

EFFECT OF ORTHO-METHOXYCINNAMIC ACID ON THE SOL-GEL TRANSITION OF METHYLCELLULOSE SOLUTIONS IN THE PRESENCE OF CETYLTRIMETHYLAMMONIUM BROMIDE

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Abstract The sol-gel transition of methylcellulose (MC) solutions in the presence of ortho-methoxycinnamic acid (OMCA) or cetyltrimethylammonium bromide (CTAB) and in the coexistence of OMCA and CTAB was determined by the rheological measurement. It has been found that the sol-gel transition temperature of MC solutions increases linearly with the concentration of either OMCA or CTAB in solution, respectively. However, in the coexistence of OMCA and CTAB, the sol-gel transition temperature of MC solutions remains invariable, independent of the concentration of CTAB in solution. The experimental results show that OMCA has priority to adsorb on the methyl group of MC chains to form polymer-bound aggregates. In particular, these aggregates inhibit the hydrophobic interaction between CTAB and the methyl group of MC chains completely. Taking into account the fact that OMCA is almost insoluble in MC-free solutions but dissolves very well in aqueous MC solutions, we propose the formation of the core-shell architecture prompted by OMCA and the methyl group of MC chains, with the methyl group of MC chains serving as the core and the self-assembly of OMCA molecules serving as the shell. Obviously, the formation of the core-shell structure increases the solubility of OMCA, improves the stability of methyl groups of MC chains at high temperatures and inhibits the hydrophobic interaction between CTAB and the methyl group of MC chains in solution. The abnormal behavior relating to the sol-gel transition of MC solutions in the presence of OMCA or in the coexistence of OMCA and CTAB is therefore explained. Upon UV irradiation, the sol-gel transition temperature of MC solutions in the presence of OMCA, or in the coexistence of OMCA and CTAB, decreases notably. However, the dependence of the sol-gel transition temperature of MC solutions as a function of OMCA concentration, or CTAB concentration in the presence of OMCA, does not change after UV irradiation.

Keywords: Methylcellulose; Ortho-methoxycinnamic acid; Cetyltrimethylammonium bromide; Sol-gel transition; Hydrophobic interaction.

INTRODUCTION

Interactions involving hydrophobically modified water-soluble polymers and surfactants in aqueous solutions have been the focus of intense research activity in recent decades^[1–3], which are not only of intrinsic fundamental interest, but also for extensive practical applications in a number of industrial and technological fields^[4–7]. Methylcellulose (MC), the hydrophobically modified derivative of cellulose, exhibits interesting thermo-reversible sol-gel transition in aqueous solutions, and the phenomenon has been fairly well studied^[8–19]. Recently, a considerable amount of research has been done to explore the factors that influence the sol-gel transition of MC, such as the type of salts, concentration of surfactants, temperature and pH.

Surfactants and salts represent the two common factors that can alter the degree of hydrophobic association and affect the sol-gel transition of MC solutions. Various systems involving surfactants such as cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl

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sulfonate (SDS) with MC have been investigated, in the meanwhile possible mechanisms have been proposed to further elucidate the effect of surfactants on the sol-gel transition of MC. Wang *et al.*^[9] and Li *et al.*^[10] studied the effect of varied concentrations of CTAB and SDS on the sol-gel transition of MC solutions using micro-differential scanning calorimetry (DSC), rheometry and turbidity. Two effects of surfactants on the sol-gel transition of MC aqueous solutions, which depend on the concentration of the surfactants, have been found. When the concentration of either CTAB or SDS is lower than its critical aggregation concentration (CAC) in MC solutions, they display a typical salt-out effect, and the sol-gel transition temperature of MC solutions decreases linearly with the concentration of surfactants. On the other hand, when the concentration of either CTAB or SDS is greater than CAC, both surfactants display a typical salt-in effect and the sol-gel transition temperature of MC solutions is found to increase linearly with the concentration of surfactants. The polymer-induced micelles, referred to as “cages”, are proposed to explain the sol-gel transition of MC solutions in the presence of surfactants with the concentration greater than CAC. Obviously, these polymer-induced micelles act as the comfortable “cages” for the hydrophobic units of MC to reside in. In order for MC solution to form a gel through the hydrophobic interaction, the cages of surfactant must be removed. A high temperature has to be applied to destroy the cages, and as a result the sol-gel transition of the MC solution shifts to a higher temperature.

