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Effects of SDS on the sol–gel transition of methylcellulose in water

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Abstract

The effects of an anionic surfactant, sodium dodecyl sulphate (SDS), on the optical transmittance, thermal, and rheological properties of methylcellulose (MC) aqueous solutions have been studied. The particular interest of this work was focused on the effects of SDS on the sol–gel transition of MC. Basically, two effects of SDS have been identified, which are 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 to occur at higher temperatures. In addition, SDS is also able to alter the pattern of gelation. Especially, when the concentration of SDS is greater than 8 mM, SDS not only delays the overall gelation of MC but also changes the pattern of MC gelation from a single mode to a bimodal one.

Keywords: Methylcellulose; Gelation; Surfactant

1. Introduction

Methylcellulose (MC) is a hydrophobically modified product of cellulose, which displays a completely thermoreversible behavior in water. Aqueous solutions of MC are able to gel in water upon heating and return back to a liquid state upon cooling. In the past decades, many studies have been carried out to examine the thermal gelation properties, the mechanism of gelation, and the gel network structure of MC using various experimental techniques [1–9].

While the gelation temperature of MC is not strongly affected by changing concentration of MC, many salts are found to be effective in altering the gelation properties of MC aqueous solutions [10,11]. Basically, two groups of salts can be classified, i.e. salt-out salts and salt-in salts. A salt-out salt can lower the gelation temperature of MC whereas a salt-in salt delays the occurrence of MC gelation. Although the gelation temperature of MC is affected linearly by the content of a salt added, the mechanism for the gelation of MC does not change with the addition of salts 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 [10,11].

We have known that a simple inorganic salt can alter the gelation behavior of MC in water [10,11]. As surfactants, especially ionic surfactants, can be considered to be made by chemically attaching a hydrophobic tail to an ion, it is interesting to know how a surfactant can affect the gelation behavior of MC in water. Anionic surfactants such as sodium dodecyl sulphate (SDS) are widely used in both industrial applications and scientific studies. SDS is well known to form micelles in water by self-assembling above its critical micellization concentration (CMC). SDS can also form the mixed micelles with polymer chains through an intermolecular binding process. After adding a surfactant, the hydrophobic association of a hydrophobically modified water-soluble polymer is expected to be affected by the interaction between the polymer and the surfactant [12–18].

Many hydrophobically modified cellulose polymers have been investigated on the polymer–surfactant interaction [19,20]. For example, hydrophobically modified hydroxylethyl cellulose (HMHEC) has been reported to interact with many surfactants [19]. Hydrophobically modified ethyl (hydroxyethyl) cellulose (HM-EHEC) [19,20] and hydroxylpropyl methyl cellulose (HPMC) [21] have also been studied. Interestingly, the interaction between surfactants and methylcellulose, the simplest form in the family of hydrophobically modified cellulose polymers, has not been found in the literature.

In this work, a commercial methycellulose is used to prepare aqueous solutions containing various concentrations of SDS,

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and the effects of SDS on the optical transmittance, thermal and rheological properties of MC solutions, especially on the sol–gel transition behaviors, have been investigated. The interesting results have been obtained and the possible mechanisms involved in these results will be proposed and discussed.

2. Experimental

2.1. Materials

A cellulose derivative, methylcellulose with a trade name of SM 4000, was kindly supplied by Shinetsu Chemical Co. Ltd, Japan. The polymer had an average degree of substitution (DS) of 1.8 and a weight-average molecular weight of 310,000 determined by light scattering. 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. Sodium *n*-dodecyl sulphate (SDS) was purchased from Sigma-Aldrich and used as received.

2.2. Sample preparation

A MC aqueous solution with a fixed concentration of 0.03 mM (about 0.93 wt%) was first 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 get a homogeneous and transparent solution. The weighed SDS was then added into the MC solution to obtain the MC–SDS solution. All samples were prepared with deionized water from a Millipore water purifier. All of the MC–SDS solutions were stored at a low temperature (below 10 °C).

2.3. Microthermal measurement

A micro differential scanning calorimeter (VP-DSC microcalorimeter, Microcal Inc.) was used to determine the thermal properties of MC–SDS solutions. Every test included heating the sample from 10 to 85 °C or higher, and then cooling back to 10 °C at a temperature scanning rate of 1 °C/min. This allowed us to examine the thermoreversibility of the 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.

