

## ARTICLE

# Sol-gel Transition of Methylcellulose Solution in the Coexistence of Hexadecyltrimethylammonium Bromide and Sodium Chloride

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(Dated: Received on January 24, 2011; Accepted on May 18, 2011)

The sol-gel transition of methylcellulose (MC) solution in the presence of NaCl and hexadecyltrimethylammonium bromide (HTAB), together with MC/NaCl solution in the presence of HTAB and MC/HTAB solution in the presence of NaCl, was investigated by the rheological measurements. It has been found that the sol-gel transition temperature of MC solution decreases linearly with the concentration of NaCl in solution but increases linearly with the concentration of HTAB in solution, respectively. However, the sol-gel transition temperature of MC/NaCl solution in the presence of HTAB keeps the same value, independent of the concentration of HTAB in solution. On the other hand, the sol-gel transition temperature of MC/HTAB solution decreases linearly with the concentration of NaCl in solution. The experimental results suggest that, for MC/NaCl solution in the presence of HTAB, the salt-induced spherical micelles of HTAB should have formed in bulk solution. For MC solution in the absence of NaCl, no spherical micelles have been formed in bulk solution, though the concentration of HTAB in our experiment is almost one order of magnitude higher than the critical micelle concentration of HTAB in polymer-free solution. In fact, due to adsorption of HTAB on MC chains, the real concentration of HTAB in bulk solution, is much less than the apparent concentration of HTAB dissolved in MC solution.

**Key words:** Sol-gel transition, Methylcellulose, NaCl, HTAB

## I. INTRODUCTION

Cellulose occurs naturally with high hydrophilicity on its chain structure. Due to the formation of the strong intermolecular hydrogen bonds between cellulose molecules, the original cellulose is insoluble in water and its practical applications are limited by the poor aqueous solubility. When a certain fraction of hydroxyl groups is substituted by hydrophobic groups such as methyl or hydroxypropyl groups, intermolecular hydrogen bonds are therefore prevented to result in a water soluble cellulose [1–3]. Methylcellulose (MC), the hydrophobically modified derivative of cellulose, exhibits interesting thermoreversible gelation property in aqueous solution, and this phenomenon has been fairly well studied [1, 4–14]. The gelation of MC is considered to result from hydrophobic association of methyl groups at higher temperatures when water becomes a poor solvent for the polymer. The solubility of MC in water at low temperatures is reported to be due to the formation of cage-like structures of water enclosing hydrophobic groups of MC.

The gelation of MC in aqueous solution has been reported to be sensitive to different environmental conditions such as temperature, solvent, and coexisting solutes including ions, pH, electrical or magnetic field, *etc.* [15–19]. Xu *et al.* have systematically studied the effects of salts and salt mixtures on the sol-gel transition of MC solution in water [11, 12]. When a salt-out salt such as NaCl is added into a MC aqueous solution, for example, the sol-gel transition temperature will shift to a lower temperature with increasing NaCl concentration. On the other hand, salt-in salt such as NaI will shift the sol-gel transition of MC solution to a higher temperature. Moreover, in the MC solutions with NaCl and NaI mixtures, the transition temperature follows a linear rule of mixing, indicating that the effect of salt on the sol-gel transition of MC is completely independent. The gelation of MC solution is affected by salts mainly because the structure of water is changed by the addition of salts.

However, the effect of surfactant on the gelation of MC solution has been proved to be much more complicated. When the concentration of surfactant is lower than the critical aggregation concentration (cac), surfactant molecules are present mainly as free unimers and able to attract water molecules. Thus, water molecules available for MC chains decrease and “water” becomes more hydrophobic for MC. As a result,

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the sol-gel transition of MC solution shifts to a lower temperature. On such an occasion, surfactant act similarly as the salt, or more precisely, as salt-out salt like NaCl. On the other hand, when the concentration of surfactant is higher than  $cac$ , the polymer-induced micelles are formed, and the hydrophobic cores of micelles act as the comfortable “cage” for the hydrophobic units of MC to reside. Obviously, the formation of the cages stabilizes MC chains in water so that the gelation of MC solution becomes more difficult. 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 MC solution shifts to a higher temperature as presented by Li *et al.* [20]. On such an occasion, the surfactant affect the gelation of MC solution mainly through the formation of cages on MC chains rather than through a water-restructuring process like salts. The effects of sodium lauryl sulphate (SLS) on the gelation of MC solution are even much more complicated. The experimental results presented by Kundu *et al.* have shown that the gelation of MC solution depends on the weight ratio  $r$  of SLS to MC present in aqueous solution. Gels are formed for the limit  $0.02 < r < 0.1$  for all MC solutions, beyond which phase separation occurs [21].