In the presence of salt the situation becomes much more complicated, mainly due to the reason that surfactants may be induced by salt to form micelles in solution. In our previous study^[20], we have shown that the effect of CTAB upon the sol-gel transition of MC solutions can be inhibited completely on condition that CTAB has been induced by NaCl to form free micelles in solution. It's already known that organic additives such as *trans*-ortho-methoxycinnamic acid (OMCA) have more efficiency in inducing the surfactants to form micelles in solution than inorganic salt such as NaCl. In particular, OMCA is a photo-responsive substances which undergoes a photo-isomerization from its *trans* to *cis* form under a certain irradiation^[21–28]. Once changed from *trans* form to *cis* form, the efficiency of OMCA in inducing the surfactants to form micelles in solution decreases considerably. In the present paper, the effect of CTAB upon the sol-gel transition of MC solutions in the presence of OMCA was studied. The OMCA acts here as a “probe”. That is to say, if CTAB molecules are induced by OMCA to form free micelles, the sol-gel transition behavior of MC solutions in the coexistence of OMCA with the *trans* form and CTAB should be quite different before and after UV irradiation. In contrast to our expectation, OMCA with the *trans*-form, even neutralized by NaOH, does not dissolve well in CTAB solution, probably due to the reason that the concentration of CTAB we used was much lower than the publication reported^[22]. In contrast, OMCA can dissolve very well in MC solution. Of particular interest is that the effect of OMCA on the sol-gel transition of MC solution is very similar to that of the traditional surfactant such as CTAB or SDS. Moreover, in the presence of OMCA, the effect of CTAB on the sol-gel transition of MC solution is inhibited completely even after irradiation. The exceptional behaviors we mentioned above indicate the formation of the core-shell structure. The methyl group of MC chains serves as the core and OMCA aggregates as the shell. The possible mechanism related to the formation of the core-shell structure and its effect upon the sol-gel transition of MC solutions in the presence of OMCA, or in the coexistence of OMCA and CTAB before and after their radiation, is proposed and explained in this manuscript.

EXPERIMENTAL

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 wt% 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. CTAB was purchased from Sinopharm Chemical Reagent Co. Ltd and used as received. OMCA in its *trans* form was purchased from Acros Chemicals, and it was greater than 98% in purity. All chemicals were used as received.

Sample Preparation

A pure MC aqueous solution of 2 wt% was first prepared by dispersing the weighed MC powder into deionized water at 70°C and kept in a refrigerator with the temperature of 20°C and kept for a minimum period of 24 h for stabilization. A homogeneous and transparent solution of MC was obtained at room temperature (25°C). Solutions containing OMCA were prepared with a slight excess of base (NaOH), and then added to MC solutions. Samples were stirred continuously under mild heating until they became homogeneous. The solutions were then left to equilibrate over night at room temperature before any experiments were conducted. The weighed CTAB was then added into the mixture to obtain all the required sample solutions. All the sample solutions were prepared with deionized water.

Rheological Measurements

Rheological measurements were conducted to determine the sol-gel point on a TA AR-G2 rheometer using a cone-plate of 40 mm diameter with cone angle of 1°. The storage modulus (G') and loss modulus (G'') were measured as a function of the temperature at an angular frequency of 1 rad/s within a linear range of viscoelasticity. The measurement temperatures were from 20°C to 70°C. A thin layer of low-viscosity silicone oil was used to cover the free surface of the solution to prevent evaporation of solvent.

Sample Response before and after UV Irradiation

MC/CTAB/OMCA samples were irradiated with UV light from an Oriel 200 W mercuryarc lamp. A dichroic beam turner with a mirror reflectance range of 280 to 400 nm was used to access the UV range of the emitted light. Samples (5 mL) were placed in a Petridish with a quartz cover, and irradiation was done for a specific duration under stirring. UV Vis spectroscopy before and after irradiation were carried out using a Varian Cary 50 spectrophotometer.

Method to Determine the Gelation Temperature

Typically, the crossover of G' and G'' is usually taken as the gelation temperature point^[17]. 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 *et al.*^[29, 30] pointed out that for a system at the sol-gel transition point there is a relationship between G' as well as G'' and ω :

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

and

$$\tan \delta = G''(\omega) / G'(\omega) = \tan(n\pi/2) \quad (2)$$

That is, $\tan \delta$ is independent of ω . In other words, at the sol-gel transition with the frequency independence, G' must be parallel to G'' . However, for some systems, 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)). However, in recent years, some authors on the basis of rheological measurements suggested that the sharp increase in G' should be taken as the gel temperature^[17, 31]. Li's group^[17] suggested that, for thermo reversible 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. Villetti *et al.*^[31] 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 more optimum choice to determine the sol-gel transition point. Thus in this work, we adopted the latter criterion to determine the gelation temperature.

RESULTS AND DISCUSSION

MC Solution in the Presence of CTAB

When the surfactant such as CTAB is added into MC solutions, the sol-gel transition of MC solutions should be changed dramatically. The mechanism related to the effect of CTAB upon the sol-gel transition of MC solutions

can be shown schematically in Fig. 1. Due to the hydrophobic interaction, the CTAB molecules will adsorb on the methyl group of MC chains. At the initial stage, the CTAB molecules bind to the methyl groups of MC chains individually. As the concentration of CTAB is higher than the critical aggregation concentration (CAC), the CTAB molecules will form cages along the MC chains. The formation of cages screens the hydrophobic interaction between the methyl groups of MC chains in solution. For the association of MC molecules through the hydrophobic interaction, these cages must be destroyed or removed. Obviously, the higher temperature is necessary for destroying the cages formed by CTAB molecules. As a result, the sol-gel transition of MC solutions increases to higher temperatures in the presence of CTAB. In particular, the increased number of cages created by the increased concentration of CTAB molecules will increase the difficulty in destructing or removing the surfactant cages. As a result, the sol-gel transition temperature of MC solutions increases with increasing the concentration of CTAB in solution as presented by Li *et al.* It should be noted that if the CTAB molecules are induced to form free micelles in solution, the effect of CTAB molecules upon the sol-gel transition of MC solutions no long exists, to which little attention has been devoted up to now.

