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Effect of Potassium Oleate on Rheological Behavior of Cationic Guar in Aqueous Solution with Varying Temperatures

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The rheology of the cationic guar (CG) solution was measured and the effects of potassium oleate (KOA) upon the rheological properties of CG solution were studied. The steady shear viscosity measurement has shown that the viscosity of CG solution increased dramatically in the presence of KOA. The viscosity enhancement of KOA upon CG solution can be approximate three orders in magnitude. The gel-like formation of CG solution is observed at the high concentration of KOA. The excess addition of KOA results in the phase separation of CG solution. The oscillatory rheological measurement has shown that the crossover modulus G_c (corresponding to either storage modulus G' or loss modulus G'' at the frequency ω_c where G' equals G'') for CG solution, decreases with the increasing the concentration of KOA in solution. On the other hand, the apparent relaxation time τ_{app} ($=1/\omega_c$) increases with increasing the concentration of KOA in solution. Our experimental results suggest that for surfactant such as KOA which has a stronger tendency to form micelles in solution, the cooperative hydrophobic interaction of polymer bound to surfactants is less necessary to the formation of aggregates in solution, especially at the high concentration of surfactants. In fact, with the increase of the concentration of KOA, the number of the aggregates which associate polymer together decreases whereas the intensity of these aggregates increases. The effect of temperature upon the aggregation is also significant. With the increase of temperature, the number of the aggregates increases whereas the intensity of these aggregates decreases, probably because the ionization of KOA increases at high temperature.

Key words: Rheological behavior, Cooperative hydrophobic interaction, Electrostatic interaction, Cationic guar, Potassium oleate

I. INTRODUCTION

Interactions between water-soluble polymers and surfactants have gained considerable interest in recent years in fundamental and applied research [1–3], mainly due to the importance of mixtures of water-soluble polymer and surfactants in a number of industrial applications including detergents, pharmaceuticals, paints, and oil recovery [4–8]. Of particular interest are the two types of interactions concerning (i) the interaction of the hydrophobically modified polymer with surfactants [9–12] and (ii) the interaction of polyelectrolyte with the oppositely charged surfactants [13–27]. These interactions can strongly affect the rheological properties of solution. For hydrophobically modified polymer solution in the presence of surfactants, the typical results are that the viscosity of solution increases dramatically at the lower surfactant concentration and decreases signif-

icantly at the higher surfactant concentration. A maximum in the viscosity is observed at a surfactant concentration close to the critical micelles concentration (cmc) of the surfactant in pure water [28]. For polyelectrolyte solution, the situation becomes much more complicated. The addition of oppositely charged surfactants into polyelectrolyte solution can lead to a large increase in solution viscosity [29–31] or in some case to phase separation [32], depending on the property of polyelectrolyte selected and the concentration of the oppositely charged surfactants in solution. A well-studied system of this class is cationic cellulose (EHEC) solution in the presence of oppositely charged surfactants. It has been reported that when an anionic surfactant, such as sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), or sodium bis(ethylhexyl) sulfosuccinate (AOT), was added to a cationic cellulosic polymer, a great increase in apparent viscosity occurred [33]. Indeed, formation of strong, clear aqueous gels was obtained at quite low levels of polymer (about 1%) with the surfactant at about one-tenth of this concentration. The effect of the chemical structure of surfactants with similar charge but with different hydrocarbon tails or

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branched type upon the rheological properties of EHEC solution was also studied in detail by Chronakis and Alexandridis [30].

