Micro-DSC and Rheological Studies of Interactions between Methylcellulose and Surfactants

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The effects of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), on the gelation of methylcellulose (MC) in aqueous solutions have been investigated by micro differential scanning calorimetry (micro DSC) and rheology. Methylcellulose had a weight average molecular weight of 310 000 and a degree of substitution of 1.8. The concentration of MC was kept at 0.5 wt % (0.016 mM) and 1 wt % (0.032 mM), and the concentration of CTAB in the MC solutions was varied from 0 to 0.6 wt % (16.5 mM). Upon heating, a single endothermic peak, which is due to the hydrophobic association and gelation of MC, shifts to lower temperatures with increasing CTAB for CTAB ≤ CMC (0.93 mM or 0.034 wt %), and then it shifts to higher temperatures lineally with CTAB for CTAB > CMC. At the same time, the endothermic enthalpy decreases with increasing CTAB concentration. Even though CTAB shows a significant “salt-in” effect on the gelation of MC, it does not affect the pattern of the sol→gel transition as well as the gel strength of MC. At the highest concentration of CTAB, 0.60 wt %, MC is still able to form a gel. At a given ratio of CTAB/MC, the effect of CTAB on MC becomes stronger when the MC concentration is lower. The results for the MC–CTAB system are compared with an ionic surfactant, SDS and the significant differences in affecting the gelation of MC between two surfactants are recognized.

Introduction

Natural cellulose possesses a high hydrophilicity in its molecular structure. However, it is insoluble in water due to strong intermolecular hydrogen bonds. Methylcellulose (MC) is one of hydrophobically modified derivatives of cellulose, which exhibits an interesting thermoreversible behavior in water. The extensive studies have been conducted to examine the thermal gelation properties, the mechanism of gelation, as well as the gel network structure of MC.1–15 It is experimentally observed that the sol→gel transition for a MC aqueous solution in a heating process occurs in the vicinity of 62 °C by showing a sharp endothermic peak and an abrupt increase of storage modulus.14 On the contrary, a MC gel returns to a liquid through a cooling process by showing a two-step pattern of dissociation.14–15 These thermoreversible features of MC are controlled by the hydrophobic association and dissociation of MC molecules. Any factors that can alter the degree of hydrophobic association or dissociation will affect the viscosity, the sol→gel transition, as well as the gel elasticity of MC. Typical factors affecting these properties can be solvent, concentration, temperature, pH, salt, surfactant, etc.16–19

The effects of salts on the gelation behavior of MC have been well studied in the literature. Many salts are found to be able to alter the gelation properties of MC aqueous solutions.16–18 For example, a salt-out salt like NaCl can lower the sol→gel transition temperature of MC whereas a salt-in salt such as NaI can enhance the gelation temperature. It is important to know that although the sol→gel transition of MC is affected by a salt added, the mechanism for the gelation of MC, which is the hydrophobic association of MC chains, does not change with the addition of a salt. This is because the presence of a salt only affects the dehydration of MC but the salt does not change directly the original feature of hydrophobic association of MC for gelation.16–18

The effects of surfactants on some hydrophobically modified cellulose polymers such as hydrophobically modified hydroxyl-ethyl cellulose (HMHEC) have been investigated.20–22 For example, the effect of a surfactant on viscosity of a HMHEC aqueous solution is recognized in terms of a surfactant binding mechanism.20,21 The viscosity of a HMHEC solution initially increases with increasing surfactant concentration, followed by a maximum viscosity and then a decrease in viscosity. The concentration of a surfactant required for the maximum viscosity, Cmax, is found to vary linearly with the critical micellization concentration (CMC) of the surfactant and for many surfactants Cmax is similar to CMC.20 For a given polymer concentration, the increase in viscosity by an added surfactant is due to the formation of the mixed micelles of surfactant molecules and hydrophobic groups of the polymer, which connect two or more polymer chains, while the decrease in viscosity at high concentrations of the surfactant is caused by the separation of the micellar connections.20