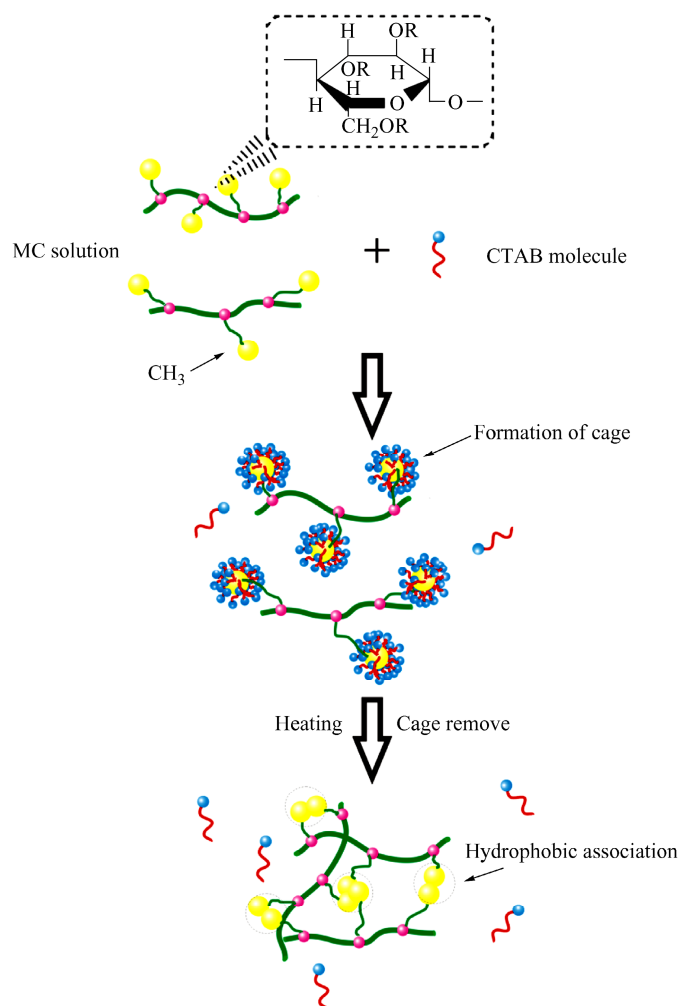


Fig. 1 Schematic diagram for the CTAB binding to methylcellulose (MC) chains to form surfactant cages and the removal of surfactant cages by heating for MC chains to associate into a gel network

Figure 2 shows the temperature dependence of storage modulus G' and loss modulus G'' for MC solutions with various contents of CTAB. It can be seen that the MC solution containing CTAB shows a liquid behavior of

$G' < G''$ at low temperatures. Besides, there is a relatively narrower temperature range in which both G' and G'' show a steeper increase. With increasing CTAB concentrations, both G' and G'' curves, as well as the sol-gel transition temperature, shift to higher temperatures, showing a salt-in like effect or a delay of MC gelation in the presence of CTAB. Figure 3 shows the dependence of sol-gel transition temperature for MC solutions as a function of CTAB concentration. It is observed that the sol-gel transition of MC solution shifts to high temperatures with increasing CTAB concentration, similar to the experimental results presented by Li *et al.*^[10] and in our previous report^[20]. It is already known that critical micelle concentration of CTAB in aqueous solution is 0.8 mmol/L, or 0.03% in weight. In our experiment, the concentration of CTAB ranges from 0.2% to 0.6% in weight, greater than CMC of CTAB in solution. Even though, the sol-gel transition of MC solution still increases linearly with the concentration of CTAB in solution as shown in Fig. 3. It should be pointed out that, due to the adsorption of CTAB on MC chains, the real concentration of CTAB in bulk solution (taking the adsorption of CTAB on MC chains into account), would be less than the apparent concentration of CTAB dissolved in solution (neglecting the adsorption of CTAB on MC chains). We define here the apparent concentration of CTAB dissolved in solution as $c_{\text{CTAB, app}}$ and the real concentration of CTAB in bulk solution as $c_{\text{CTAB, real}}$. In our experiment, the average degree of substitution (DS) is about 15% and the number of hydrophobic unit of MC is sufficiently larger than the number of CTAB molecules added into solution, implying that a great number of

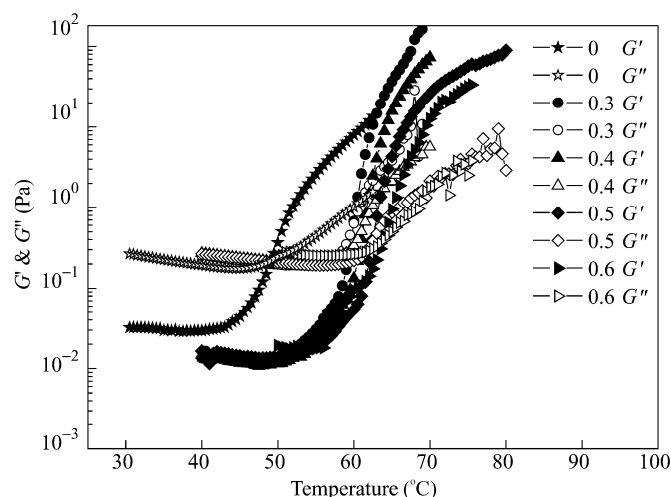


Fig. 2 Storage modulus G' and loss modulus G'' as a function of temperature for 2 wt% MC solutions containing CTAB
A heating rate of about 1 K/min was used. The CTAB concentrations in wt% are indicated.

