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Effect of β -Cyclodextrin Upon the Sol-gel Transition of Methylcellulose Solutions in the Presence of Sodium Dodecyl SulfateHua-yu Li^a, Xiang Hao^a, Yong-jun Xie^a, Hai-yang Yang^{a*}, He Liu^b, Jian-hui Luo^b*a. Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China**b. Research Institute of Science and Technology, China National Petroleum Corporation, Beijing 100083, China*

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The sol-gel transition temperature of methylcellulose (MC) solution in the presence of sodium dodecyl sulfate (SDS) as well as the mixtures of SDS and β -cyclodextrin (β -CD) was measured, and the effect of the two competing interactions, the hydrophobic interaction between SDS and MC and the inclusion interaction between SDS and β -CD, upon the sol-gel transition of MC solution was studied. It has been found that the inclusion interaction between SDS and β -CD is much greater than the hydrophobic interaction between SDS and MC. As a result, in the coexistence of SDS and β -CD, the sol-gel transition temperature of MC solution keeps the same value, independent of the concentration of SDS in solution on condition that the concentration of SDS is less than β -CD. Our experimental results not only suggest that the effect of SDS upon the sol-gel transition of MC solution can be screened by β -CD completely but also indicate the inclusion ratio of SDS to β -CD can be determined quantitatively by using rheological measurement. The inclusion ratio of SDS to β -CD is 1:1, which is in good agreement with the inclusion ratio of SDS to β -CD in the presence of poly(vinyl pyrrolidone) determined by the viscosity measurement but is critically different from the inclusion ratio of SDS to β -CD in the presence of the oppositely charged polyelectrolyte by using the rheological measurement, mainly due to the reason that the mechanism of the interaction between SDS and MC is critically different from the mechanism of the interaction between SDS and the oppositely charged polyelectrolyte.

Key words: Methylcellulose, Sodium dodecyl sulfate, β -CD, Sol-gel transition, Inclusion interaction

I. INTRODUCTION

Hydrophobic modified polymers that can exhibit controllable rheology behavior of fluids are commercially important in a number of industrial applications such as pharmaceutical formulations, food additives, cosmetic products and environment-friendly paints *etc.* [1–3]. Methylcellulose (MC), derivated from cellulose, is such a hydrophobic modified polymer which has drawn considerable attention in recent years [4–11]. The peculiar interest exhibited by MC is its unusual solution property that not only experiences sol-gel transition at physiological temperature, pH and ionic strength, but also can be modified by small molecules additive [12–15]. In particular, the MC aqueous solution combined with surfactants has been taken as the model system for the basic study of the interaction between polymer and surfactants as well as the good candidate for the practice

application. The mechanism about the effect of surfactant on the rheology behavior of MC solution has been proposed by Li *et al.* [15, 16]. It has been pointed out that, due to the hydrophobic interaction between MC and surfactants, the surfactants will self-assemble around the methyl groups of MC to form cage-like aggregates as the concentration of surfactants is greater than its critical aggregation concentration (CAC). The formation of cage-like aggregates provides the comfortable “cages” for hydrophobic groups of MC to reside in, screening the hydrophobic interaction between the methyl groups in solution. As a result, the gelation temperature of MC solution increases in the presence of surfactant. However, in the coexistence of surfactants and salts, the situation becomes much more complicated and contradictory. On one hand, the addition of salt will encourage the surfactants to adsorb on the methyl groups of MC to form cage-like aggregates, increasing the sol-gel transition temperature of MC solution. On the other hand, the addition of salt may induce the surfactants to form free micelles in solution, inhibiting the effect of the surfactants upon the sol-gel tran-

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sition of MC solution. Our experimental results have shown that in the coexistence of HTAB and NaCl, the sol-gel transition of MC solution keep the same value, independent of the concentration of HTAB in solution [17].