We have recently studied the effects of an anionic surfactant, sodium dodecyl sulfate (SDS), on the optical transmittance, thermal, and rheological properties of MC aqueous solutions.19 Two effects of SDS on a 0.03 mM MC aqueous solution were found: the salt-out and salt-in effects at low (≤6 mM) and high (>6 mM) concentrations of SDS, respectively. The salt-out effect of SDS is to bring the gelation of MC to lower temperatures, whereas the salt-in effect of SDS is to make the gelation of MC occur at higher temperatures. More interestingly, when the concentration of SDS is greater than 8 mM, SDS changes the pattern of MC gelation from a single mode to
a bimodal one. The molecular binding of SDS to MC delays the hydrophobic association of those SDS-bound MC chains but the SDS-free MC chains can undergo the hydrophobic association more early (i.e., at lower temperatures). As a result, a two-step gelation takes place.19

From the literature, we have noted that there is still a lack of studies on the effect of surfactants on MC. Especially, the effects of cationic surfactants on MC have not been extensively examined. The aims of the present work are (1) to investigate the effects of a typical cationic surfactant, cetyltrimethylammonium bromide (CTAB), on the so-gel transition of MC in aqueous solutions using micro DSC and rheology, and (2) to compare with the effects of SDS, a typical ionic surfactant, on MC to examine the effects of surfactant type and CMC. CTAB is selected because of two reasons: it is cationic and has a low CMC. The CMC of CTAB is 0.92 mM,23 which is about one-ninth of the CMC (8.1 mM) of SDS.

Experimental

Materials. A cellulose derivative, methylcellulose with a trade name of SM4000, was kindly supplied by Shinetsu Chemical Co. SM4000 has an average degree of substitution (DS) of 1.8 and a weight-average molecular weight of 310 000 determined by light scattering. The viscosity reported by the manufacturer was 4.54 Pa.s at 20 °C for a 2 wt % aqueous solution. The material was used as received. Prior to use, it was vacuum-dried at 55 °C for 24 h and kept in a desiccator at room temperature. Cetyltrimethylammonium bromide (CTAB) was purchased from Sigma-Aldrich and used as received.

Sample Preparation. Two MC aqueous solutions with concentrations of 1 wt % (about 0.032 mM) and 0.5 wt % (about 0.016 mM), respectively, were prepared by dispersing the weighed MC powder into deionized water at 70 °C and then kept in a refrigerator at about 10 °C for overnight to become homogeneous and transparent solutions. The weighed CTAB was then added into the MC solutions and thus the MC–CTAB solutions were obtained. The concentration of CTAB in the 1 wt % MC solution ranged from 0 to 0.60 wt %, while the concentration of CTAB in the 0.5 wt % MC solution varied from 0 to 0.30 wt %. All the MC–CTAB solutions were prepared with deionized water from a Millipore water purifier and stored at a low temperature (below 10 °C) before use.

Microthermal Analysis. A micro differential scanning calorimeter (VP-DSC microcalorimeter, Microcal Inc.) was used to determine the thermal properties of the MC–CTAB solutions. The sample cell had a volume of 0.516 mL. Every test included heating the sample from 10 to 85 °C and then cooling back to 10 °C at a scanning rate of 1 °C/min. This allowed us to examine the thermoreversibility of each sample. Deionized water was used as the reference. Before each test, the sample cell was cleaned thoroughly with a water baseline session to ensure a non-contamination condition.

Rheological Measurement. A fluid rheometer (ARES 100FRTN1, Rheometric Scientific) with a geometry of parallel plates of 50 mm diameter was used. The dynamic viscoelastic functions such as shear storage modulus G’ and loss modulus G” were measured as a function of temperature. To prevent dehydration during the rheological measurements, a thin layer of low viscosity silicone oil was placed on the periphery surface of the solution held between the plates.