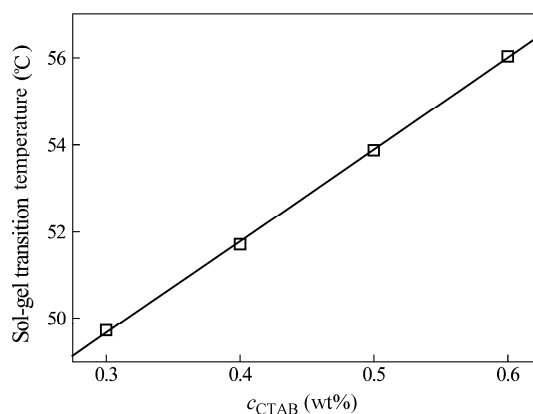


Fig. 3 Dependence of sol-gel transition temperature for MC solutions as a function of CTAB concentration

CTAB molecules will adsorb on MC chains. As a result, the real concentration of CTAB in bulk solution, $c_{\text{CTAB,real}}$ is still less than CMC of CTAB in polymer free solution. This explains why the sol-gel transition of MC solutions still increases linearly with the concentration of CTAB in solution as indicated in Fig. 3.

MC Solution in the Presence of OMCA

It is already known that OMCA has more efficiency in inducing the surfactants to form micelles in solution than inorganic salt such as NaCl. Far from our expectation is that OMCA with the *trans*-form, even deprotonated by NaOH, cannot dissolve well in either pure water or in CTAB aqueous solution, but dissolve very well in MC solution. Of particular interest is that the effect of OMCA on the sol-gel transition of MC solutions is very similar to the traditional surfactant such as CTAB or SDS.

Figure 4 shows the storage modulus G' and loss modulus G'' for MC solutions with various OMCA (with the *trans*-form and deprotonated by NaOH) contents as a function of temperature at a heating rate of 1 K/min. It is observed that MC solutions in the presence of OMCA show a liquid behavior of $G' < G''$ at low temperatures. Within a narrow temperature range subsequently, both G' and G'' show a steeper increase. Upon increasing the OMCA concentration, both G' and G'' curves, as well as the sol-gel transition temperature, shift to higher temperatures, showing a salt-in like effect or a delay of MC gelation. The variation of sol-gel temperature of MC solutions against the concentration of OMCA as shown in Fig. 5 further elucidates the effect of OMCA upon the sol-gel transition of MC solutions. It can be seen that the sol-gel transition temperature of MC solutions increases linearly with increasing OMCA concentration, indicating that the effect of OMCA upon the sol-gel transition of MC solutions is very similar to that of traditional surfactants such as CTAB and SDS. To get a better understanding of the effect of OMCA upon the sol-gel transition of MC solutions, we have to explain why OMCA (with the *trans*-form and deprotonated by NaOH) cannot dissolve well in either pure water or in aqueous CTAB solution, but dissolve very well in MC solution.

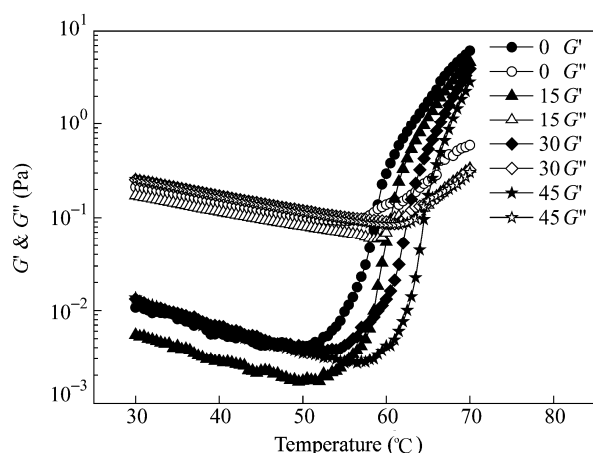


Fig. 4 Storage modulus G' and loss modulus G'' as a function of temperature for 2 wt% MC solutions with OMCA prior to irradiation. A heating rate of about 1 K/min was used. The OMCA concentrations in mmol/L are indicated.