2.4. Turbidity measurement

An Ultraviolet–visible spectroscopy system (Agilent 8453, UV–VS, HP Co.) equipped with a temperature controller was employed for the turbidity measurements. Deionized water was used as the reference. The sample cell was covered by a plastic cap to prevent evaporation. The turbidity measurement was then carried out at a wavelength of 500 nm, in which the sample was first heated from 20 to above 80 °C, and subsequently cooled down to 20 °C at the heating and cooling rates of 1 °C/min. The absorbance due to the sample's turbidity was recorded, and then converted to transmittance according to the Beer's Law.

2.5. Rheological measurement

The 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 of the dynamic viscoelastic measurements were carried out at an angular frequency of 1 rad/s. G' and G'' were measured during a heating process from about 20 to 80 °C. The heating rate was adjusted to be 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 linear region of viscoelasticity.

3. Results and discussion

3.1. Turbidity

Fig. 1(a) and (b) shows the optical transmittance at the wavelength of 500 nm for the 0.03 mM MC solutions

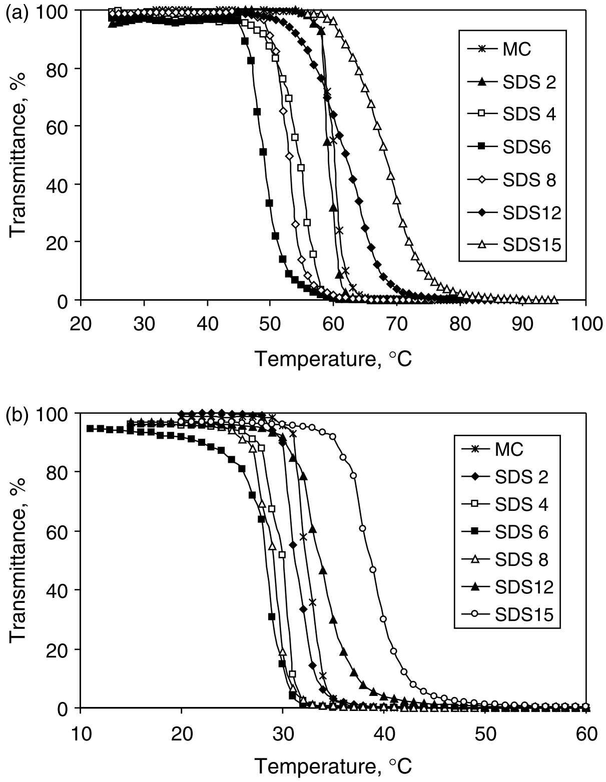


Fig. 1. Optical transmittance at a wavelength of 500 nm for 0.03 mM MC solutions containing various concentrations (in mM) of SDS during (a) heating and (b) subsequent cooling at a temperature scanning rate of 1 °C/min.

containing various concentrations (in mM) of SDS upon heating and cooling, respectively. For each solution, the heating was followed by the cooling.

As shown in Fig. 1(a), at low temperatures (≤45 °C), all of the MC–SDS solutions display a high transmittance (nearly 100%), indicating that the solutions are optically clear and the transmittance is independent of the solution composition. However, after being heated to a certain temperature, which is dependent on the solution composition, each transparent solution starts to become turbid, followed by the sharp decrease in transmittance. At the high temperatures, each sample becomes completely opaque within a narrow temperature range, and the transmittance drops to about zero, indicating the formation of a cloudy gel as further confirmed later by the rheological measurements.

Besides the general feature on the turbidity of MC solutions, the effect of SDS on the turbidity can be observed clearly from these transmittance curves. First, the starting point for becoming turbid and the ending for becoming zero-transmitting occur differently for a different concentration of SDS but they do not follow a decreasing or increscent order with increasing the concentration of SDS. For simplicity, let us take the 50% transmittance as a critical transition point at which the corresponding temperature can be defined as the clouding point or the sol–gel transition temperature. This definition is reasonable because the transmittance always decreases with temperature to reach the maximum rate approximately at the 50% transmittance. The clouding points obtained based on the 50% transmittance are plotted against SDS concentration in Fig. 6 and we will use Fig. 6 to discuss the effect of SDS in the later text.