It is already known that cyclodextrins (CDs) represent another important class of additives which can affect the interaction between polymer and surfactants in solution significantly. Unlike the salt such as NaCl, CDs can neither encourage the adsorption of the surfactants on polymer chains nor induce the surfactants to form free micelles in solution. Instead, CDs with cyclic oligosaccharides of 6–8 D-glucose units, envelop and sequester the hydrophobic part of the surfactants in solution. The rheological behavior of polymer solution in the presence of surfactants is therefore changed by the addition of CDs accordingly. For example, polyrotaxanes of α -CD on polyethylene glycol with $M_w > 2 \times 10^3$ were reported to be hydrogelators [18]. Jiang *et al.* have found that the addition of CDs to an zwitterionic surfactant (tetradecyldimethylammonium propane sulfonate, TDPS) solution can form hydrogel possessing of multiple response [19]. Nakahata *et al.* reported a transparent, self-healing, and redox-responsive supramolecular hydrogel quickly forms upon mixing poly(acrylic acid) (PAA) possessing β -CD as a host polymer with pAA possessing ferrocene as a guest polymer [20]. The more information of controllable inclusion complex have been reviewed by Chen and Jiang [21].

In this work, we study the effect of β -CD upon the sol-gel transition of MC solution in the presence of SDS. The practical significance of this research work lies in the fact that the thermo-sensitive polymer solution often coexisted with ionic surfactant under usage environment, especially for oil recovery. Sometimes the existence of surfactant is beneficial to the application because the sol-gel transition temperature of MC solution can be increased by the surfactants. But more often than not, we prefer to inhibit the influence of surfactants upon the sol-gel transition of MC solution completely in order to fit for the temperature of the oil reservoir. The sol-gel transition behavior of MC solution depends on two competing interactions, the hydrophobic interaction between SDS and MC and the inclusion interaction between SDS and β -CD. Our experimental results have shown that effect of SDS upon the sol-gel transition of MC solution can be screened completely by β -CD. Of particular interest is our experimental results also show that the inclusion ratio of β -CD to SDS can be determined quantitatively by the rheological measurement.

II. EXPERIMENTS

A. Materials

A cellulose derivative, methylcellulose with a trade name of M450, was obtained from Sinopharm Chemical

Reagent Co. Ltd. The polymer had an average degree of substitution (DS) of 1.5 and, the viscosity was 0.45 Pa·S at 25 °C for a 2% aqueous solution. The material was used as received without further purification. Prior to use, it was vacuum-dried at 55 °C for 24 h and kept in a desiccator at room temperature (25 °C). SDS and β -CD were purchased from Sinopharm Chemical Reagent Co. Ltd., and used as received.

B. Sample preparation

A pure MC aqueous solution was first prepared by dispersing the weighed MC powder into deionized water at 70 °C and kept in a refrigerator for stabilization. A homogeneous and transparent solution of MC was obtained at room temperature. The weighed SDS or/and β -CD was then added into the MC solution to obtain all the required sample solutions. All the sample solutions were prepared with deionized water. Unless stated otherwise, the MC concentration in this work is fixed at 2%.

C. Rheological measurements

Rheological measurements were conducted on a TA AR-G2 rheometer using 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). The storage modulus G' and loss modulus G'' were measured as a function of temperature at an angular frequency of 1 rad/s within a linear range of viscoelasticity. The measurement temperatures were from 30 °C to 80 °C. A thin layer of low-viscosity silicone oil was used to cover the free surface of the solution to prevent evaporation of solvent.

D. Method to determine the gelation temperature

The crossover of G' and G'' is traditionally used as an indication of the sol-gel transition temperature [24]. Although this method is simple and convenient, the sol-gel transition temperature obtained by this method is dependent on the measurement frequency ω . Chambon and Winter pointed out that for a system at the sol-gel transition point there is the relationship between G' as well as G'' and ω [25–27]:

$$G' \sim G'' \propto \omega^n \quad (1)$$

$$\tan \delta = \frac{G''(\omega)}{G'(\omega)} = \tan \frac{n\pi}{2} \quad (2)$$

here, $\tan \delta$ is independent of ω . In other words, at the sol-gel transition with the frequency independence, G' must be parallel to G'' . Using this method, Dai *et al.*