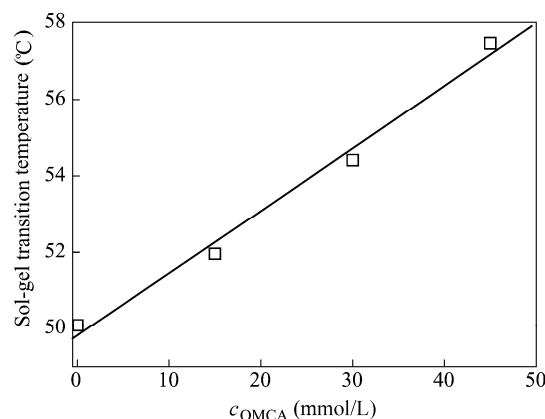


Fig. 5 Dependence of sol-gel transition temperature for MC solution as a function of OMCA concentration

It is already known that OMCA with the *trans*-form also has hydrophilic and hydrophobic groups, similar to the traditional surfactants. If OMCA is treated here as a surfactant, the hydrophobic tail of OMCA is short and rigid. The possible self-assembly architecture for OMCA can be shown in Fig. 6(a), with one end of this possible self-assembly architecture hydrophilic while the other end hydrophobic. This architecture is unstable in water of course. This explains why OMCA is almost insoluble in pure water. If deprotonated by NaOH, as shown in Fig. 6(b), the packing parameter of OMCA will be changed due to the electro-static repulsion. However, due to

the limitation that the hydrophobic part of OMCA is short and rigid, the possible architecture for the self-assembly of OMCA is a hollow sphere as shown in Fig. 6(c). The inner surface of the sphere is hydrophobic, whereas the out surface of the sphere is hydrophilic. Obviously, this hollow sphere is unstable and cannot exist in aqueous solutions. As a result, the OMCA cannot dissolve well in aqueous solution even in the presence of NaOH.

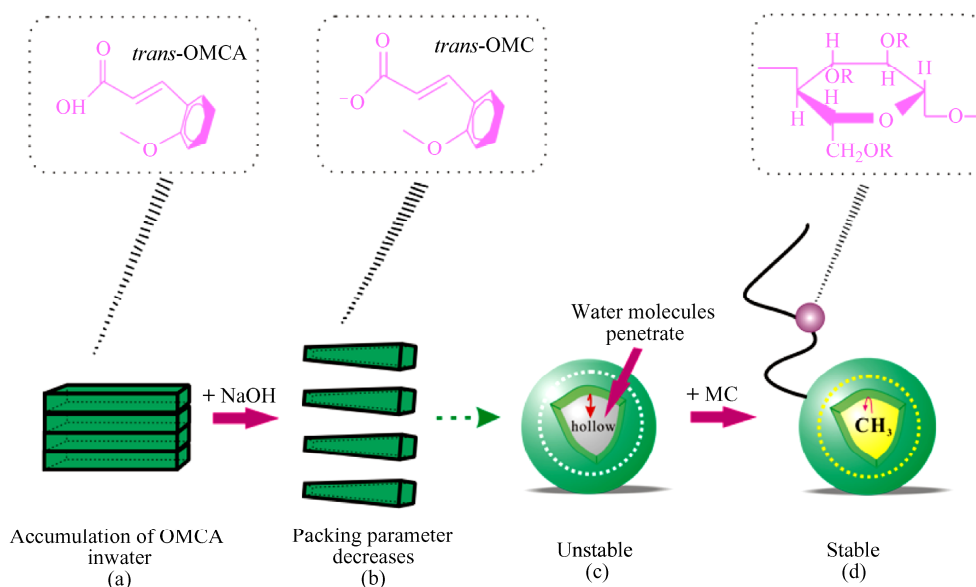


Fig. 6 Mechanism of the adsorption of OMCA on the methyl group of MC chains in NaOH aqueous solution: (a) the unstable packed structure of OMCA in water, (b) the unstable structure of OMCA in NaOH solution, (c) the unstable structure of OMCA in MC solution, (d) stable solid sphere due to the existence of methyl group of MC chains

In the presence of MC, the situation becomes critically different. The methyl groups of MC chains, referred to as the hydrophobic sphere approximately, can just fulfill the hollow sphere self-assembled by OMCA to form a core-shell structure, with methyl groups of MC chains serve as a core and the self-assembly OMCA molecules serve as the shell, as shown in Fig. 6(d). The formation of the core-shell structure make the architecture created by the methyl groups of MC chains and the aggregates of OMCA molecules become stable in water. As a result, OMCA dissolves very well in the MC solution. Obviously, the formation of core-shell structure inhibits the hydrophobic interaction between the methyl groups of MC chains in solution. This suggests that the sol-gel transition of MC solutions should increase in the presence of OMCA, which is verified by the experimental results as shown in Fig. 5.

It should be noted that the efficiency of OMCA and CTAB in enhancing the sol-gel temperature of MC solutions is quite different. From Fig. 3 and Fig. 5 it can be seen that within the temperature range, for example, from 52°C to 56°C, the concentration required for CTAB is about 0.11 mmol/L to 0.165 mmol/L, whereas the concentration needed for OMCA is markedly ranged from 20 mmol/L to 45 mmol/L.