The decrease in transmission on heating is believed to be due to the formation of large clusters or aggregates and eventually a gel network structure, which leads to the strong light scattering. It should be true that the denser a gel network formed, the lower the optical transmission is. Slootmaekers et al. [22] in their studies on the clouding behavior of carrageenan solutions and Nossal's work [23] on polyacrylamide gels proved that the spatial variations and dynamic concentration fluctuation of the polymers in the gelled state resulted in strong light scattering. In our study of MC gelation, the light scattering is considered to be caused by the hydrophobic aggregates of MC appearing at enhanced temperatures.

In the subsequent cooling process (Fig. 1(b)), the turbidity remains unchanged at high temperatures until another critical temperature, at which the opaque gel begins to dissolve, and the transmittance recovers rapidly back to the high value within a narrow temperature range. From the fact that the sample turns back to the transparent solution again after completing the thermal cycle, we may conclude that the MC gelation is thermoreversible although the cooling curve is not a mirror image of its corresponding heating one.

The outstanding hysteresis between heating and cooling indicates that the thermally induced hydrophobic dissociation is not an exact reversal of the hydrophobic association caused in the heating process. All of the MC–SDS solutions showed the complete thermoreversibility that was not changed by the addition of SDS. Thus, we may draw another conclusion that SDS does not affect the basic feature of MC gelation or in other words SDS does not alter the inherent mechanism of MC gelation, which is based on the hydrophobic association of MC chains. Similarly, we use the 50% transmittance to define the clear point (i.e. the gel–sol transition) for each transmittance curve in the cooling process and then plot it in Fig. 6.

3.2. Thermal behaviors

The thermal behaviors of MC–SDS solutions have been studied by means of micro-DSC, and the results are shown in Fig. 2. The temperature scanning rates were 1 °C/min. The relative thermal capacity C_p with a unit of cal/L °C was used after the conversion of the sample volume of 0.516 mL to 1 L.

All of the MC–SDS solutions show the endothermic behaviors. Before adding SDS, the MC solution shows a narrow endothermic peak with a peak temperature of about 60 °C, which corresponds to the sol–gel transition of MC. When the SDS concentration is lower than 8 mM (i.e. 2, 4, and 6 mM), the respective heating curve remains one single endothermic peak with the peak temperature slightly shifting to the lower temperature than the SDS-free MC solution. For example, the MC solution with 2 mM SDS exhibits a similar sharp peak as the pure MC solution, except that the peak slightly moves to the left side, indicating a weak effect of SDS on MC. This effect is a salt-out like effect because the gelation of the MC–SDS solution occurs earlier (or at a lower temperature) than the SDS-free MC solution.

With further increasing SDS concentration, the peak still slightly shifts to the left until about 6 mM but it becomes wider and more moderate, implying a stronger effect of SDS on the hydrophobic association and gelation of MC. When the SDS concentration reaches 8 mM, an obvious shoulder is observed at the higher temperature side next to the primary peak. The primary peak at 8 mM SDS does not further shift to the left and begins to shift to the right with a reduced peak

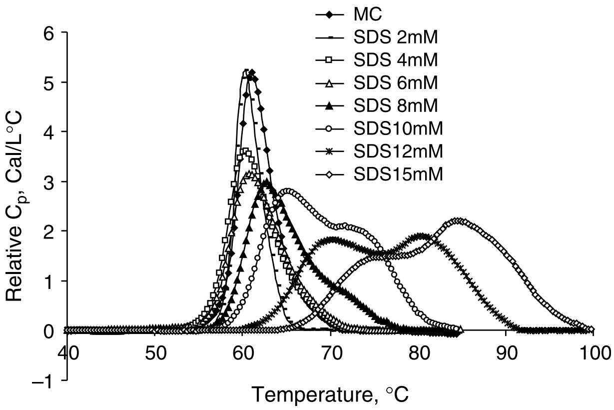


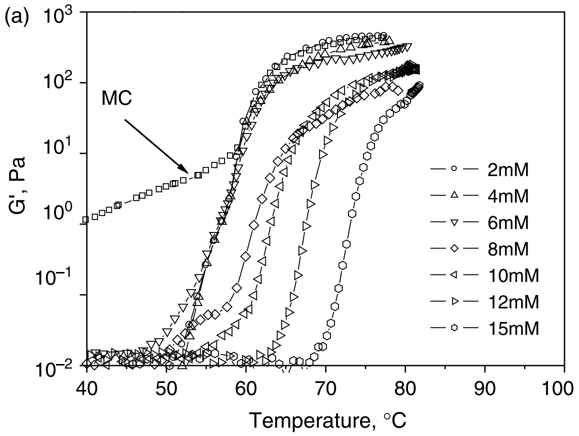
Fig. 2. Relative capacity, C_p, as a function of temperature for 0.03 mM MC solutions with various concentrations of SDS (in mM) during heating at a rate of 1 °C/min.