Salts are known to favor the aggregation of surfactant in either polymer or polymer-free solution, mainly due to that salts can be referred to as the counterions which screen the electrostatic repulsive interactions between the head-group of surfactant in solution. For instance, Wang *et al.* presented that the added NaBr decreases both the critical micelle concentration ( $cmc$ ) and the  $cac$  of dodecyltrimethylammonium bromide (DTAB) in polymer-free and sodium carboxymethylcellulose (NaCMC) solutions, respectively [22]. Kjoniksen *et al.* and Nyström *et al.* demonstrated that the added salts promote the polymer-bound aggregation of ionic surfactant [23–25]. Moreover, Dubin *et al.* showed that counterions furnished by surfactant play a direct role in the stabilization of polyethylene oxide (PEO)/sodium dodecyl sulfate (SDS) complexes, similar to the effects of added salts on polymer/surfactant complex formation [26]. We originally regard that NaCl will favor the surfactant HTAB to form cages on MC chains in solution. If it is true, the sol-gel transition of MC/HTAB solution should increase with the concentration of NaCl dissolved in solution. However, the experimental results show that the sol-gel transition of MC/HTAB solution decreases with increasing the concentration of NaCl in solution. In particular, the sol-gel transition of MC/NaCl solution in the presence of HTAB keeps the same value, independent of the concentration of HTAB dissolved in solution. The formation of salt-induced spherical micelles in bulk solution, as presented in this study, should be responsible for the results. Though the interactions between HTAB and MC in the presence of NaCl as well as hydrophobic salts including sodium

benzoate (NaBz) and sodium hexanoate ( $NaH_x$ ) has been investigated by rheological and fluorescence probing experiments, and the  $cac$ ,  $cmc$ , micellar aggregation number ( $N$ ), micellar micropolarity index and viscosity curve of the polymer-surfactant mixed system as a function of HTAB concentration were presented [27], the investigations describing the effect of coexisting salt and surfactant on the sol-gel transition of MC solution, to our knowledge, are still limited.

## 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 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. The salt NaCl and surfactant hexadecyltrimethylammonium bromide (HTAB) was purchased from Sinopharm Chemical Reagent Co. Ltd., and used as received.

### B. Sample preparation

A pure MC aqueous solution of 2% 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 for 24 h. A homogeneous and transparent solution of MC was obtained at room temperature (25 °C). The weighed NaCl or/and HTAB was then added into the MC solution to obtain all the required sample solutions. All the sample solutions were prepared with deionized water.

### C. 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.

## III. RESULTS

### A. Sol-gel transition of MC solution in the presence of NaCl

Figure 1 shows both  $G'$  and  $G''$  of 2% MC solutions in the absence and presence of NaCl with various con-

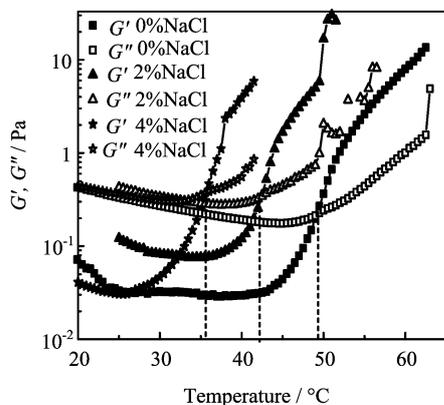


FIG. 1  $G'$  and  $G''$  as function of temperature for 2% MC solutions containing NaCl with different concentrations. The heating rate was about  $1\text{ }^{\circ}\text{C}/\text{min}$ .

tents, for some selected samples (NaCl=0, 2%, and 4%) as a function of temperature in a heating process with heating rate of about  $1\text{ }^{\circ}\text{C}/\text{min}$ . As shown, at low temperatures, all of the samples display a liquid behavior of  $G' < G''$ . Noting that the pure MC solution sample studied by Wang *et al.* behaves as  $G' > G''$  at lower temperatures due to the weakly entangled structure [14], which is quite different from ours. The possible reason is that the studied MC chain in this work is much shorter than that used by Wang *et al.* (the viscosity of 2% MC solution in this work is  $0.45\text{ Pa}\cdot\text{s}$ , also much lower than  $4.54\text{ Pa}\cdot\text{s}$  studied by Wang *et al.* [11, 14]) and difficult to form entangled structure. However, by increasing the temperatures, both  $G'$  and  $G''$  increase rapidly. Especially,  $G'$  increases by more than 2 decades to reach a plateau at high temperatures, which is more significant than  $G''$  (by about 1 decade). The crossover of  $G'$  and  $G''$  indicates the turning point from a viscous solution to a viscoelastic gel, which is a traditional and convenient method used for the determination of the sol-gel transition point.