It is already known that OMCA is an optical isomer. Under a certain irradiation, OMCA undergoes a photoisomerization from its *trans* to its *cis* form as shown in Fig. 7. Figure 8 shows the storage modulus G' and loss modulus G'' for MC solutions with various OMCA (deprotonated by NaOH) contents as a function of temperature at a heating rate of 1 K/min after UV irradiation. The variation of sol-gel temperature of the MC solution against the concentration of OMCA is shown in Fig. 9. It is noted that the effect of OMCA with the *cis* form upon the sol-gel transition of MC solutions is very similar to that of OMCA with the *trans* form. However, there is a slight difference which has to be noted here. By comparing Fig. 9 with Fig. 5, we can see that the sol-gel transition of MC solution in the presence of OMCA with the *trans* form decreases after UV irradiation. Ketner *et al.*^[22] have studied the factors which influence the association of *trans*- and *cis*-OMCA with CTAB

micelles. They believe that there are two related factors which have to be taken into account in this regard: (i) the geometry of the two OMCA isomers and (ii) their hydrophobicities^[22]. We extend this view point to propose a reasonable interpretation as to the question of why the sol-gel transition temperature of MC solutions undergoes decreasing after UV irradiation in the presence of OMCA with the *trans* form.

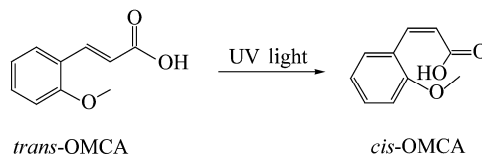


Fig. 7 Schematic behavior of the *trans* to *cis* photoisomerization of OMCA

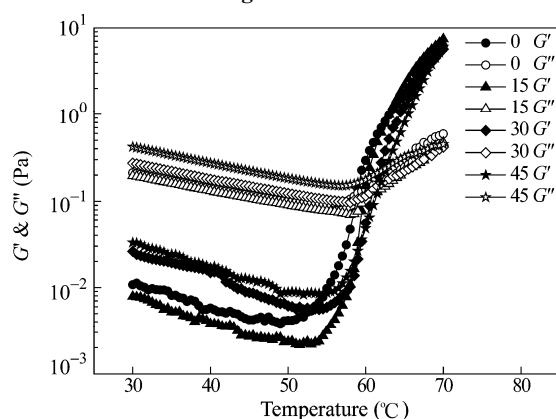


Fig. 8 Storage modulus G' and loss modulus G'' as a function of temperature for 2 wt% MC solutions containing OMCA after UV irradiation. A heating rate of about 1 K/min was used. The OMCA concentrations in mmol/L are indicated.

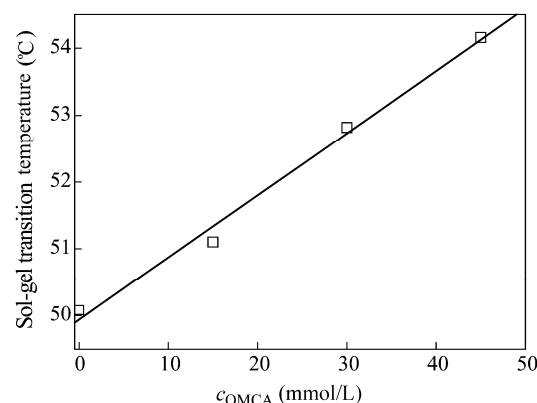


Fig. 9 Dependence of sol-gel transition temperature for MC solution as a function of OMCA concentration radiated by UV

The first argument concerns the relative different configurations of the two isomers. As shown in Fig. 7, the carboxyl of benzene ring of OMCA with the *trans* form stretches out of the ring-like structure whereas the carboxyl of benzene ring of OMCA with the *cis* form embeds in the ring-like structure. These slight structural differences must not be neglected because they play a particular important role in the formation of aggregates related to OMCA molecules. If the carboxyl of benzene ring of OMCA with the *cis* form embeds in the ring-like structure, the hydrophobic interaction of OMCA with the *cis* form becomes weaker than OMCA with the *trans* form. This suggests that the core-shell structure created by OMCA and the methyl group of MC chains becomes less stable and can be removed at the lower temperature. As a result, the sol-gel transition temperature of MC solutions undergoes decreasing after UV irradiation in the presence of OMCA with the *trans* form.

A second related argument concerns the relative hydrophobicity of the two isomers, which has been documented that *trans*-OMCA is more hydrophobic than *cis*-OMCA^[22]. A relatively high hydrophobicity of the *trans* isomer has been noted for a variety of compounds, including olefinic and azobenzene derivatives. For example, in azobenzene-based surfactants, the greater hydrophobicity of the *trans* form gives it a lower critical micelle concentration or CMC^[4, 32]. This difference in hydrophobicity has been attributed to the lower net dipole moment of the *trans* isomer compared to the *cis* isomer: *i.e.*, the dipoles add up in the *cis* form, while they tend to cancel each other in the *trans* form. Equivalently, here is greater charge delocalization in the *cis* form^[4, 32].

Moreover, studies of Ketner *et al.* further confirm the differences in hydrophobicity. In the absence of base, they find that OMCA with either *trans* form or *cis* form has a limited solubility in deionized water. But while the solubility of OMCA with the *cis* form is measured to be 8.6 mmol/L, the solubility of OMCA with the *trans* form is just 0.26 mmol/L, *i.e.*, more than a factor of 30 less. This confirms that OMCA with the *trans* form is

much more hydrophobic than OMCA with the *cis* form. Obviously, with the increase of the hydrophilicity of OMCA with the *cis* form, the hydrophobic interaction between OMCA and the methyl group of MC chains decreases accordingly. The core-shell structure created by OMCA and the methyl group of MC chains becomes less stable. This explains why the sol-gel transition temperature of MC solutions undergoes decreasing after UV irradiation in the presence of OMCA with the *trans* form.