In our previous study we have shown that the viscosity of cationic guar (CG) solution increases dramatically by adding SDS into solution [31]. The similar gel-like formation is observed for CG solution as the concentration of CG is 0.6% in weight and the concentration of SDS is greater than 0.01% in weight. It is generally accepted that the interaction of polyelectrolyte with the oppositely charged surfactants is enhanced for the surfactant with the longer hydrocarbon tail. The surfactant chain length dependence for the formation of the aggregates in polymer solution is similar to the alkyl chain length dependence for the formation of surfactant micelles in polymer-free solution [3, 34]. It is already known that potassium oleate (KOA) is more hydrophobic and has a stronger tendency to form micelles in solution than SDS. In fact, the cmc of KOA is 0.81 mmol/L [35], which is one order of magnitude less than SDS with cmc of 8.2 mmol/L [10]. We are therefore convinced that KOA is more efficient in enhancing the viscosity of CG solution than SDS. However, the experimental results presented in this work have shown that KOA is less efficient in enhancing the viscosity of CG solution than SDS. Further, we show that the crossover modulus G_c of CG solution decreases upon increasing the concentration of KOA. In contrast, the crossover modulus G_c of CG solution almost keeps the same upon increasing the concentration of SDS. Our experimental results reveal that, for surfactant such as KOA which has a stronger tendency to form micelles, the cooperative hydrophobic interaction of polymer bound surfactants is less necessary to the formation of aggregates in solution, especially as the concentration of surfactants is sufficiently high. The effect of temperature upon the rheology of CG solution in the presence of KOA is also studied 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. The regular guar is a galactomannane polysaccharide, and its backbone is constituted of mannose sugar units, which bear some randomly distributed galactose units. The ratio mannose to galactose is close to 2. KOA with the purity greater than 99.9% was obtained from Sinopharm Chemical Reagent Co. Ltd. and used as received without any further purification. The structure of KOA is shown in Fig.1. 3-chloride-2-hydroxypropyl N,N,N-trimethylammonium chloride was A. R. grade and purchased from Shanghai Chemical Reagent Company. The structure is also shown in Fig.1. The reagents such as sodium hydroxide, acetic acid, isopropyl alcohol, and acetone were all A. R. grade and

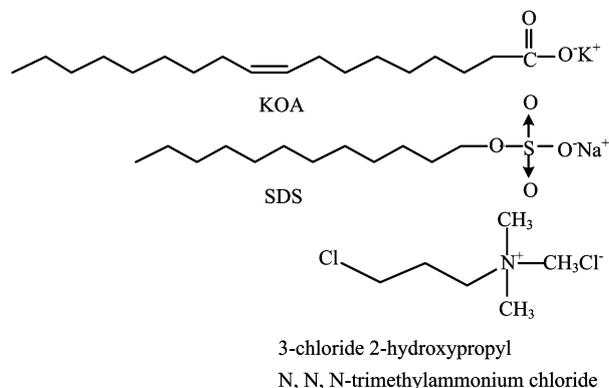


FIG. 1 Chemical structure of KOA, SDS, and 3-chloride-2-hydroxypropyl N,N,N-trimethylammonium chloride.

purchased from Shanghai Chemical Reagent Company.

B. Grafting

CG was obtained by grafting hydroxypropyl trimethylammonium chloride groups both on mannose and galactose units of guar gum according to Chowdhary's method [36]. 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 is stirred for an additional 15 min. 50% NaOH solution was added over a 15 min period 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. 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 were believed to be randomly distributed along the chains. The degree of cationic substitution, determined by nitrogen analysis according to Kjeldahl analysis [37], was found to be 13.8%.

C. Sample preparation

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 one 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 are in all cases perfectly homogeneous and transparent for the concentration employed.

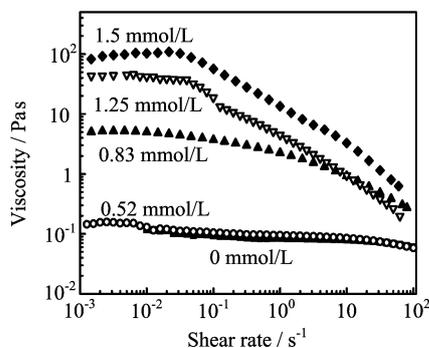


FIG. 2 The viscosity as a function of shear rate for CG solution in the presence of KOA with various concentrations at 25 °C. The concentration of CG is kept to be 0.6%.

D. Rheological measurements

Oscillatory shear and steady shear measurements were performed using a TA AR-G2 rheometer using the cone plate system (diameter of 35 mm, angle of 2°) or the system of coaxial cylinders (stator inner radius of 15.00 mm, rotor inner radius of 14.00 mm, cylinder immersed height of 42 mm), depending on the viscosity of the sample. 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 a certain temperature prior to conducting measurements. The storage modulus G' and loss modulus G'' were measured over the frequency range 10^{-3} – 10^2 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 are independent of applied stress.