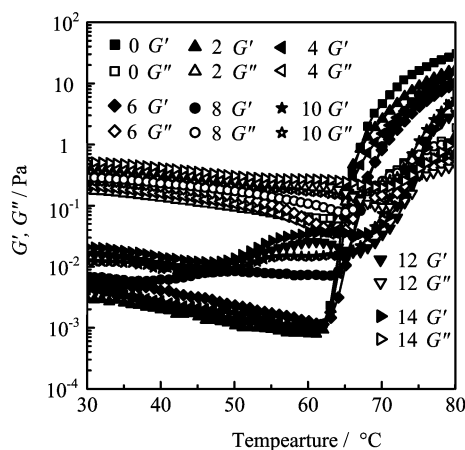


FIG. 1 Storage modulus G' and loss modulus G'' as a function of temperature for MC solutions containing SDS with various concentrations of 0, 2, 4, 6, 8, 10, 12, and 14 mol/L. A heating rate of about $1\text{ }^\circ\text{C}/\text{min}$ was used.

determined the sol-gel transition temperature for aqueous gellan gum solutions with different salt concentrations [28]. However, for some systems [5], the condition that G' must be parallel to G'' does not exist for satisfying the requirement in applying Winter's scaling law at the sol-gel transition (Eq.(1)). Li's group suggested that, for thermoreversible gels, the temperature at which an abrupt increase of G' occurs is more suitably defined as the sol-gel transition temperature for it correlates excellently with the endothermic peak observed by the micro-DSC measurements [4]. Villetti *et al.* conducted work on the physicochemical properties of MC and DTAB in aqueous medium, in which the temperature at which an abrupt increase of G' occurs is considered the optimum choice to determine the sol-gel transition point [29]. In this work, we adopted the latter criterion to determine the gelation temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows both storage modulus G' and loss modulus G'' of MC solutions in the absence and presence of SDS with various contents as a function of temperature in a heating process with a constant heating rate of $1\text{ }^\circ\text{C}/\text{min}$. As can be seen, at low temperatures, all of the samples show a predominant liquid behavior of $G' < G''$. However, by increasing the temperature, both G' and G'' increases rapidly in a relatively narrow range of temperature for each MC-SDS sample. Especially, G' increases by about 4 decades to reach a plateau at high temperature, which is more significant than G'' (by 2 decades). It is believed that the sol-gel transition occurs within the temperature range for an abrupt increase in G' . Moreover, the samples containing 0, 2, 4 and 6 mmol/L of SDS show the similar transition curves, whereas the samples with the higher SDS concentrations (≥ 8 mmol/L) shift to the high temperature

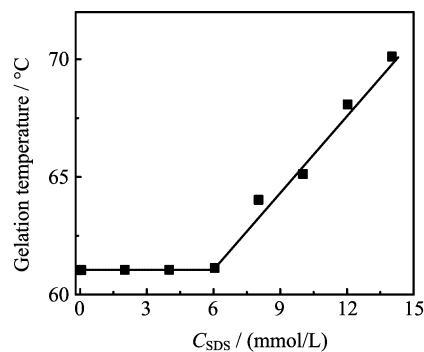


FIG. 2 Gelation temperature as a function of SDS concentration for MC solutions containing SDS.

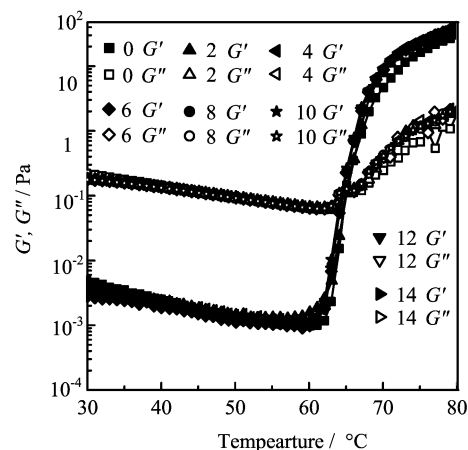


FIG. 3 Storage modulus G' and loss modulus G'' as a function of temperature for MC solutions containing β -CD with various concentrations of 0, 2, 4, 6, 8, 10, 12, and 14 mol/L. A heating rate of about $1\text{ }^\circ\text{C}/\text{min}$ was used.

side significantly, indicating a salt-in effect.

The sol-gel transition temperature for each sample, obtained from the temperature at which an abrupt increase of G' occurs, as a function of SDS concentration is plotted in Fig.2. It can be seen that, for $C_{\text{SDS}} \leq 6$ mmol/L, the sol-gel transition temperature of MC is independent of SDS concentration. However, the temperature increases linearly with increasing SDS from 6 mmol/L, showing a "salt-in" effect. Note that the transition point (6 mmol/L) is smaller than the CMC of SDS, it thus be defined as the CAC of SDS in the presence of MC, which is in accordance with results reported by other groups [15]. When SDS concentration is lower than the CAC, unimers are presented and no micelle-like aggregates of SDS are expected to form surrounding the hydrophobic block of MC. It also should be pointed that a salt-out effect for $C_{\text{SDS}} \leq 6$ mmol/L was observed in the previous study [15] which differed from our experimental results. We postulated that such result may be attributed to the limit of our experimental instrument precision.