height. Interestingly, with increasing SDS content to exceed 8 mM, the shoulder grows to become a secondary peak whereas the primary peak shrinks in height. Eventually, the secondary peak becomes bigger than the primary peak at 15 mM SDS. The overall trend is that with increasing SDS concentration a MC–SDS solution exhibits its thermal behavior of interest over a broader range of temperature and the gelation tends to occur at higher temperatures.

3.3. Viscoelastic properties

In Fig. 3, storage modulus G' and loss modulus G'' for the 0.03 mM MC solutions with various SDS contents are shown as a function of temperature in a heating process at a heating rate of about 1 °C/min. The SDS-free MC solution is also shown in the figures. Four features can be observed from the figures. (1) At low temperatures, all of the samples show a liquid behavior of $G' < G''$. (2) For each MC–SDS sample, there is a relatively narrow range of temperature in which both G' and G'' show an abrupt increase. Especially, G' increases by more than 4 decades to reach a plateau at high temperatures, which is much more significantly than G'' (by 2 decades). It is believed that the sol–gel transition occurs within the temperature range for the abrupt increase in G'. (3) The samples containing 2, 4, and 6 mM of SDS show the similar transition curves, whereas the samples with the higher SDS concentrations (≥ 8 mM) shift to the high temperature side significantly, indicating a salt-in like effect. (4) Before the sol–gel transition region, the SDS-free MC solution behaves differently from the MC solutions with the low concentrations of SDS. That is, both G' and G'' values for the SDS-free MC solution are much larger than those of the MC solutions of the low concentrations of SDS (≤ 6 mM) in the same temperature range before the sol–gel transition. This distinctive phenomenon can be explained by a possible mechanism that the weekly entangled structure of MC chains in solution, which contributes to the high G' and G'' values as pointed out by Kobayashi et al. [24], is destroyed by SDS or unable to form in the presence of SDS. Due to the salt-out effect of SDS at the low concentrations (≤ 6 mM), the MC chains would tend to become more condensed from a looser state in the absence of SDS, so that the possibility of molecular entanglements of MC would be considerably reduced. On the other hand, if the molecular entanglements of MC are formed by the weak association of some highly hydrophobic segments of the MC chains, the binding of SDS molecules to the hydrophobic segments of MC chains would make the hydrophobic association impossible. As a result, the molecular entanglements of MC would become impossible also.

To further elucidate the effect of SDS on the viscoelastic properties of the MC solutions, the G' and G'' curves of some selected samples (SDS = 0, 2, and 15 mM) are drawn in Fig. 4. 2 and 15 mM were chosen because they were the lowest and highest concentrations of SDS used in this work. G' is already superior to G'' at the low temperatures for the SDS-free sample, whereas the SDS-containing samples behave in a way of $G' < G''$. There is a crossover point of G' and G'' each for the samples with SDS whereas no crossover point exists for the SDS-free sample. The crossover



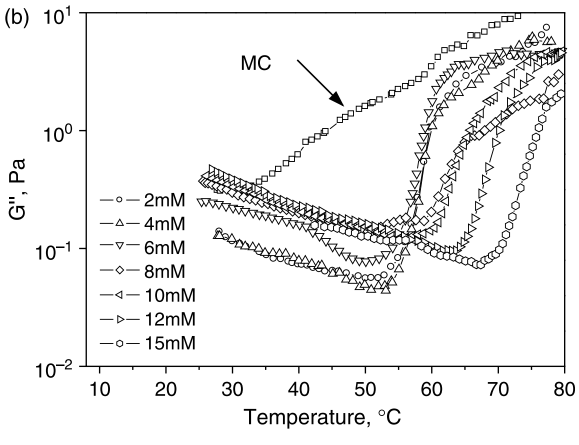


Fig. 3. Storage modulus G' and loss modulus G'' for 0.03 mM MC solutions with various SDS concentrations as a function of temperature at a heating rate of about 1 °C/min: (a) G' and (b) G''.