All the dynamic viscoelastic measurements were carried out at an angular frequency of 1 rad/s. The small and constant frequency was used because the effect of frequency on the sol–gel transition is not studied in this work. More importantly, at such a low frequency, it is easy to meet the condition for linear viscoelasticity. The sample in the liquid state was first loaded on to the bottom plate of the rheometer at room temperature and tested through a temperature sweep mode, in which G’ and G” were measured during a heating process from about 20 to 80 °C. The heating rate was adjusted to about 1 °C/min, which was similar to that used in the micro DSC measurements. Large strains (>5 %) were applied before the vicinity of the sharp increase of G’ and G” to meet the minimum torque requirement that the transducer could detect, whereas after the sharp increase of G’ and G” (i.e., the sol–gel transition), the strains applied were adjusted to be below 5 % gradually to ensure that the gel like sample was tested in the region of linear viscoelasticity.

Results and Discussion

1. Effects of CTAB and CTAB/MC Ratio on Thermal Properties. The micro DSC curves on heating and cooling are shown in Figures 1 and 2, respectively, where the MC concentration in each sample is 1 wt % (or 0.032 mM). The significant changes in the thermal properties of a MC solution are observed as a function of CTAB concentration. For the endothermic peaks shown in Figure 1, three features can be identified. (1) There is only a single endothermic peak (denoted as peak 1) for each sample. (2) The endothermic peak (the peak temperature is defined as Tp) shifts to the right side (i.e., higher temperature) of the peak of the pure MC when the CTAB concentration ≥0.15 wt %, whereas it shifts the left side (i.e., lower temperature) when the CTAB concentration <0.15 wt %. (3) For CTAB ≥0.15 wt %, the endothermic peak also decreases in height and becomes broader as the concentration of CTAB increases.

However, the effects of CTAB on the cooling curves (exothermic peaks) of DSC are much different from the heating ones. As observed from Figure 2 where (a) all exothermic curves are plotted and (b) the selected curves are shown for a purpose of identifying the features, when CTAB <0.15 wt % (including the pure MC), each sample exhibits a single exothermic peak (denoted as peak 2) with a shoulder. At CTAB = 0.15 wt %, the shoulder appears as a small peak (denoted as peak 3). Peak 3 increases in height with increasing CTAB, and eventually becomes higher than peak 2. However, it is interesting to note that the peak temperatures of peak 1 and peak 2 remain nearly
independent of CTAB concentration, suggesting that the degradation mechanism of a MC gel is not changed by CTAB.

Figure 3 shows the DSC heating curves for a 0.5 wt % MC solution containing CTAB. The endothermic peak shifts to the right with increasing CTAB and at the same time the peak height decreases and broadens significantly.

On the basis of the above results, the effects of CTAB can be further analyzed and understood. For the 1 wt % MC solutions, the peak temperatures of peak 1, peak 2, and peak 3 are obtained from Figures 1 and 2, listed in Table 1, and plotted as a function of CTAB concentration in Figure 4. In Figure 4, for CTAB ≤ 0.04 wt %, the temperature of peak 1 decreases with increasing CTAB, showing a weak “salt-out” effect. On the other hand, the temperature increases with increasing CTAB from 0.04 wt %, showing a “salt-in” effect. As CMC of CTAB is 0.034 wt % (0.93 mM),\textsuperscript{23} the transition at 0.04 wt % from the salt-out effect to the salt-in one is considered to be caused by a balance between two actions: competition of water molecules with MC chains and the formation of surfactant cages through molecular binding to MC. For the first action, we propose a mechanism to explain how it could cause the salt-out effect. When the concentration of CTAB is lower than the CMC (0.93 mM), CTAB molecules are present as free unimers and able to attract water molecules. Thus, water molecules available for MC chains decrease and “water” becomes more “hydrophobic” for MC. This effect is similar to the addition of a salt-out salt like NaCl or the increase in temperature.\textsuperscript{16–18} As a result, MC undergoes the hydrophobic association at a lower temperature. However, this salt-out effect is not strong because the maximum decrease in the peak temperature is only about 2 °C at the transition point. This is due to the small CMC of CTAB.