Figure 3 showed the storage modulus G' and loss

modulus G'' for MC solutions with six concentrations (0–10 mmol/L) of β -CD as a function of temperature. It can be seen that both G' and G'' curves for MC solutions with various contents of SDS coincide perfectly with the two curves for the SDS-free MC sample, respectively. That is to say, the addition of β -CD has no influence on the sol-gel transition of MC, where the sol-gel transition temperatures of MC are plotted as a function of β -CD concentration. As is well known, The interior of β -CD is hydrophobic and has the tendency to bind to the hydrophobic $-\text{CH}_3$ groups along MC chains. However, the $-\text{CH}_3$ groups are too short, resulting in the weak interaction between β -CD and MC and the great steric hindrance effect from the back-bone of MC chains. In this case, β -CD molecules cannot bind to the $-\text{CH}_3$ groups along MC chains, and therefore has little effect on the sol-gel transition of MC.

Once β -CD is added into MC/SDS mixture solutions, things would change and become quite different. The effect of the added β -CD on the rheology of the MC/SDS mixture solutions is illustrated in Fig.4, where G' and G'' versus temperature data are presented for mixtures containing MC/14 mmol/L SDS. On the one hand, similar to the MC/SDS case (Fig.1), the MC/SDS/ β -CD systems exhibit a typical liquid behavior with $G' < G''$ at lower temperatures, while heating samples to a higher temperature an abrupt increase is shown for both G' and G'' . On the other hand, both G' and G'' curves of MC/SDS mixture, as well as the temperature at which an abrupt increase of G' occurs (gelation temperature), shift to lower temperatures with the addition of β -CD. Interestingly, these curves can eventually coincide with those of the MC solution in the absence of SDS. This is a nice demonstration of the ability of β -CD to bind and “deactivate” the surfactant and thus reverse the delay of sol-gel transition caused by SDS. Since the addition of β -CD does not affect the sol-gel transition of MC aqueous SDS-free solution (Fig.3), the effects are mainly as a result of the interactions between β -CD and SDS.

To further elucidate the effect of β -CD, the variation of sol-gel transition temperature of MC/14 mmol/L SDS mixture solution against the concentration of β -CD is plotted in Fig.5. As shown, for $C_{\beta\text{-CD}} < 8$ mmol/L, the gelation temperature of MC/14 mmol/L SDS mixture solution decreases linearly with increasing β -CD concentration. On the other hand, a temperature plateau is shown from $C_{\beta\text{-CD}} \geq 8$ mmol/L. The initial gelation temperature decrease and down to a plateau eventually observed with increasing β -CD concentration is contrasted to the effect of SDS on the sol-gel transition of MC shown in Fig.2. Similar results for the effect of β -CD on the gelation temperature of MC/12 mmol/L SDS and MC/10 mmol/L SDS mixture solutions are also obtained (Fig.5). Besides, the temperature plateaus of all three MC/SDS mixture systems at high β -CD concentrations have the same change trend and equal to that of MC sample in the absence or presence of SDS below the CAC.

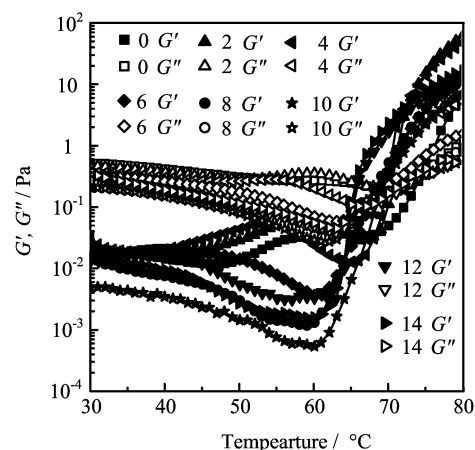


FIG. 4 Storage modulus G' and loss modulus G'' of MC/SDS mixtures at a fixed SDS concentration (14 mmol/L), as a function of temperature, for different β -CD concentrations. The β -CD concentrations in mmol/L are indicated.