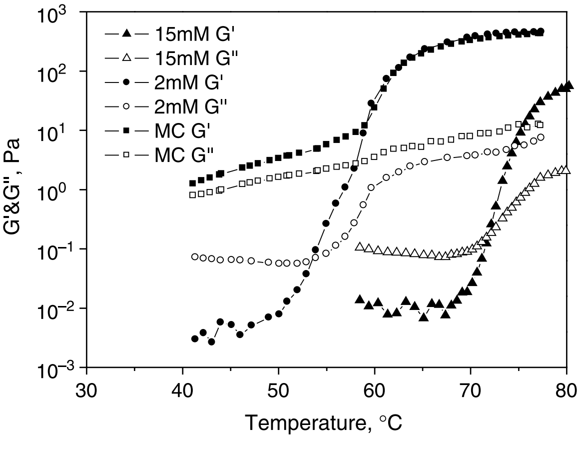


Fig. 4. G' and G'' for the 0.03 mM MC solutions with various SDS concentrations (SDS = 0, 2, and 15 mM) as a function of temperature at a heating rate of about 1 °C/min.

of G' and G'' indicates the turning point from a viscous solution to a viscoelastic gel, which is traditionally used as the sol–gel transition point. The crossover of G' and G'' shifts to the right with increasing the SDS concentration, showing a salt-in like effect or a delay of gelation by SDS.

Where gelation of MC occurs? In our previous studies on gelation of MC [1], we have found that the abrupt increase in G' in a heating process is consistent with the endothermic peak of the DSC heating curve. Thus, the consistence between the G' abrupt increase and the endothermic peak has been used to define the gel point. When the endothermic peak is not a single and narrow peak but a bimodal and broad peak, however, a question raised here is which endothermic peak (i.e. primary or secondary) can be used as an indication of the gel point. To find the answer for the question, we plotted G' and C_p against temperature in Fig. 5 for the MC solutions with various SDS concentrations from 2 to 15 mM. For a better view, six concentrations of SDS are divided into two groups and shown in Fig. 5(a) and (b), respectively.

In Fig. 5(a), where the concentrations of SDS are low (≤ 8 mM), all of the endothermic peaks are relatively narrow and no secondary peaks are clearly observed. It can be seen that the onset and offset of each C_p curve correspond to the onset and offset of the abrupt increase of G', respectively, beyond which a plateaus is reached. Thus, in this case, the endothermic peak, which is within the abrupt increasing region of G', can still be used as the gel point for each MC–SDS solution. This behavior is similar with our previous studies for the pure MC in water [1]. On the other hand, at the high contents of SDS (Fig. 5(b)), the C_p curves are featured by the broadened and bimodal peaks. The bimodal peak is an indication of a two-stepped gelation process. Taking the 10 mM SDS sample in Fig. 5(b) as an example, we can see that the most part of the sharp increasing curve of G' falls in the same region of the first peak of the C_p curve. Thus, it is reasonable to consider that the first peak at the lower temperature side is directly related to the starting of gelation. However, the gelation is not completed after the first peak because G' is still growing. Importantly, it is observed that the offset of the secondary peak is consistent with the onset of the G' plateau. If the onset temperature for the G' plateau can be considered as the ending point of gelation, the second endothermic peak is necessary for a complete gelation process. While we have known the endothermic heat, which is attributed to the fist endothermic peak, is necessary for destroying the cage-like structures of water for MC molecules to associate hydrophobically, a new question is what the secondary endothermic peak is for. In other words, why the MC–SDS solutions have to absorb heat by two steps?