When the concentration of CTAB is higher than the CMC (0.034 wt %), the polymer-induced micelles or mixed micellar aggregates\textsuperscript{20} are formed, and their hydrophobic cores can act

### Table 1: Peak Temperatures of DSC Curves in Figures 1 and 2 for 1 wt % SM4000 Solutions Containing CTAB

<table>
<thead>
<tr>
<th>CTAB (wt %)</th>
<th>peak 1 (°C)</th>
<th>peak 2 (°C)</th>
<th>peak 3 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>61.9</td>
<td>31.9</td>
<td></td>
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<tr>
<td>0.02</td>
<td>60.1</td>
<td>31.8</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>59.9</td>
<td>31.5</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>60.0</td>
<td>31.4</td>
<td></td>
</tr>
<tr>
<td>0.08</td>
<td>60.1</td>
<td>31.6</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>61.1</td>
<td>31.8</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>62.5</td>
<td>32.1</td>
<td>38.1</td>
</tr>
<tr>
<td>0.20</td>
<td>63.7</td>
<td>32.5</td>
<td>38.0</td>
</tr>
<tr>
<td>0.25</td>
<td>64.8</td>
<td>32.6</td>
<td>37.9</td>
</tr>
<tr>
<td>0.30</td>
<td>66.4</td>
<td>32.8</td>
<td>37.9</td>
</tr>
<tr>
<td>0.40</td>
<td>68.4</td>
<td>33.1</td>
<td>37.8</td>
</tr>
<tr>
<td>0.50</td>
<td>70.8</td>
<td>33.0</td>
<td>38.0</td>
</tr>
<tr>
<td>0.60</td>
<td>73.3</td>
<td>32.9</td>
<td>38.0</td>
</tr>
</tbody>
</table>

![Figure 2](image1.png)  
**Figure 2.** Thermal capacity \( C_p \) as a function of temperature for 1 wt % SM4000 solutions containing CTAB upon cooling at 1 °C/min.

![Figure 3](image2.png)  
**Figure 3.** Thermal capacity \( C_p \) as a function of temperature for 0.5 wt % SM4000 solutions containing CTAB upon heating at 1 °C/min.
as the comfortable "cages" for the hydrophobic groups of MC to reside. The schematic concept about the formation of surfactant cages will be shown in Figure 11 later. Since the shells of the CTAB micelles are highly hydrophilic, the formation of the surfactant cages is able to stabilize MC chains in water so that the gelation of MC becomes more difficult. In order for MC to form a gel through the hydrophobic association, the surfactant cages must be removed. A higher temperature has to be applied to destroy the surfactant cages, and as a result the so-called salt-in effect is observed. The salt-in effect is approximately a linear function of CTAB concentration within the concentration range studied.

However, it should be noted here that the true effect of salt-in is observed only when CTAB ≥ 0.15 wt %. The true effect means the real increment in the peak temperature from that for the surfactant-free MC solution. In this case, it is the increment from 61.9 °C. Before 0.15 wt % of CTAB, the salt-out effect and the salt-in effect compete each other and they cancel completely at a CTAB concentration near 0.15 wt %. The concentration of 0.15 wt % is approximately 4.4 times the CMC of CTAB.

In the cooling process, peak 2 and peak 3 (it is a shoulder at low concentrations of CTAB) are observed. Although the peak heights vary with CTAB concentration significantly, the peak positions are almost independent of CTAB concentration.

The endothermic enthalpy changes \( \Delta H \) are shown in Figure 5 as a function of CTAB concentration for the 1 wt % MC aqueous solution. Except for the few points at the low concentrations of CTAB, \( \Delta H \) decreases approximately linearly with increasing CTAB. At the highest concentration of CTAB, \( \Delta H \) becomes lower than 1/5 of that for the pure MC solution.