The transition temperature for each sample, obtained from this traditional definition (*i.e.* the crossover of  $G'$  and  $G''$ ), as a function of NaCl concentration is plotted in Fig.2. It has been suggested by Li *et al.* that the abrupt increase of  $G'$  is more suitably defined as the sol-gel transition temperature for MC aqueous solution [10]. In our experiment, the transition temperatures obtained from traditional method and Li *et al.*'s definitions are well consistent [10]. By adding NaCl into the MC aqueous solution, the sol-gel transition shifts to low temperatures, which is consistent with the prior experimental observations [11, 12]. As indicated from Fig.2, the transition temperature of MC solution decreases linearly with the concentration of NaCl in solutions. That is to say, NaCl displays a typical salt-out effect. As well known,  $\text{Cl}^-$  furnished by adding NaCl, which tend to have a stronger interaction with water molecules than the interaction between water molecules

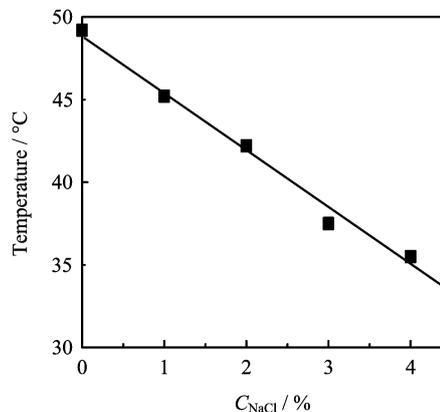


FIG. 2 Sol-gel transition temperature for MC solution as a function of NaCl concentration.

themselves, destruct part of original hydrogen-bonding network formed by water, leading to the decrease of MC solubility in the water. Therefore, the sol-gel transition of MC solution in the presence shifts to a lower temperature. In fact, the salt-out effect of NaCl can also be seen from Fig.1. With increasing NaCl concentration in the solution, both of the curves of  $G'$  and  $G''$  shift to the lower temperatures.

## B. Sol-gel transition of MC solution in the presence of HTAB

Figure 3 shows the temperature dependence of  $G'$  and  $G''$  for 2% MC solutions with various contents of HTAB. Similar to MC solution in the presence of NaCl, the MC solution containing HTAB shows a liquid behavior of  $G' < G''$  at low temperatures. And, there is a relatively narrower temperature range in which both  $G'$  and  $G''$  show a steeper increase. However, in contrast to the effect of added NaCl, both  $G'$  and  $G''$  curves, as well as the sol-gel transition temperature, shift to the higher temperatures with increasing the HTAB concentration, showing a salt-in like effect or a delay of MC gelation by HTAB. To quantitatively elucidate the HTAB effect on the sol-gel transition of MC, the variation of sol-gel temperature of MC solution against the concentration of HTAB is shown in Fig.4. It is observed that the gelation temperature of MC solution increases linearly by increasing HTAB concentration, indicating that the salt-in effect is approximately a linear function of HTAB concentration within the concentration range studied. As widely accepted by many researchers [20, 21], when the concentration of HTAB in the solution is above a certain value, the hydrophobic tails of HTAB bind to the hydrophobic units or groups of MC chains to form surfactant cages. Since the shells of these surfactant cages are high hydrophilic, the formation of these HTAB cages is able to stabilize (or in another word, solubilize) MC chains in water so that the gelation of MC becomes more difficult. In order for

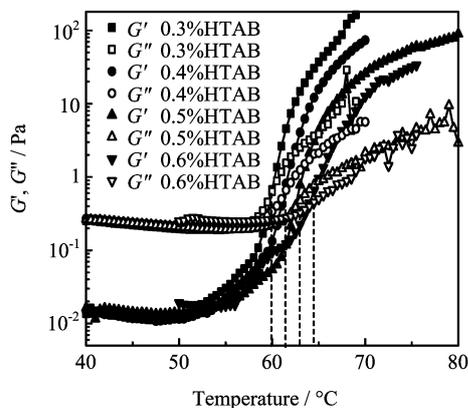


FIG. 3  $G'$  and  $G''$  as a function of temperature for 2% MC solutions containing HTAB with different concentrations. The heating rate was about  $1\text{ }^{\circ}\text{C}/\text{min}$ .

MC to form a gel through the hydrophobic association, the HTAB cages must be removed. A higher temperature has to be applied to destruct the formed HTAB cages, and thus the so-called salt-in effect is observed. However, the gelation mechanism of a MC gel is not changed by adding HTAB, which has been proved by micro-DSC measurement [20]. Moreover, a slight salt-out effect of HTAB on MC solution has been observed when the concentration of HTAB in the solution is very low, and the mechanism is still not clear [20]. Unfortunately, due to the sensitivity of the rheological method, this slight salt-out effect of HTAB on MC has not been observed in our study.