III. RESULTS AND DISCUSSION

A. Steady viscosity measurement of CG solution in the presence of KOA

A characteristic feature of many associating polymer systems is the strong shear-rate dependence of the viscosity [38–42]. Figure 2 shows the effect of shear-rate on the measured viscosity for CG solutions in the presence of various amounts of KOA at 25 °C. The concentration of CG is kept to be 0.6% but the concentration of KOA is selected to be 0, 0.52, 0.83, 1.25, and 1.5 mmol/L, respectively. From Fig.2 it can be seen that, in the absence of KOA, CG solution exhibits almost Newtonian behavior. That is, its viscosity is independent of shear rate. The viscosity of CG solution is almost two orders of magnitude greater than that of the water (1 mPas), arising from the high molecular weight and polyelectrolyte nature of CG, as well as from the relative stiffness of saccharide backbone of CG chains. In the presence of KOA, however, CG solution switches to a

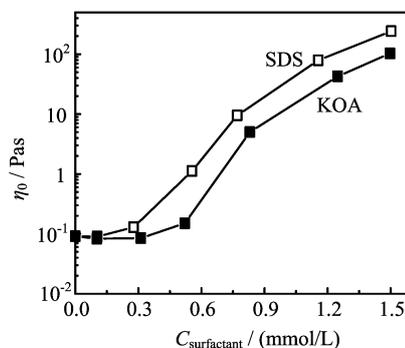


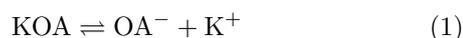
FIG. 3 The zero-shear viscosity as a function of KOA or SDS concentration for aqueous CG solutions at 25 °C.

shear-thinning response, with a plateau in the viscosity at low shear rates, followed by a drop in viscosity at higher shear rates. In particular, the zero-shear viscosity of CG solution increases approximate three orders of magnitude as the concentration of KOA in CG solution increases from 0.52 mmol/L to 1.5 mmol/L. The excess addition of KOA into CG solution results in phase separation. The strong shear-rate dependence of the viscosity, together with the dramatically viscosity enhancement of CG solution in the presence of KOA, indicates the existence of network in solution. This network originates from the polymer-bounded aggregates which associate CG chains in solution together like cross-linkers.

To further demonstrate the effects of KOA upon the viscosity of CG solution, we plot in Fig.3 the zero-shear viscosity η_0 of the CG solution as a function of KOA concentration at 25 °C. It can be seen that η_0 keeps constant at low concentrations of KOA and increases abruptly when the concentration of KOA is higher than a certain value namely C_s , which is 0.52 mmol/L in present work. In our previous study, the effect of SDS, another anionic surfactant with a short hydrophobic tail, on the rheological behaviors of CG solutions has been investigated. A similar viscosity enhancement of SDS upon CG solutions has been observed [31]. The result is also shown in Fig.3. Two features can be identified from Fig.3, (i) The critical concentration C_s at which the abrupt increase of η_0 begins for KOA is quite larger than that for SDS, though the cmc of the former is much lower than that of the latter. (ii) KOA is less efficient in enhancing the viscosity of CG solution than SDS, though KOA has a longer hydrophobic tail and a stronger tendency to form micelles in polymer-free solution than SDS. The former feature is greatly associated with the hydrophilic head-groups of surfactants whereas the later feature is associated with the hydrophobic tails of surfactants, respectively and interestingly.

It is already known that, when adding an oppositely charged surfactant into a concentrated polyelectrolyte solution, the surfactant molecules are prior to bind to the polyelectrolyte chains due to the electrostatic attractions between the head-groups of the surfactant and

oppositely charged units or groups of the polyelectrolyte chains [13–27, 31]. If the number of the surfactant molecules binding to the polyelectrolyte chains is sufficient, *i.e.*, the surfactant added into the polyelectrolyte solution is above a critical concentration, the polymer-bounded surfactants will form aggregates through the cooperative hydrophobic interaction. These aggregates associate polymer chains together like cross-linkers. For rigid polyelectrolyte such as cationic or anionic cellulose, the inter-chain association is predominant over the intra-chain interaction in solution. As a result, the viscosity of polyelectrolyte solution increases dramatically by the formation of aggregates in solution and gel-like solution can be observed at the proper concentration of surfactants [32, 34, 43, 44]. On the other hand, for flexible polyelectrolyte based on repeated vinyl chemistry structure units, the intra-chain association is predominant over the inter-chain interaction in solution. On such an occasion, the formation of aggregates in solution usually results in phase separation [45]. In our previous study we have shown that the solution viscosity of CG, a semi-rigid polyelectrolyte, can be increased dramatically due to the formation of aggregates SDS in solution and the gel-like CG solution was observed at the proper concentration of SDS [31]. Obviously, the formation of aggregates are associated with both the number of surfactants binding to polymer chains through the electrostatic interaction and the tendency of polymer-bounded surfactants to the associated together through the hydrophobic interaction. SDS is a strongly acidic salt and its molecules ionize completely in solution and each head-group of SDS possesses one negative charge. However, KOA is a weakly acidic salt as shown in Fig.1 and its molecules ionize incompletely in the solution. There is an ionization balance for KOA molecules in the solution,



