environment.

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