### C. Sol-gel transition of MC/NaCl solution in the presence of HTAB

As shown in many experimental observations and presented above [11, 12, 20], the addition of NaCl or HTAB alone shifts the sol-gel transition to lower or higher temperatures, respectively. However, if both NaCl and HTAB are dissolved in MC solution, the situation becomes much more complicated. Figure 5 shows the temperature dependence of  $G'$  and  $G''$  for MC/NaCl solution in the presence of HTAB ranging from 0.2% to 0.6%. It is observed that both  $G'$  curves and  $G''$  curves display similar patterns for all samples. At low temperatures,  $G' < G''$  corresponds to a typical liquid behavior. An abrupt increase is shown for both  $G'$  and  $G''$  upon heating samples to higher temperatures. However, in contrast to the effect of HTAB on MC gelation in the absence of NaCl (Fig.4), both  $G'$  and  $G''$  curves for all samples overlap respectively with increasing HTAB concentration, implicating that the crossover of  $G'$  and  $G''$ , *i.e.*, the transition temperature of MC/NaCl solution is independent of the concentration of HTAB. Therefore, the typical salt-in effect of HTAB in the absence of NaCl can not apply to MC solutions containing NaCl, and the mechanism for this interesting observation will be dis-

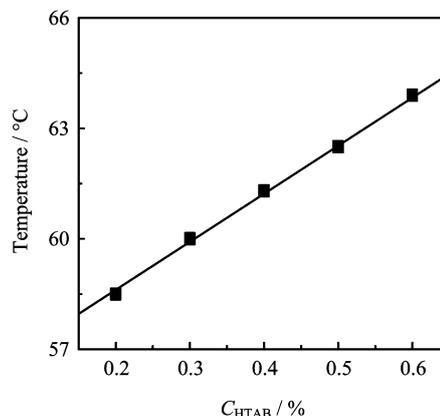


FIG. 4 Sol-gel transition temperature for MC solution as a function of HTAB concentration.

cussed in the next section.

### D. Sol-gel transition of MC/HTAB solution in the presence of NaCl

Figure 6 shows the temperature dependence of  $G'$  and  $G''$  for MC/HTAB solution in the presence of NaCl ranged from 1% to 5% at heating rate of  $1\text{ }^{\circ}\text{C}/\text{min}$ . NaCl still shows a typical salt-out effect on MC solution in the presence of HTAB, as observed from the crossover point of  $G'$  and  $G''$  shifting to the lower temperatures with increasing NaCl concentration. To quantitatively elucidate the effect of added NaCl on the sol-gel transition of MC/HTAB solution containing a series of fixed concentrations of HTAB, the dependence of the sol-gel transition temperature for MC/HTAB solution as a function of NaCl concentration is shown in Fig.7. For comparison, the curve for the sample in the absence of HTAB is also plotted. It is observed that NaCl shows a similar salt-out effect on MC gelation for the MC samples containing HTAB as those without HTAB. Since the transition temperature is independent of HTAB concentration as illustrated in Fig.5, the lines for all samples contain various concentrations of HTAB overlap. The slopes of the lines for the samples containing HTAB are the same as those for the HTAB-free samples. It is also noted that the increase of the sol-gel transition temperature of MC solution induced by HTAB is the same in the presence of NaCl, although HTAB concentration varies from 0.2% to 0.6%.

## IV. DISCUSSION

### A. Why does the sol-gel transition temperature of MC solution still increase with HTAB concentration greater than its critical micelle concentration?

It is already known that the critical micelle concentration of HTAB is 0.81 mmol/L, or 0.03% in weight [20]. In our experiment the concentration of HTAB is much

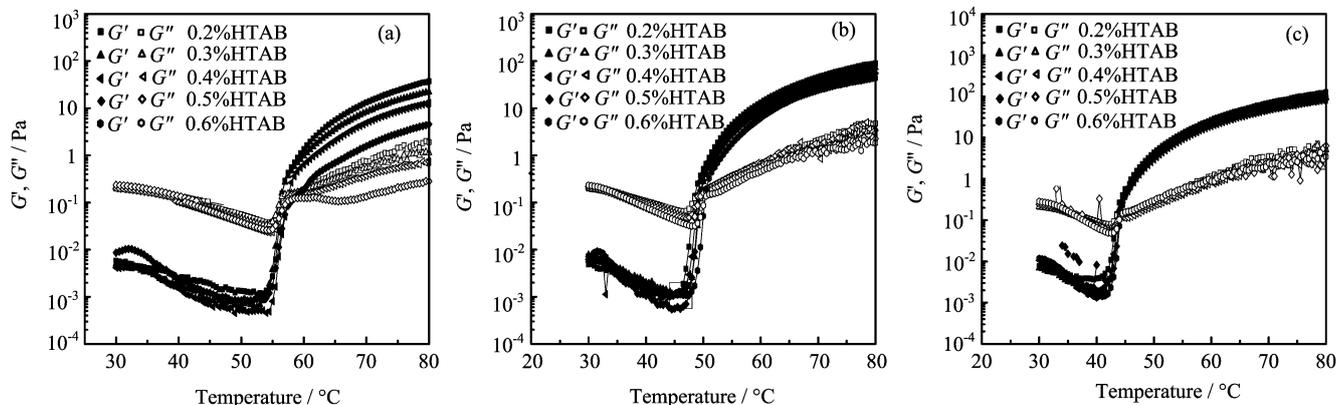


FIG. 5 Temperature dependence of  $G'$  and  $G''$  for MC/NaCl solution in the presence of HTAB ranging from 0.2% to 0.6% at the heating rate of  $1\text{ }^{\circ}\text{C}/\text{min}$ . The concentration of MC is kept to be 2%. The concentration of NaCl is selected to be (a) 1%, (b) 3%, and (c) 5%, respectively.