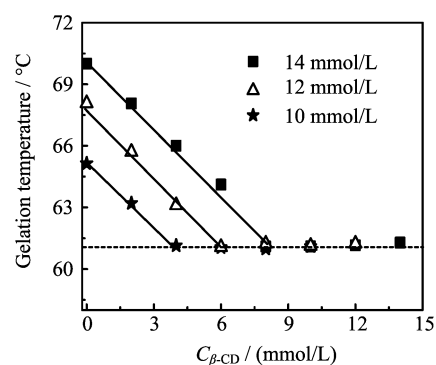


FIG. 5 Decrease in gelation temperature of MC/14 mmol/L SDS, MC/12 mmol/L SDS and MC/10 mmol/L SDS mixture solutions, resulting from the addition of β -CD at different concentrations. The dashed line indicates the gelation temperature value of SDS-free MC solution.

As mentioned in the Introduction, CDs are able to form inclusion complexes with a wide variety of hydrophobic guest molecules. For surfactant solutions with concentrations above its CMC, the addition of CDs introduces an additional equilibrium (inclusion of surfactant molecule into the CD cavity), which competes with the self-assembly process, thus causing the destruction of the micelle aggregates [30–32]. Therefore, in MC/SDS mixture solutions, the added β -CD molecules have the potential to bind to the hydrophobic moieties of the SDS unimers in bulk solution and thus reduce the tendency of SDS molecules to associate with $-\text{CH}_3$ groups of MC chains and form micelle-like aggregates surrounding them. This reduces the aggregation number of those SDS aggregates surrounding $-\text{CH}_3$ groups of MC chains and thus shifts the sol-gel transition of MC to lower temperatures. Evidently, the interaction between β -CD and SDS molecules is strong enough to

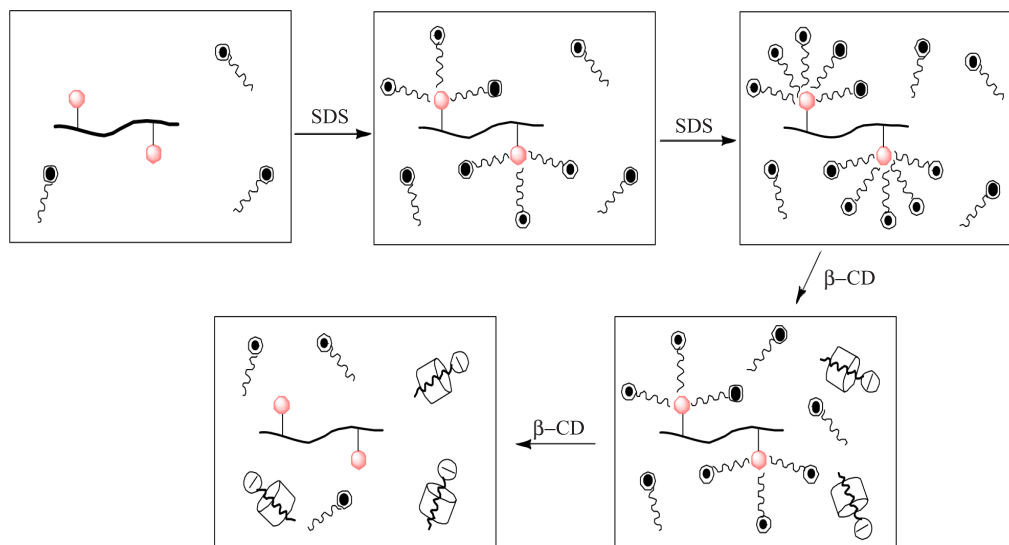


FIG. 6 Schematic representation of the formation of SDS aggregates surrounding the side groups along MC chains and the aggregate disassociation and complete disruption for the formation of inclusion complexes between SDS and the further added β -CD.

disrupt the aggregates surrounding $-\text{CH}_3$ groups of MC chains completely. Note that the appropriate “milestone” in the polymer-surfactant system is the CAC. In MC/SDS/ β -CD system, the aggregates of SDS have been destroyed when the rest SDS molecules (do not form inclusion complexes with β -CD) is below the CAC. Figure 5 indicates the gelation temperature value of MC aqueous solution in the absence of SDS (also that of MC aqueous solution in presence of SDS below the CAC, in which SDS molecules are present as unimers and the aggregates are unexpected to form). As mentioned above, upon the addition of sufficient amount of β -CD, the gelation temperatures for three all MC/SDS mixture systems can decrease to the gelation temperature value of MC in the absence of SDS.