In Figures 1 and 3, we note that the endothermic peak shifts to the right (higher temperature) more sensitively with increasing CTAB for the 0.5 wt % MC solution than the 1 wt % MC solution. This may imply that there would be an effect of MC concentration. To verify this hypothesis, the endothermic peak temperatures are plotted against the weight ratio of CTAB/MC in Figure 6 for the 0.5 and 1 wt % MC solutions. The peak temperature for a pure MC aqueous solution has been known to be almost independent of MC concentration.\(^{15}\) This conclusion is verified again in Figure 6. However, when CTAB is added, the dependence of the peak temperature on MC concentration comes visible. It is shown in Figure 6 that the increment in the peak temperature by CTAB for one unit mass of MC is higher when the MC concentration in the aqueous solution is lower. This result can be explained by the more effective interaction between CTAB and MC when the MC concentration is lower.

2. Effects of CTAB on Rheological Behavior. Storage modulus \( G' \) and loss modulus \( G'' \) are shown in Figure 7 for the 1 wt % MC solutions with seven concentrations (≥0.05 wt %) of CTAB, where the seven curves that reach the gel plateau with modulus >100 Pa are the \( G' \) curves. Three features can be observed from the figure. (1) At low temperatures, all of the samples show a predominant liquid behavior of \( G' < G'' \). (2) For each MC–CTAB sample, \( G' \) and \( G'' \) increase with temperature rapidly, and a crossover of \( G' \) and \( G'' \) appears. After the crossover, \( G' > G'' \) is shown. In particular, \( G' \) increases by more than 4 decades to reach a plateau at high temperatures, which is much more significant than \( G'' \) (by 2 or less decades). It is believed that the sol–gel transition occurs within the temperature range for the abrupt increase in \( G' \). (3) Both \( G' \) and \( G'' \) curves shift to the right (higher temperature) with increasing CTAB, indicating the same salt-in effect as observed from the thermal properties.

The correlation between microthermal and rheological behaviors of MC has been confirmed to be very good through our previous studies on MC.\(^ {15,19} \) For the MC/CTAB solutions, an example is given in Figure 8 to show the correlation of the
Figure 8. Storage modulus $G'$, loss modulus $G''$, and thermal capacity $C_p$ as a function of temperature for a 1 wt % SM4000 solution containing 0.40 wt % CTAB.

Figure 9. Crossover temperature of $G'$ and $G''$ as a function of CTAB concentration for 1 wt % SM4000 aqueous solutions containing CTAB.

Figure 10 shows $T_{\text{DSC}}$ and $T_{\text{CP}}$ as a function of the surfactant/MC ratio in a unit of mol/mol for the MC–CTAB system and the MC–SDS system respectively. The surfactant/MC ratio with the unit of mol/mol also means the number of surfactant molecules available for one chain of MC in a given solution. Although the clouding points for the MC–CTAB system have not been measured, we believe that they are similar to the correponding $T_{\text{DSC}}$. Thus, to use $T_{\text{DSC}}$ for the MC–CTAB system will not affect our comparison with $T_{\text{CP}}$ of the MC–SDS system. In Figure 10, the effect of surfactant type is clearly shown. First, there is a similarity found between CTAB and SDS, which is the transition from salt-out to salt-in effects on MC. For both surfactants, there is a critical value below which a salt-out effect appears while a salt-in effect becomes evident.

TABLE 2: Crossover Temperature of $G'$ and $G''$ for 1 wt % SM4000 Solutions with CTAB

<table>
<thead>
<tr>
<th>CTAB (wt %)</th>
<th>Crossover temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>54.0</td>
</tr>
<tr>
<td>0.10</td>
<td>54.2</td>
</tr>
<tr>
<td>0.20</td>
<td>57.3</td>
</tr>
<tr>
<td>0.30</td>
<td>59.1</td>
</tr>
<tr>
<td>0.40</td>
<td>61.1</td>
</tr>
<tr>
<td>0.50</td>
<td>62.7</td>
</tr>
<tr>
<td>0.60</td>
<td>63.7</td>
</tr>
</tbody>
</table>

riological properties with thermal properties. It is noted here again that the endothermic peak corresponds nicely to the abrupt increase in $G'$ and $G''$. Importantly, it is observed that the temperature (61 °C) for the crossover of $G'$ and $G''$ is consistent with the onset temperature (about 61 °C) of the endothermic peak. This means that the hydrophobic association of MC leading to gelation occurs almost immediately after the dehydration of MC.