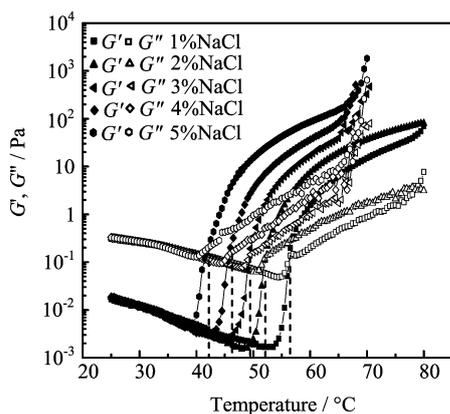


FIG. 6 Temperature dependence of  $G'$  and  $G''$  for MC/HTAB solution in the presence of NaCl ranging from 1% to 5% at the heating rate of  $1\text{ }^{\circ}\text{C}/\text{min}$ . The concentration of MC is kept to be 2%. The concentration of HATB is selected to be 0.2%.

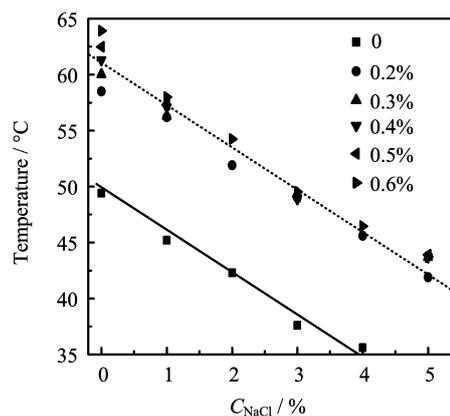
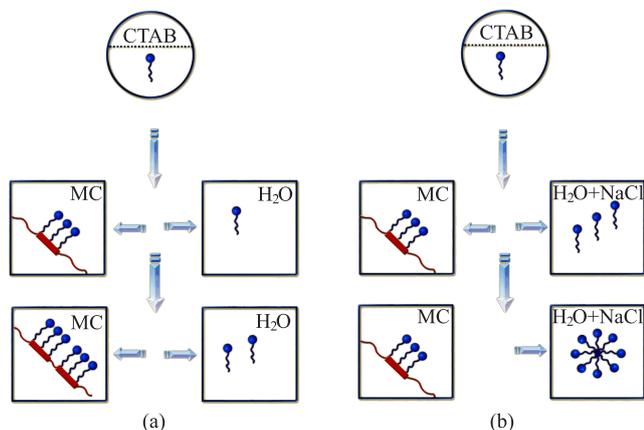


FIG. 7 Sol-gel transition temperature for MC/HTAB solution as a function of NaCl concentration. The concentration of MC is kept to be 2%. The concentration of HTAB is fixed and selected to be 0.2%, 0.3%, 0.4%, 0.5%, and 0.6%.

greater than the cmc of HTAB. Due to the adsorption of HTAB molecules to MC chains, the concentration of HTAB in bulk solution is less than the concentration of HTAB dissolved in solution. In our experiment the average DS is about 29% and the number of the hydrophobic units of MC is sufficiently larger than the number of HTAB molecules added into solution. This suggests that a great number of HTAB molecules will adsorb on MC chains. As a result, the real concentration of HTAB in bulk solution (taking into account the adsorption of HTAB on MC chains) is sufficiently less than the apparent concentration of HTAB dissolved in solution (neglecting the adsorption of HTAB on MC chains). We define here the apparent concentration of HTAB dissolved in solution as  $C_{\text{HTAB,app}}$  and the real concentration of HTAB in bulk solution as  $C_{\text{HTAB,real}}$ . According to the model presented by Li *et al.* [20], the adsorbed HTAB molecules on MC chains will form cages

as the concentration of surfactant is higher than its cac. Since MC undergoes the sol-gel transition through the hydrophobic association, the surfactant cages must be destroyed or removed in order for MC to associate hydrophobically. As the binding of surfactant to MC is strong, temperature has to be enhanced to weaken the surfactant cages and eventually destruct them to expose hydrophobic units or groups of MC to water. When the exposed hydrophobic units of MC meet, they are able to form hydrophobic aggregates that will act as junctions for the formation of a gel network. Obviously, the destruction of surfactant cages is a necessary precursor for MC to form a gel in the presence of surfactant. The dependence of the sol-gel transition temperature of MC on surfactant concentration can be explained by the number of surfactant cages, which is dependent on the surfactant concentration. The increased number of surfactant cages by the increased concentration of surfactant, as indicated in Scheme 1(a), will increase the difficulty