MC Solution in the Coexistence of CTAB and OMCA

Figure 10 shows the temperature dependence of storage modulus G' and loss modulus G'' for MC solutions in the coexistence of CTAB and OMCA (deprotonated by NaOH) prior to the UV irradiation at a heating rate of 1 K/min. It can be seen that the curves of G' or G'' almost coincide with each other, the difference merely lies in the different plateaus reached, that is to say, different gel strength. More precisely, sol-gel temperature of MC solution remains constant, independent of the concentration of CTAB in the presence of OMCA which can be intuitively seen from Fig. 11. The possible interpretation is that CTAB molecules have been induced by OMCA to form micelles in solution as mentioned above. However, there are several reasons which challenge this presumption critically.

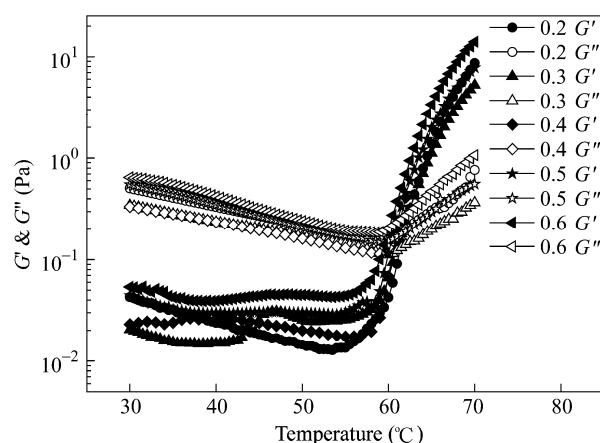


Fig. 10 Storage modulus G' and loss modulus G'' as a function of temperature for MC solutions in the coexistence of CTAB and OMCA prior to irradiation. A heating rate of about 1 K/min was used. The concentration of OMCA is fixed at 30 mmol/L, and CTAB concentrations in wt% are indicated.

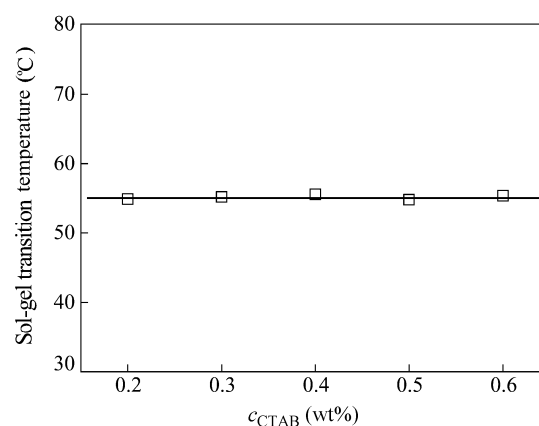


Fig. 11 Dependence of sol-gel transition temperature for MC solutions as a function of CTAB concentration in the presence of OMCA with the *trans* form

First, if CTAB molecules were induced to form micelles in solution, then, in MC free solutions, the situation will be the same. However, the experimental results have shown that OMCA, even neutralized by NaOH, can not dissolve well in aqueous CTAB solution. Second, if CTAB molecules were induced by OMCA to form micelles in solution, then, upon UV irradiation, the association of OMCA with CTAB micelles will be changed. As a result, the sol-gel transition of MC solutions in the coexistence of CTAB and OMCA should change significantly. However, the experimental results, as shown in Fig. 12 and Fig. 13, indicate that UV irradiation has little effect upon the sol-gel transition of MC solutions in the coexistence of CTAB and OMCA.

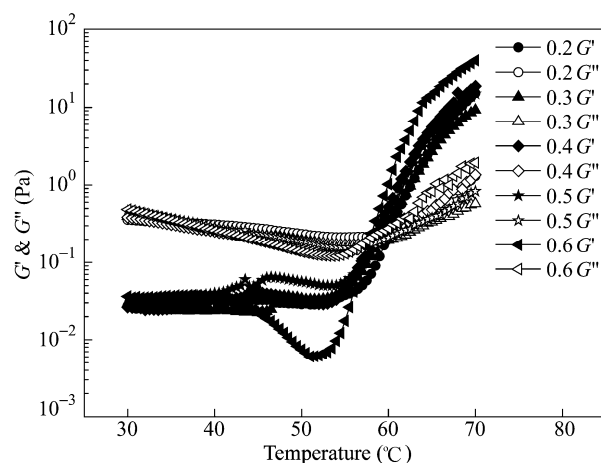


Fig. 12 Storage modulus G' and loss modulus G'' as a function of temperature for MC solutions in the coexistence of CTAB and OMCA after UV irradiation. A heating rate of about 1 K/min was used. The concentration of OMCA is fixed at 30 mmol/L, and CTAB concentrations in wt% are indicated.