A schematic representation of the interaction between MC, SDS, and β -CD is given in Fig.6. First the SDS molecules with concentrations below its CAC in MC solutions are present as unimers and they thus affect little the sol-gel transition of MC. For MC solutions in the presence of SDS above its CAC, the micelle-like aggregates of SDS are formed around $-\text{CH}_3$ groups of MC chains, with some SDS molecules still present as unimers in the bulk solution, and lead to the sol-gel transition to the higher temperatures. Once the β -CD are added, the inclusion complex formation between β -CD molecules and the hydrophobic moieties of SDS unimers in the bulk solution leads to the disassociation of the SDS aggregates surrounding $-\text{CH}_3$ groups of MC chains, a disruption of the aggregates, and to the decrease of MC gelation temperature.

Though most commonly claimed stoichiometric ratio for CD complexes is 1:1 guest-host, the molar ratio of CD to guest molecule is still controversial [33]. From our experimental results (Fig.5) and considering

the CAC of SDS we find that the concentrations of β -CD required to “deactivate” (*i.e.*, low down the gelation temperature to that of MC in the absence or presence of SDS below the CAC) SDS are 10, 8 and 6 mmol/L, respectively, which corresponds to 1 guest SDS molecule per 1 host β -CD molecule. That is to say, the molar ratios for the SDS- β -CD inclusion complex in three mixture systems studied are all 1:1. However, the apparent stoichiometric ratios for SDS- β -CD inclusion complex in polyelectrolyte/SDS mixture systems are found to vary in the range of 1:1 and 1:2 guest-host ratios, depending on the SDS concentration in the mixture [23]. This discrepancy may mainly be due to the different interaction mechanism of SDS as well as β -CD with polymer chains. In the case of polyelectrolyte/SDS mixture systems, SDS molecules bind to polyelectrolyte chains via electrostatic interactions with their hydrophobic moieties exposed in the aqueous environment. Therefore the free (unassociated) SDS molecules and those having bound to polyelectrolyte chains can both form inclusion complexes with the added β -CD molecules, and they exhibit different binding properties with β -CD. On the other hand, some β -CD molecules bind to side groups along polymer chain and thus cannot participate in the inclusion complex formation with SDS. These lead to a variant apparent stoichiometric ratio for SDS- β -CD inclusion complex with the concentration of SDS. However, in MC/SDS mixture systems, SDS molecules form aggregates surrounding $-\text{CH}_3$ groups on MC chains with their charged head groups outer. Therefore, only the free SDS molecules (do not form the aggregates) can form inclusion complexes with β -CD. Moreover, the added β -CD molecules cannot bind to the side groups along MC chains, as been proved above. The expected stoichiometric ratio (1:1) is thus observed in the mix-

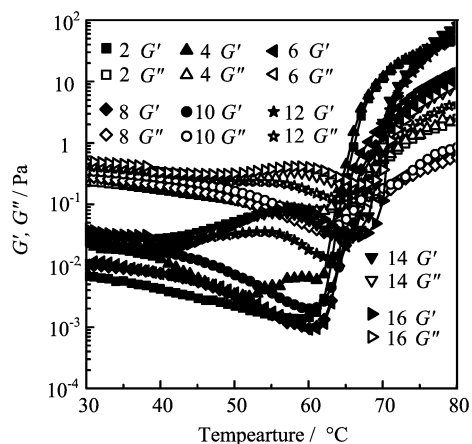


FIG. 7 Storage modulus G' and loss modulus G'' of MC/ β -CD mixtures at a fixed β -CD concentration (4 mmol/L), as a function of temperature, for different SDS concentrations. The SDS concentrations in mM are indicated.

ture systems.