The crossover temperatures of $G'$ and $G''$, which are obtained from Figure 7, are listed in Table 2 and plotted in Figure 9 against CTAB concentration. The crossover temperature can be approximately expressed as a positive function of CTAB concentration, showing a strong effect of “salt-in”.

3. Comparison between CTAB and SDS. Recently, we have reported the effects of SDS on the sol–gel transition of MC.24,25 Three important effects of SDS have been identified: (a) the salt-out effect at SDS < CAC (critical association concentration), (b) the salt-in effect at SDS > CAC, and (c) the two-step gelation accompanied with a bimodal endothermic peak at high concentrations of SDS (≥10 mM). CAC is an important critical concentration for the so-called polymer-induced micellization.23,25 CAC is generally smaller than CMC and dependent on the polymer-surfactant interaction.24,25 For SDS in the aqueous solution of MC, we found that CAC is about 6 mM,19 whereas CMC of SDS is reported to be 8 mM in the literature.23 For comparison, we recall the thermal and rheological results on the MC–SDS system.19

From our previous studies,14,18 it has been known that the endothermic peak temperature ($T_{\text{DSC}}$) correlates very well with the clouding point ($T_{\text{CP}}$) at which the storage modulus increases abruptly. But they occur somewhat differently in an order of $T_{\text{DSC}} < T_{\text{CP}} < T_G$.18 For example, the difference between $T_{\text{DSC}}$ and $T_{\text{CP}}$ or the difference between $T_{\text{CP}}$ and $T_G$ is less than 2 °C. Therefore, one may simply use one of them to estimate the sol–gel transition temperature of MC.
200 mol/mol, the sol–gel transition temperature has decreased by about 14 °C from the pure MC solution.

Beyond the individual transition from salt-out to salt-in, both surfactants exhibit the linear behaviors of salt-in but with different strengths. If one only looks at the slopes, it would be concluded that SDS has a stronger salt-in effect than CTAB. Since the salt-in curve of CTAB is always higher than that of SDS in the range of molecular ratio (below 515) studied, however, CTAB is a stronger salt-in surfactant for MC than SDS at a given molecular ratio of surfactant/MC. Another important difference between CTAB and SDS is the concentration or the molecular ratio at which the sol–gel transition temperature of MC recovers to that of a pure MC solution. For CTAB, the recovery concentration is 3 mM (or 100 mol/mol), while the recovery concentration for SDS is 12 mM (or 400 mol/mol). Thus, it is interesting to note that the difference in the recovery concentration between CTAB and SDS is 4 times. Furthermore, it is understood that the recovery point is the critical point at which the salt-out and the salt-in effects are cancelled each other.

Another big difference between CTAB and SDS is that in the gelation process of MC, SDS causes the appearance of a bimodal endothermic peak (at SDS ≥ 10 mM)\(^9\) while CTAB still results in a single endothermic peak (see Figure 1). We consider this difference to be caused by the different binding strength of each surfactant to the polymer, MC. From the difference in CMC between SDS and CTAB, one may know that CTAB is a stronger surfactant than SDS because the former can form micelles at a lower concentration than the latter. The stronger MC–CTAB interactions allow CTAB to bind to MC chains at lower ratios of surfactant/MC, while the weaker MC–SDS interactions require SDS to bind to MC to form the surfactant cages at higher ratios of surfactant/MC. Except at very low ratios of surfactant/MC, CTAB shows the strong effect of “salt-in” on MC over the range of surfactant/MC ratios. The simple and strong binding of CTAB to MC leads to the single endothermic peaks of the MC/CTAB system.