Scheme 1 Schematic diagram for the HTAB binding to MC chains to form surfactant cages and residing in bulk solution to aggregate into spherical micelles or present as free unimers.

in destructing or removing the surfactant cages. As a result, the sol-gel transition of MC solution shifts to a higher temperature. In our experiment, the sol-gel transition temperature increases linearly with HTAB concentration, indicating that the number of cages increases subsequently by adding HTAB into solution. On the other hand, if HTAB molecules have formed the spherical micelles in bulk solution, the numbers of cages on MC chains will no longer increase. This suggests that the sol-gel transition temperature no longer increase by adding HTAB into solution. However, our experimental results as indicated in Fig.4 have shown that the sol-gel transition temperature increases linearly with HTAB concentration. We are therefore convinced that the real concentration of HTAB in bulk solution,  $C_{\text{HTAB,real}}$ , is still less than its cmc, though the apparent concentration of HTAB dissolved in solution,  $C_{\text{HTAB,app}}$ , is already much higher than cmc.

### B. Why is the sol-gel transition temperature of MC solution independent of HTAB concentration in the presence of NaCl?

Because the effect of NaCl and HTAB upon the sol-gel transition of MC solution is completely different as shown in Fig.2 and Fig.4, we originally regard that the sol-gel transition of MC solution should depend on the ratio of HTAB/NaCl. However, the experimental results in Fig.5 have shown that the sol-gel transition of MC/NaCl solution is independent of the concentration of HTAB. This suggests that the number of cages on MC chains will be no longer increased by adding HTAB into solution in the presence of NaCl. The reasonable interpretation is that the HTAB molecules have formed spherical micelles in bulk solution in the presence of NaCl. In fact, the cmc of surfactant can be decreased significantly in the presence of salt due to the screening

of electrostatic repulsive interaction of surfactant in solution. We therefore propose a mechanism to interpret the dependence of the sol-gel transition temperature of MC/HTAB solution on the concentration of HTAB, which is shown in Scheme 1. In NaCl-free solution, although the apparent concentration of HTAB dissolved in solution,  $C_{\text{HTAB,app}}$ , is higher than cmc, the real concentration of HTAB in bulk solution,  $C_{\text{HTAB,real}}$ , is still less than cmc. On one hand, with the addition of HTAB into NaCl-free solution successively, the number of the surfactant cages on MC chains increases accordingly as indicated in Scheme 1(a). As a result, the sol-gel transition temperature of MC solution increases with increasing HTAB concentration as shown in Fig.4. On the other hand, in the presence of NaCl, the salt-induced spherical micelles of HTAB begin to form in bulk solution. On such an occasion, the added HTAB molecules prefer to form spherical micelles in bulk solution rather than adsorb on MC chains to increase the number of cages as indicated in Scheme 1(b). This interprets why the sol-gel transition temperature of MC/NaCl solution is independent of the HTAB concentration as shown in Fig.5. Another possible interpretation may be that in the presence of NaCl the adsorption of HTAB becomes saturated as the concentration of HTAB is higher than 0.2% in weight. However, the detailed analysis of the data as shown in Fig.1–Fig.4 does not support this assumption. The sol-gel transition temperature of MC solution is 48.5°C in the absence of HTAB as shown in Fig.2 and almost 64°C in the presence of HTAB with the concentration of 0.6% in weight as shown in Fig.4. That is to say that the sol-gel transition temperature of MC solution can increase 14.5°C as the concentration of HTAB in solution increase from 0 to 0.6% in weight. Even though, the adsorption of HTAB to MC chains is still unsaturated. In the presence of NaCl with the concentration of 1% in weight, the sol-gel transition temperature of MC solution is almost 45°C as shown in Fig.2, *i.e.*, the sol-gel transition temperature of MC solution decreases approximately 3.5°C in the presence of 1% NaCl. If the adsorption of HTAB to MC chains were already saturated in the presence of 1% NaCl, the sol-gel transition temperature of MC solution would have been higher than 64°C. Further, if we take the effect of 1% NaCl into account, the sol-gel transition temperature of MC solution is still expected to be higher than 60.5 °C. From Fig.5(a) it is observed that the sol-gel transition temperature of MC solution in the presence of NaCl with the concentration of 1% in weight is 56°C and keeps constant as the concentration of HTAB increases from 0.2% to 0.6% in weight. We are therefore convinced that the sol-gel transition temperature of MC/NaCl solution is independent of the HTAB concentration as shown in Fig.5 due to the formation salt-induced spherical micelles in MC-free part of solution.