That is to say, only some molecules of KOA are ionized in the solution while the others are still electric neutral. In other words, the number of OA^- is much less than that of SD^- in solution, even though the concentration of KOA and SDS in solution maybe the same. Furthermore, due to the reason that $-\text{SO}_4^-$ is easier to polarize than $-\text{COO}^-$ as presented by Hansson [46], we believe that the electrostatic interaction of SDS with CG chain should be stronger than that of KOA with CG chain. These indicate that the number of SDS binding to CG chains is sufficient to form aggregates even at a lower concentration of SDS. This interprets why C_s at which the abrupt increase of η_0 begins for KOA is quite larger than that for SDS as shown in Fig.3. It is already known that KOA is more hydrophobic and has a stronger tendency to form micelles in solution than SDS. In fact, the cmc of KOA is 0.81 mmol/L, which is one order of magnitude less than SDS with the cmc of 8.2 mmol/L. Considering that the formation of aggregates associating polymer chains together is due to

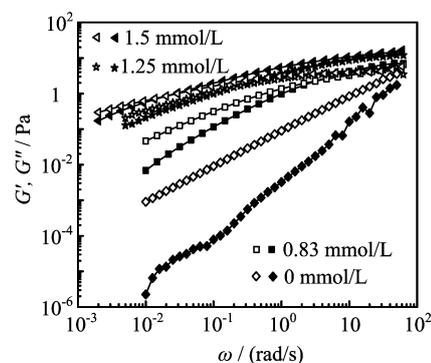


FIG. 4 Frequency dependences of the storage modulus G' (solid symbols) and the loss modulus G'' (open symbols) for aqueous CG solution in the presence of KOA with various concentration at 25 °C.

the cooperative hydrophobic interaction of surfactants, we believe that KOA should be more efficient in enhancing the viscosity of CG solution than SDS. The experimental result, as shown in Fig.3, is contrary to our expectation. The reason will be discussed in the following section.

B. Oscillatory rheological measurement of CG solution in the presence of KOA

Additional information on polymer-surfactant complex networks can be obtained from frequency sweep rheological experiments, by determining the dependence of the network structural parameters on the oscillatory frequency. The profiles of the dynamic G' and G'' of CG solution in the presence of KOA, obtained from such experiments are presented in Fig.4. The concentration of CG is kept to be 0.6% whereas the concentration of KOA is selected to be 0, 0.52, 0.83, 1.25, and 1.5 mmol/L respectively. For a better view, only the curves for some selected samples ($C_{\text{KOA}}=0, 0.83, 1.25,$ and 1.5 mmol/L) are drawn in Fig.4. From Fig.4 it can be seen that for CG solution in the absence of KOA, the sample exhibits a viscous behavior, with $G'' > G'$ within the whole frequency range. However, when the KOA concentration added into the CG solutions is equal or higher than 0.52 mmol/L, the sample shows a typical viscoelastic behavior, with $G'' > G'$ (viscous behavior) at low frequencies and $G' > G''$ at higher frequencies where the elastic response dominates. If the rheological behavior can be described by the single Maxwell model, G' and G'' can be expressed as [47].

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

$$G''(\omega) = G_{\infty} \frac{\tau \omega}{1 + \tau^2 \omega^2} \quad (3)$$

In agreement with the results on hydrophobically modified cellulose ethers in the presence of surfactants

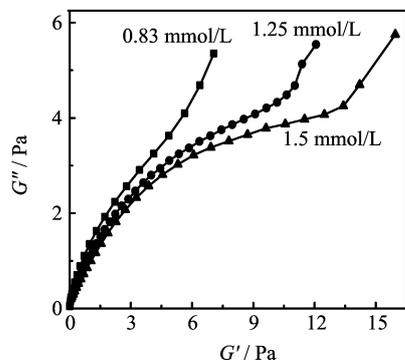


FIG. 5 Cole-cole plots of aqueous CG solution in the presence of KOA with various concentrations at 25 °C.