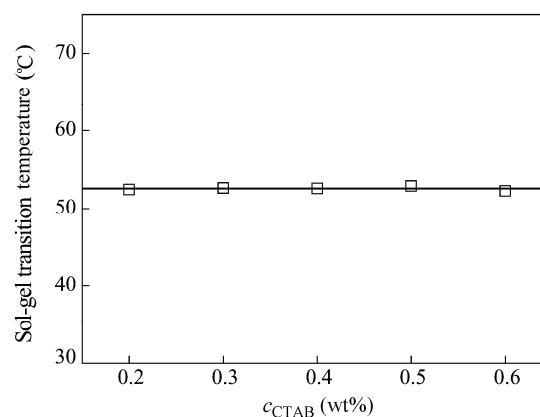


Fig. 13 Dependence of sol-gel transition temperature for MC solutions as a function of CTAB concentration in the presence of OMCA with the *cis* form

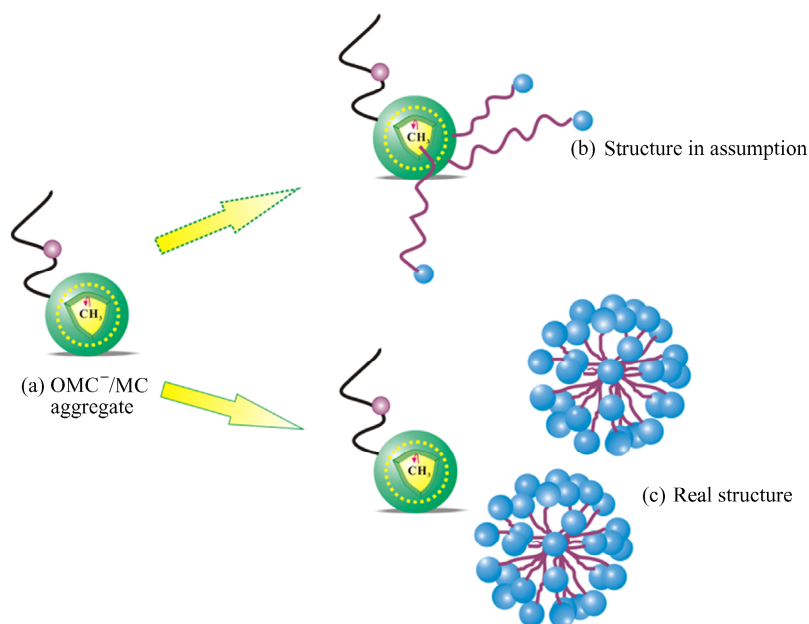


Fig. 14 (a) The aggregation of OMC^- formed on the MC chains, (b) the unstable structure illustrating the assumed aggregation of CTAB on the MC chains, (c) the real structure of OMCA and CTAB in MC solution

We are therefore convinced that the mechanism related to the sol-gel transition of MC solutions in the coexistence of OMCA and CTAB can be shown in Fig. 14. For MC solutions in the coexistence of OMCA and CTAB, OMCA has priority to adsorb on the methyl group of MC chains to form core-shell structure as shown in Fig. 14(a). When CTAB is added, the possible structure can be shown as Fig. 14(b), with the long carbon chain of CTAB exposing to water molecules. Obviously, the architecture formed in this way is quite unstable. On such an occasion, the CTAB molecules with the long hydrophobic tails would form free micelles rather than penetrating into core-shell structure to form mixed micelles in solution as shown in Fig. 14(c). In a word, due to

the formation of the core-shell structure created by OMCA and the methyl group of MC chains, the hydrophobic interaction of CTAB with the methyl group of MC chains is inhibited completely. As a result, in the coexistence of OMCA and CTAB, the sol-gel transition of MC solutions keep the same value, independent of the concentration of CTAB in solution.

CONCLUSIONS

This study has demonstrated that OMCA can shift the sol-gel transition of MC solutions to the higher temperatures like the traditional surfactants such as CTAB. The effect of OMCA upon the sol-gel transition of MC solutions, together with the dissolution of OMCA in the presence of MC, can be attributed to the formation of the core-shell structure created by OMCA and the methyl groups of MC chains, with the methyl groups of MC chains serving as the core and OMCA aggregates as the shell. The formation of the core-shell structure inhibits either the hydrophobic interaction between the methyl groups of MC chains in solution, or the hydrophobic interaction between CTAB and the methyl group of MC chains in solution. The sol-gel transition temperature of MC solutions, therefore, increases in the presence of OMCA, or keeps the same value in the coexistence of OMCA and CTAB, independent of the concentration of CTAB in solution. Our experimental results also confirm that the sol-gel transition temperature of MC solutions in the presence of OMCA, or in the coexistence of OMCA and CTAB, decreases notably upon UV irradiation. However, the dependence of the sol-gel transition temperature of MC solutions with the concentration of OMCA, or the concentration of CTAB in the presence of OMCA, does not changed by UV irradiation. Due to the change of the configuration of OMCA, both the hydrophobic interaction between OMCA molecules in solution and the hydrophobic interaction between OMCA and the methyl group of MC chains, which are essential to the stable of the core-shell structure created by OMCA and the methyl group of MC chains, decrease accordingly. The instability of the core-shell structure caused by UV irradiation is taken to account for the decrease of the sol-gel transition temperature of MC solutions in the presence of OMCA.

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