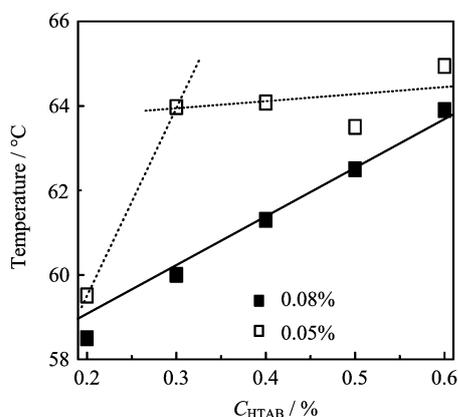


FIG. 8 Sol-gel transition temperature for MC/NaCl solution as a function of HTAB ranging from 0.2% to 0.6% at heating rate of 1 °C/min. The concentration of MC is kept to be 2%. The concentration of NaCl is selected to be 0.05% and 0.08%, respectively.

### C. Dependence of the sol-gel transition temperature of MC solution on the concentration of HTAB in the presence of NaCl with extremely lower concentrations

We have previously argued that the sol-gel transition temperature of MC/NaCl solution is independent of the HTAB concentration due to the formation of salt-induced spherical micelles in bulk solution. If the concentration of NaCl is sufficiently low, the induction of salt on the formation of spherical micelles in bulk solution is not significant. On such an occasion, the sol-gel transition temperature of MC/NaCl solution should still increase with HTAB concentration, similar to the case that without NaCl in the solution. Figure 8 shows the sol-gel transition temperature of MC/NaCl solution as a function of HTAB concentration. The concentration of MC is kept to be 2% whereas the concentration of NaCl is selected to be 0.05% and 0.08%, respectively. From Fig.8 it can be seen that the sol-gel transition temperature of MC/NaCl solution increases linearly with  $C_{\text{HTAB}}$  when the concentration of NaCl in solution is selected to be 0.05%, similar to the sol-gel transition of MC in NaCl-free solution as indicated in Fig.4. On such an occasion, the screening effect of NaCl is insufficient to facilitate the formation of the free micelles of HTAB in bulk solution. As a result, the HTAB molecules tend to bind to the hydrophobic units of MC chains to increase the number of the hydrophobic cages. However, when the concentration of NaCl is selected to be 0.08%, the sol-gel transition temperature of MC/NaCl solution increases at the lower concentration of HTAB but keeps almost the same value at the higher concentration of HTAB as indicated in Fig.8. The experimental results in turn verify our assumption that the sol-gel transition of MC/NaCl solution is independent of the concentration of HTAB due to the formation salt-induced spherical micelles in bulk solution. Obviously, the formation

of salt-induced spherical micelles in bulk solution depends both on the concentration of HTAB in bulk solution and on the concentration of NaCl in bulk solution. When the concentration of NaCl is selected to be 0.08%, the salt-induced spherical micelles cannot form at the lower concentration of HTAB in bulk solution. As a result, the sol-gel transition temperature of MC/NaCl solution increases with  $C_{\text{HTAB}}$  at the lower concentration of HTAB. On the other hand, at the higher concentration of HTAB, the salt-induced spherical micelles have formed in bulk solution. On such an occasion, the added HTAB molecules prefer to form spherical micelles in bulk solution rather than adsorbing on MC chains to increase the number of cages in solution. This interprets why the sol-gel transition temperature of MC/NaCl solution increases initially at the lower concentration of HTAB but keeps almost the same at the higher concentration of HTAB as indicated in Fig.8.

### V. CONCLUSION

In this work, the effects of the coexisting NaCl and HTAB on sol-gel transition of MC solution have been investigated systematically using rheological measurements. It has been found that the sol-gel transition of MC solution decreases linearly upon increasing the concentration of NaCl but increases linearly upon increasing the concentration of HTAB. The typical salt-out and salt-in effects on MC gelation have been observed for NaCl and HTAB, respectively. However, the sol-gel transitions of MC/NaCl solution keep the same value, independent of the concentration of HTAB dissolved in solution. On the other hand, the sol-gel transitions of MC/HTAB solution decrease linearly upon increasing the concentration of NaCl in solution. Our experimental results show that the effects of NaCl and HTAB on sol-gel transition of MC solution are synergic. In the presence of NaCl, the NaCl-induced micelles form in bulk solution. On such an occasion, the added HTAB molecules no longer adsorb on the hydrophobic units of MC chains to form new cages but aggregate into spherical micelles in bulk solution. As a result, the sol-gel transition temperature of aqueous solution of MC/NaCl mixtures is independent of the concentration of HTAB dissolved in solution. On the other hand, in the absence of NaCl, even though the apparent concentration of HTAB dissolved in solution,  $C_{\text{HTAB,app}}$ , is already higher than the cmc of HTAB in polymer-free solutions, the real concentration of HTAB in bulk solution,  $C_{\text{HTAB,real}}$ , may be still less than the cmc of HTAB. As a result, in the absence of NaCl, the added HTAB molecules prefer to adsorb on MC chains to increase the number of cages covering the hydrophobic units of MC chains rather than form spherical micelles in bulk solution. This interprets why the sol-gel transition temperature of MC solution in the absence of NaCl increases linearly upon increasing the concentration of HTAB in solution. When the concentration of NaCl is