[12] as well as cationic cellulose in oppositely charged surfactants, the curves of G' and G'' could not be fitted to a single Maxwell element. In fact, within the accessible frequency window the limiting slopes of 2 or 1 as indicated by Eq.(2) and Eq.(3), cannot be obtained respectively from the plot of $\lg G'$ and $\lg G''$ versus $\lg \omega$ as shown in Fig.4. Furthermore, G' and G'' cannot be indicated as a cole-cole plot as shown in Fig.5. Consequently, neither the terminal relaxation times nor the plateau moduli can be extracted from the oscillatory measurements on these samples. We have therefore used the crossover coordinates to characterize the mechanical spectra as presented by Piculell *et al.* [28]. These coordinates will be referred to as the crossover modulus G_c and angular frequency ω_c , respectively. From ω_c , the apparent relaxation time τ_{app} can be defined as

$$\tau_{app} = 1/\omega_c \quad (4)$$

The parameter τ_{app} and G_c can be used for indicating the changes in the lifetime and the number of aggregates associating polymer chain together, respectively. The dependence of τ_{app} as well as the crossover modulus, G_c , on the concentration of KOA added into the CG solutions is plotted in Fig.6. For comparison, the dependence of G_c and τ_{app} upon the concentration of SDS is also shown in Fig.6. From Fig.6 it can be seen that τ_{app} increases successively whereas G_c decreases linearly with increasing the concentration of KOA in CG solutions. The effects of KOA upon G_c and τ_{app} of CG in aqueous solution are very similar to the effects of surfactants upon G_c and τ_{app} of hydrophobically modified polymers in aqueous solution as presented either by Piculell *et al.* [28] or by Zhao and Chen [48]. Obviously, G_c of CG solution decreases with increasing KOA in solution indicates that the number of aggregates associating polymer chain together decreases upon increasing KOA in solution. This interprets why KOA is less efficient in enhancing the viscosity of CG solution than SDS as discussed above. However, there are two questions arise from the experimental results as shown in Fig.6. (i) why does G_c of CG solution decrease with in-

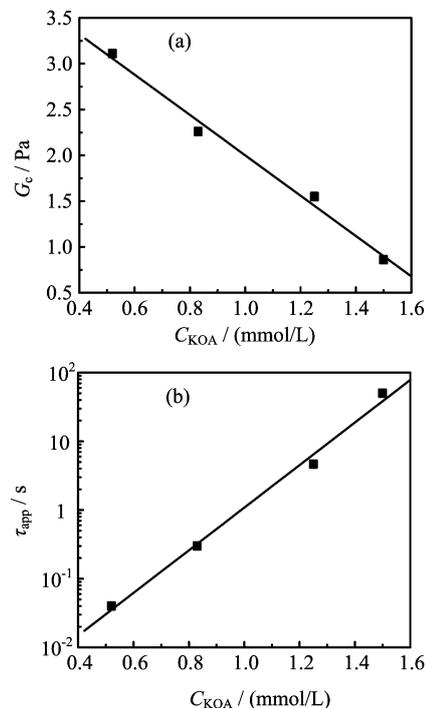


FIG. 6 The crossover modulus G_c (a) and apparent relaxation time τ_{app} (b) of aqueous CG solutions in the presence of KOA with various concentrations at 25 °C.

creasing KOA in solution? (ii) In particular, why does G_c of CG solution keep constant with increasing SDS in solution? It should be noted here that the concentration range of KOA used here is just the same as the concentration range of SDS in our previous study. It has been reported that cmc of SDS in polymer-free solution is 8.2 mmol/L. In our experiment, the concentration of SDS is less than 1.5 mmol/L. This suggests that no spherical micelles of SDS can be formed in MC-free part of solution. It should be noted that the cmc of KOA in polymer-free solution is 0.81 mmol/L. In our experiment, the concentration of KOA in CG solution, $C_{KOA,app}$, ranges from 0.1 mmol/L to 1.5 mmol/L. However, due to the adsorption of KOA to CG chains, the concentration of KOA in MC-free part of solution, $C_{KOA,real}$, should be still less than 0.81 mmol/L. As a result, the free spherical micelles in MC-free part of solution do not exist. On such an occasion, the added KOA will be adsorbed the existed aggregates to increase the number of surfactants in aggregates rather than form the free spherical micelles in MC-free part of solution. τ_{app} increases successively upon increasing the concentration of KOA in solution, verifying our assumption completely. In particular, G_c of CG solution decrease already as the concentration of KOA is less than cmc of KOA as shown in Fig.6. In a word, the difference between the rheological behavior of CG solution in the presence of KOA and in the presence of SDS is not due to the formation of spherical micelles in