In addition, the SDS- β -CD inclusion complexes in polyelectrolyte/SDS mixtures are thought to participate in the mixed micelles which are still able to sustain cross-links in the polyelectrolyte network [23]. That is to say, SDS molecules having bound to β -CD can also participate in the formation of the aggregates. However, an opposite observation is obtained in this work. In MC/SDS mixture systems, the inclusion complexes of SDS molecules with the added β -CD are present in bulk solution and cannot form the micelle-like aggregates surrounding $-\text{CH}_3$ groups along MC chains. In fact we observe that, within the experimental error, the gelation temperature of MC/SDS mixture in the presence of a certain concentration of β -CD coincides with that of MC solutions in the presence of $(C_{\text{SDS}}-C_{\beta\text{-CD}})$ SDS for all three MC/SDS mixture systems studied. Here C_{SDS} and $C_{\beta\text{-CD}}$ are the concentrations of SDS and β -CD in the mixture, respectively. Therefore, the SDS- β -CD inclusion complexes do not participate in the formation of SDS aggregates, otherwise the expected gelation temperature of MC/SDS in the presence of β -CD would be higher than that observed.

Further, the effects of the SDS on MC/ β -CD mixture solutions were also measured. Figure 7 shows the storage modulus G' and loss modulus G'' of MC/4 mmol/L β -CD mixture solutions as a function of temperature in presence of variant amounts of SDS. When SDS is below 10 mmol/L, the G' and G'' curves of all samples almost overlap, respectively. On the other hand, the G' and G'' curves of MC/ β -CD mixture solutions shift to higher temperatures with increasing the SDS concentration from $C_{\text{SDS}} \geq 10$ mmol/L. The dependence of the gelation temperature of MC/4 mmol/L β -CD mixture solution on the SDS concentration is plotted in Fig.8. As shown, the gelation temperature keeps constant for $C_{\text{SDS}} \leq 10$ mmol/L whereas it increases linearly with

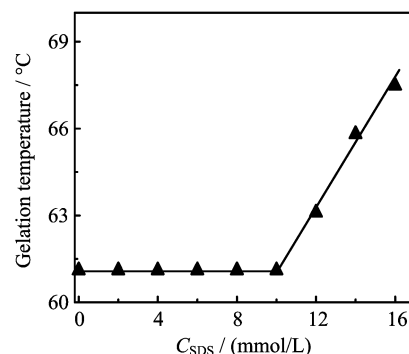


FIG. 8 Gelation temperature for MC/4 mmol/L β -CD mixture solutions as a function of SDS concentration.

further increasing the SDS concentration. Comparing Fig.8 with Fig.2 it can be seen that the transition point of MC in presence of 4 mmol/L β -CD is delayed from 6 mmol/L to 10 mmol/L. Moreover, the gelation temperature of MC/ β -CD mixture solutions with various amounts of SDS coincides with those of MC samples in presence of $(C_{\text{SDS}}-4)$ mmol/L SDS within the experimental error. Here C_{SDS} indicates the concentration of the added SDS into MC/ β -CD mixture solutions. So, it can be concluded that the SDS- β -CD inclusion complexes do not participate in the formation of the micelle-like aggregates surrounding $-\text{CH}_3$ groups along MC chains. The stoichiometric ratio of 1:1 for SDS- β -CD inclusion complexes are obtained accordingly.

IV. CONCLUSION

In this work, interactions between MC, SDS, and β -CD in aqueous solution have been studied using rheological measurements. Our experimental results have shown that the inclusion interaction between β -CD and SDS is much greater than the hydrophobic interaction between SDS and the methyl groups of MC chains. As a result, in the coexistence of β -CD and SDS, the sol-gel transition temperature of MC solution keeps the same value, independent of the concentration of SDS in solution. This results not only suggest that the effect of surfactant upon the sol-gel transition of MC solution can be screened by β -CD completely but also indicate that the inclusion ratio of β -CD and SDS can be determined quantitatively by the rheological measurement. In our experiment, the inclusion ratio of β -CD and SDS in the presence of MC is 1:1, which is in good agreement with our previous study but is critically different from the uncertain inclusion ratio of β -CD and SDS in the presence of polyelectrolyte with the opposite charge of SDS, mainly due to the reason that the mechanism of the interaction between SDS and the hydrophobic modified polymer MC is critically different from the mechanism of the interaction between SDS and the oppositely charged polyelectrolyte.

V. ACKNOWLEDGEMENTS

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