sufficiently low, the induction of the formation of spherical micelles in bulk solution is negligible. On such an occasion, the sol-gel transition temperature of MC/NaCl solution still increases with HTAB concentration, similar to the case without NaCl. Our experimental results show that due to the adsorption of HTAB on the hydrophobic units of MC chains, the real concentration of HTAB in bulk solution,  $C_{\text{HTAB,real}}$ , is significantly less than the apparent concentration of HTAB dissolved in solution,  $C_{\text{HTAB,app}}$ . In particular, as soon as the NaCl-induced micelles begin to form in solution, the synergic effects of NaCl and HTAB upon the sol-gel transition of MC solution become significant.

## VI. ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology of China (No.2007CB936401). We thank Prof. Guang-zhao Zhang and Dr. Xiao-yun Xu for valuable discussions.

- [1] J. Guent, *Thermoreversible Gelation of Polymers and Biopolymers*, London: Academic Press, (1992).
- [2] N. Sakar, *J. Appl. Polym. Sci.* **24**, 1073 (1979).
- [3] F. Tanaka and M. Ishida, *J. Chem. Soc., Faraday Trans.* **91**, 2663 (1995).
- [4] L. Li, *Macromolecules* **35**, 5990 (2002).
- [5] A. Haque and E. R. Morris, *Carbohydr. Polym.* **22**, 161 (1993).
- [6] C. Chevillard and M. A. V. Axelos, *Colloid Polym. Sci.* **275**, 537 (1997).
- [7] M. Hirrien, C. Chevillard, J. Desbrieres, M. A. V. Axelos, and M. Rinaudo, *Polymer* **25**, 6251 (1998).
- [8] S. Ghosh and S. P. Moulik, *Indian J. Chem. A* **38A**, 201 (1999).
- [9] T. Chakraborty, I. Chakraborty, and S. Ghosh, *Langmuir* **22**, 9905 (2006).
- [10] L. Li, H. Shan, C. Y. Yue, Y. C. Lam, K. C. Tam, and X. Hu, *Langmuir* **18**, 7291 (2002).
- [11] Y. Xu, C. Wang, K. C. Tam, and L. Li, *Langmuir* **20**, 646 (2004).
- [12] Y. Xu, L. Li, P. J. Zheng, Y. C. Lam, and X. Hu, *Langmuir* **20**, 6134 (2004).
- [13] Y. Xu and L. Li, *Polymer* **46**, 7410 (2005).
- [14] Q. Wang, L. Li, L. Liu, Y. Xu, and J. Liu, *Polymer* **4**, 1372 (2006).
- [15] G. Wanka, H. Hoffman, and W. Ulbricht, *Colloid Polym. Sci.* **268**, 107 (1990).
- [16] J. Byeongmoon, W. K. Sung, and H. B. You, *Adv. Drug Delivery Rev.* **54**, 37 (2002).
- [17] S. G. Starodoubtev, A. R. Khokhlov, E. L. Sokolov, and B. Chu, *Macromolecules* **28**, 3930 (1995).
- [18] R. A. Siegel and B. A. Firestone, *Macromolecules* **21**, 3254 (1988).
- [19] B. D. Chin and H. H. Winter, *Rheol. Acta* **41**, 265 (2002).
- [20] L. Li, E. Liu, and C. H. Lim, *J. Phys. Chem. B* **111**, 6410 (2007).
- [21] P. P. Kundu and M. Kundu, *Polymer* **42**, 2015 (2001).
- [22] X. Wang, Y. Li, J. Li, J. Wang, Y. Wang, Z. Guo and H. J. Yan, *J. Phys. Chem. B* **109**, 10807 (2005).
- [23] A. L. Kjoniksen, B. Nyström, and B. Lindman, *Macromolecules* **31**, 1852 (1998).
- [24] B. Nyström, A. L. Kjoniksen, and B. Lindman, *Langmuir* **12**, 3233 (1996).
- [25] B. Nyström and B. Lindman, *Macromolecules* **28**, 967 (1995).
- [26] P. J. Dubin, J. H. Gruber, J. Xia, and H. Zhang, *J. Colloid Interface Sci.* **148**, 35 (1992).
- [27] A. A. Dar, A. Garai, A. R. Das, and S. Ghosh, *J. Phys. Chem. A* **114**, 5083 (2010).