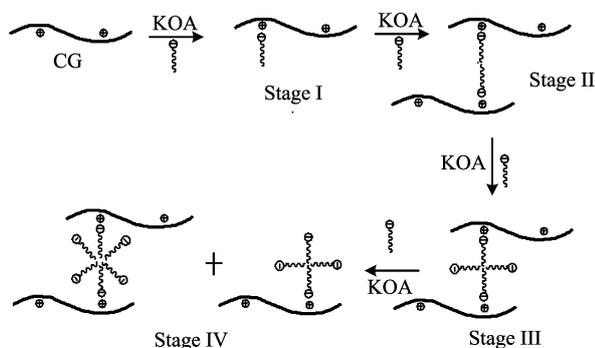


FIG. 7 The interaction mechanism of KOA with CG in aqueous solution.

CG-free part of solution. We are therefore convinced that the mechanism concerning the interaction of KOA with CG in aqueous solution is quite different from the interaction of SDS with CG in aqueous solution.

C. Mechanism of the interaction of KOA with CG in aqueous solution

We have shown the rheological behavior of CG solution in the presence of KOA. Now we need to gain a better understanding of the mechanism of the interaction of KOA with CG in aqueous solution. Obviously, if the ionic surfactant was added into oppositely charged polymer solution, the ionic surfactant should adsorb the oppositely charged units of polymer chains individually as indicated in Fig.7. In the initial stage I, with the increase of the concentration of surfactants in solution, the number of surfactants binding to polymer chains increases accordingly. As the number of surfactants binding to polymer chains increase to a certain value, the cooperative hydrophobic interaction between the polymer-bound surfactants in solution should be introduced. On such an occasion, the hydrophobic tails of polymer-bound surfactants would associate together to form associative units through the hydrophobic interaction. We refer to this stage in which the cooperative hydrophobic interaction occurs as the second stage II. Obviously, the associative units formed in this way are unsteady. If more surfactants are added into solution, the added surfactants can either bind to the oppositely charged units of polymer chains individually or bind to the associative units to form aggregates.

In our experiment, the degree of cationic substitution of CG is 13.8%, the concentration of CG is 0.6%. The cationic sites of CG chains should be approximately 2.5 mmol/L. That is to say that there are enough cationic units to which the oppositely charged surfactants bind. The zero-shear viscosity of CG solution increases sharply as the concentration of KOA is higher than 0.05 mmol/L which suggests the formation of cross-linkers of CG chains in the presence of KOA.

That is to say, if more surfactants are added into solution, the added surfactants prefer to adsorb on the associative units through hydrophobic interaction rather than bind to oppositely charged units of polymer chains through electrostatic interaction. The associative unit acts as a nuclear by which the aggregate grows up in solution. We refer to this stage in which the associative unit grows to aggregates as stage III. If our presumption is correct, in the stage III τ_{app} of polyelectrolyte solution should increase by the addition of surfactants whereas G_c should keep the same by the addition of surfactants. The rheological behavior of CG solution in the presence of SDS verified this assumption completely.

However, G_c of CG solution in the presence of KOA decreases gradually by the addition of KOA in solution as indicated in Fig.6. The similar experimental results have also been obtained for the study of the mixture systems of the non-ionic polymer, hydrophobically modified hydroxyethyl cellulose (HMHEC) solution and surfactants such as sodium tetradecyl sulfate (STS), sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium bromide (HTAB), *etc.* We are therefore convinced that the excess addition of surfactants will result in the formation of the polymer-bounded aggregates. For discriminating, we here refer to the aggregates grown from the associative unit as polymer-associated aggregates. There are three differences between polymer-bounded aggregates and polymer-associated aggregates. (i) The polymer-associated aggregates grow up from the associative unit and therefore the cooperative hydrophobic interaction is needed to the formation of aggregates. On the other hand, the cooperative hydrophobic interaction is not necessary to the formation of polymer-bounded aggregates. (ii) The polymer-associated aggregates associate polymer chains together like cross-linkers. As a result, the viscosity of solution increases dramatically due to the formation of polymer-associated aggregates in solution. In contrast, the polymer-bounded aggregates have less influence upon the viscosity of solution. (iii) The polymer-associated aggregates can form at the low concentration of surfactants.