On the contrary, the MC/SDS system shows the bimodal endothermic peaks and the two-step gelation particularly when SDS concentrations are higher than 8 mM.\(^9\) Here we use the weak binding mechanism of SDS to explain the bimodal phenomenon, which does not conflict with our previous discussion.\(^9\) At a given surfactant/MC ratio, it is reasonably considered that the number of SDS molecules bound to MC chains is much less than that of CTAB molecules bound to MC because SDS is a relatively weaker surfactant than CATB. Thus, some of hydrophobic units of MC are not bound by SDS. These unbound hydrophobic units may associate first upon heating, leading to the first endothermic peak and the first step of gelation. Subsequently, the further heating will destroy the SDS–MC binding forces (or more conveniently the SDS cages) to allow the hydrophobic association of these units of MC, resulting in the second endothermic peak and the second step of gelation.

The experimental observations by Ballerat-Busserolles et al.\(^{26}\) strongly support our above argument that CTAB is able to form a stronger polymer-surfactant complex than SDS.

**4. The Mechanism for Effects of CTAB on MC.** We have shown the thermal and rheological results for the MC–CTAB system and also compared with the MC–SDS system. Now we need to understand the mechanism for CTAB to affect the sol–gel transition of MC.

Since CTAB has a small CMC, the critical association concentration (CAC) is expected to be small or the effect of MC on CAC of CTAB is expected to be weak. Although we have observed the salt-out effect before CMC, the primary effect of CTAB is to shift the sol–gel transition of MC to higher temperatures, which is the so-called salt-in effect. The salt-in effect of CTAB is achieved through the formation of surfactant cages by molecular binding of CTAB to MC. A schematic diagram is presented in Figure 11 to describe the formation of CTAB cages and the hydrophobic association of MC after the surfactant cages are removed by heating. In Figure 11, it is proposed that the hydrophobic tails of CTAB bind to the hydrophobic units or groups of MC chains to form the surfactant cages. For this cage formation to be possible, the CTAB concentration must be higher than its CMC. The CTAB binding to MC occurs at room temperature or any temperature below the onset of the sol–gel transition. 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 CTAB to MC is strong, temperature has to be enhanced to weaken the surfactant cages and eventually destroy them to expose MC’s hydrophobic units or groups 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. The destruction of surfactant cages is a necessary precursor for MC to form a gel in the presence of CATB.

The dependence of the sol–gel transition temperature of MC on CTAB concentration can be explained by the number of surfactant cages, which is dependent on the CTAB concentration. The increased number of surfactant cages by the increased concentration of CTAB will increase the difficulty in destroying or removing the surfactant cages. A simple solution is to enhance temperature. As a result, the salt-in effect is shown. As all the endothermic peaks are single (not bimodal), we do not consider that the MC–CTAB solution has to undergo a two-step gelation process as proposed for the MC–SDS system.\(^9\) Also, the gelation mechanism of MC, which is the hydrophobic association, is not affected by the addition of a surfactant like CTAB or SDS.

**Conclusions**

In this work, the effects of a cationic surfactant, CTAB, on the sol–gel transition of methylcellulose (MC) have been
examined micro-thermally and rheologically. By gradually increasing the surfactant concentration from 0 to 0.6 wt % (16.5 mM), a transition from a salt-out effect to a salt-in one on MC is observed, which is near to the critical micellization concentration (CMC) of CTAB. Beyond the transition, the salt-in effect of CTAB is found to be a linear function of CTAB concentration. The salt-in effect is also dependent on the MC concentration: the lower the MC concentration is, the stronger the effect is. A good correlation between the micro thermal properties and the rheological properties has been obtained. The effects of CTAB have been compared with an ionic surfactant, SDS. It is found that both CTAB and SDS show the transition from the salt-out to the salt-in. Since CTAB has a much smaller CMC than SDS, however, the salt-out effect of CTAB is much weaker than SDS. CTAB is more likely to act as a strong salt-in agent for MC rather than a salt-out surfactant. Finally, a schematic diagram is proposed to explain the mechanism for the salt-in effect of CTAB. In this mechanism, the formation and destruction of surfactant cages are presented. In addition, this mechanism also explains why the gelation of MC in the presence of CTAB still has the same mechanism or pattern as a pure MC.

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