However, polymer-bounded aggregates can only form at the high concentration of surfactants or at low concentration of surfactants on condition that these surfactants have a long hydrophobic tails and have the strong tendency to form micelles in solution. We refer to the stage in which the polymer-bounded aggregates occur as stage IV. Obviously, in stage IV the polymer-bounded aggregates are also stable for these surfactants with a long hydrophobic tails and at the high concentration. On such an occasion, one polymer-associated aggregate may be divided into two or more polymer-bounded aggregates. That is to say, in stage IV the polymer-bounded aggregates co-exist with polymer-associated aggregates in solution together. It is already known that KOA has a long hydrophobic tail and has a strong tendency to form micelles in solu-

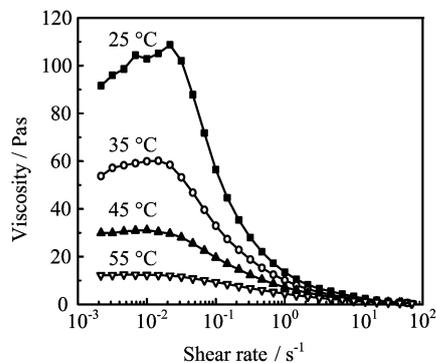


FIG. 8 The steady viscosity as a function of frequency for aqueous CG solutions in the presence of KOA at various temperatures. The concentrations of CG and KOA are 0.6% and 1.5 mmol/L, respectively.

tion. The excessive addition of KOA results in both the growth of polymer-associated aggregates and the formation polymer-bounded aggregates. As a result, τ_{app} of CG solution increases by the addition of KOA whereas G_c of CG solution decreases by the addition of KOA as shown in Fig.6. The stage IV is very similar to the model developed by Piculell *et al.* [28] to interpret the viscosity behavior of the aqueous solution of hydrophobic modified polymer in the presence of surfactants. The detailed mechanism of the interaction of KOA with CG is shown in Fig.7.

Obviously, for SDS which has a less tendency to form micelles in solution, the polymer-bounded aggregates can only form at the higher concentration of SDS. However, the excess addition of SDS into CG solution, as presented in our previous study, results in the phase separation of CG solution. This interprets why G_c of CG solution in the presence of SDS is independent of the concentration of SDS.

D. Effect of temperature upon the rheological properties of CG solution in the presence of KOA

Figure 8 shows the shear-rate dependence of steady viscosity of the CG solution in the presence of 1.5 mmol/L KOA at various temperatures. It can be seen that the viscosity of CG solution in the presence of KOA decreases continuously with increasing the temperature. The zero-shear viscosity of CG solution decreases by one order of magnitude as the temperature increases from 25 °C to 55 °C. The further frequency sweep rheological measurements reveal that G_c increases steady with increasing the temperature T whereas a directly opposite trend for τ_{app} is observed as indicated in Fig.9. It is already known that with increasing the temperature, the ionization degree of KOA increases, and the ionization balance of KOA (Eq.(1)) shifts to the right. That is to say, more OA^- are formed in the solution. The number of OA^- binding to CG

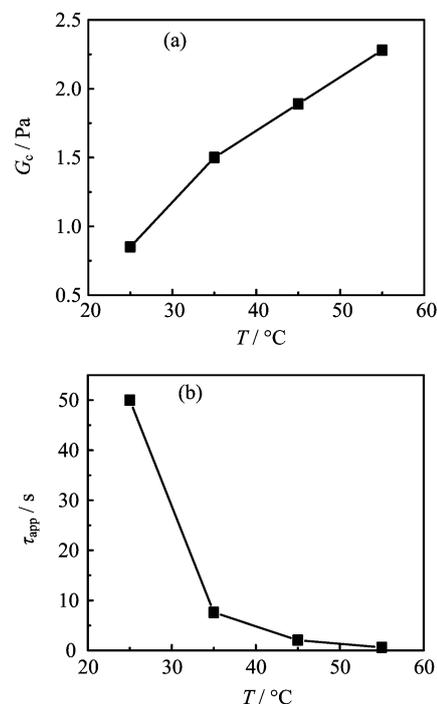


FIG. 9 The crossover modulus G_c (a) and apparent relaxation time τ_{app} (b) of aqueous CG solutions in the presence of 1.5 mmol/L KOA at different temperatures.

chains increases and hence the polymer-associated aggregates increase accordingly with increasing temperature. On the other hand, the cooperative hydrophobic interactions among the tails of KOA should decrease with the increase of the temperature. As a result, τ_{app} of the polymer-associated aggregates decreases accordingly. Figure 10 shows a logarithmic plot of τ_{app} of the CG solution in the presence of KOA against the inverse of the temperature, $1/T$. A clear linear relationship between τ_{app} and $1/T$ can be seen, indicating the temperature dependence of τ_{app} may follow the Arrhenius behavior

$$\tau_{\text{app}} \propto e^{E_m/RT} \quad (5)$$

where E_m is the flow activation energy for one mol of OA^- transferring from the polymer-associated aggregates into the water and R is gas constant. The value of E_m is thus obtained from the slope of the line, which is 118.8 kJ/mol. In our previous study, the value of E_m is 94.3 kJ/mol [31]. It is noted that the value of E_m corresponding to CG solution in the presence of KOA is larger than that corresponding to CG solution in the presence of SDS, mainly due to the reason that KOA has a longer hydrophobic tail and has a stronger tendency to form micelles in solution than SDS. As a result, the polymer-associated aggregates of KOA are more stable at high temperature than that of SDS.

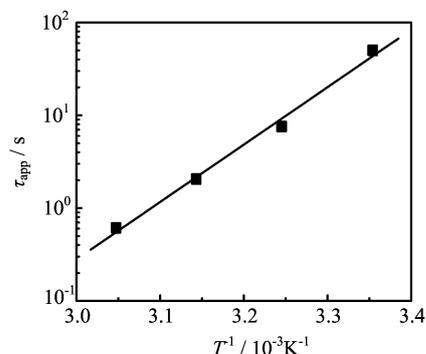


FIG. 10 The apparent time τ_{app} of the CG solution in the presence of KOA against the inverse of the temperature T^{-1} .

IV. CONCLUSION

In this work, the effect of KOA on rheological properties of CG solutions has been investigated using steady and oscillatory rheological measurements. It has been found that the viscosity of CG solution increases dramatically as the concentration of KOA is higher than C_s , due to the formation of the polymer-associated aggregates of KOA which associates polymer chains together like cross-linkers. The critical concentration C_s corresponding to CG solution in the presence of KOA is higher than that corresponding to CG solution in the presence of SDS, mainly due to the reasons that KOA is a weakly acidic salt and the interaction of the head-group of KOA with cationic unit of CG chains is less than the interaction of the head-group of SDS with cationic unit of CG chains. Oscillatory rheological measurements show that the crossover modulus G_c of CG solution decreases by the addition of KOA whereas τ_{app} of CG solution increases by the addition of KOA into solution. The dependence of G_c on the concentration KOA in CG solution can be explained as the formation of polymer-bounded aggregate in solution. For KOA which has a long hydrophobic tail and has a strong tendency to form micelles in solution, the cooperative hydrophobic interaction of polymer bound surfactants, or the associative unit, is less necessary for KOA to form aggregates in solution. As a result, the excessive addition of KOA results in both the growth of polymer-associated aggregates and the formation of polymer-bounded aggregates in solution. For SDS which has a less tendency to form micelles in solution, the associative unit is needed to the formation of aggregates in solution. As a result, G_c of CG solution in the presence of SDS is independent of the SDS concentration at the range investigated. The effect of temperature upon the viscosity of CG solution in the presence of KOA is significant. In fact, the zero-shear viscosity of CG solution decreases by one order of magnitude as the temperature increases from 25 °C to 55 °C. The flow E_m corresponding to CG solution in the presence of KOA is larger than that corresponding to CG solution

in the presence of SDS, mainly due to the reason that KOA has a longer hydrophobic tail and has a stronger tendency to form micelles in solution than SDS.

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