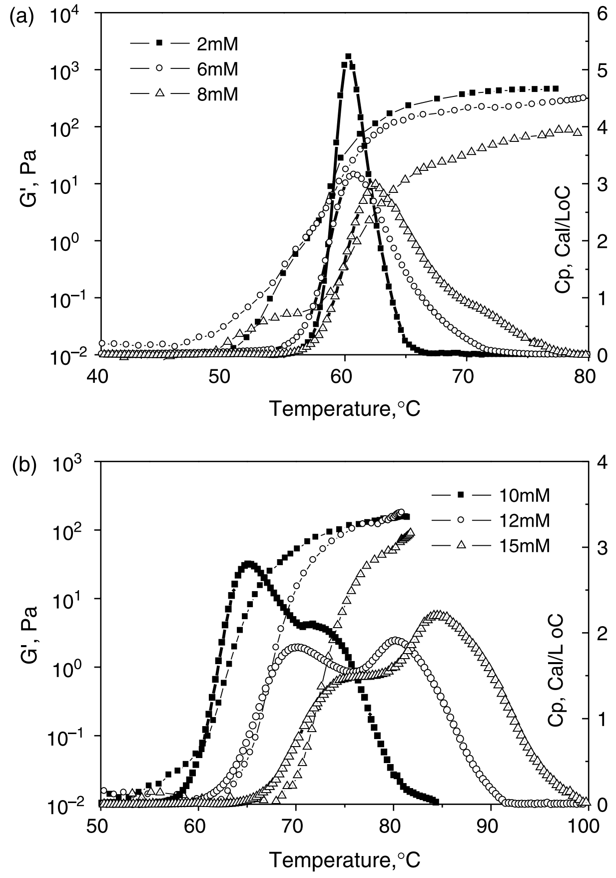


Fig. 5. C_p and G' as a function of temperature for 0.03 mM MC solutions with various concentrations of SDS: (a) 2, 6 and 8 mM; (b) 10, 12, and 15 mM.

We propose a mechanism here to explain the two-step gelation of MC in the presence of SDS. In the first step, the endothermic heat is mainly used to destroy the cage-like structures of water, which surround MC chains. Then, the hydrophobic association of MC begins and G' starts to increase. This is the same mechanism as that in a pure MC solution. However, since the binding of SDS molecules to the MC chains should be stronger than those of cage-like structures of water, a higher energy is required to remove the bound SDS molecules from the MC chains, resulting in the secondary endothermic peak. At the same time, more hydrophobic groups of MC are exposed and they then associate to form new junctions for the gel network. Eventually, all of the bound SDS molecules are removed and a complete network of MC is then formed. The two-step gelation can be also seen from the G' curves for 12 and 15 mM of SDS: there is the shoulder, followed by the continuous growth (but with a higher slope) in G'. This phenomenon becomes much clearer in the 15 mM SDS curve.

Unfortunately, due to the limitation of the rheometer, we were unable to measure G' at temperatures higher than about 82 °C so that the completed second plateau of G' could not be fully observed.

3.4. The role of SDS in affecting hydrophobic association and gelation of MC

We have shown all of the optical, thermal, and rheological results in Figs. 1–3, respectively, for the MC–SDS aqueous solutions. Based on these results, we further elucidate the role of SDS in affecting the hydrophobic association and gelation of MC.

3.4.1. Salt-out and salt-in effects

Two effects of SDS on the gelation of MC have been observed, which are the salt-out like effect at the low concentrations of SDS and the salt-in effect at the high concentrations of SDS. Regarding the two effects, the great consistence among the three types of properties (i.e. optical, thermal, and rheological properties) has been verified from Figs. 1–3. Here, let's take the optical properties as an example to discuss about the salt-out and salt-in effects of SDS. For convenience, we use the temperature at which 50% transmittance is reached to define the sol–gel transition (i.e. clouding point) on heating or the gel–sol transition (i.e. clear point) on cooling. This definition is reasonable because the decreasing rate of transmittance on heating (or the increasing rate of transmittance on cooling) reaches the maximum in the vicinity of 50% transmittance. The results are shown in Table 1 and Fig. 6.

In Fig. 6, the significant effects of SDS can be observed from the clouding-point curve, whereas the clear-point curve shows the weak effect of SDS. On heating, the salt-out and salt-in effects of SDS are shown at low (≤6 mM) and high (>6 mM) concentrations of SDS, respectively. The transition point is 6 mM, which is interesting to know because it is near the critical micellization concentration (CMC, 8 mM) of SDS in water. For the salt-out effect, one possible mechanism can be applied, which is the modification of water's hydrophobicity by SDS. In this mechanism, when the concentration of SDS is lower than the CMC (8 mM), SDS molecules are present as free unimers and able to attract water molecules so that water molecules available for MC chains decrease and 'water' becomes more 'hydrophobic' for MC. When the concentration of SDS is low, the micelles of SDS are not expected to form to surround the hydrophobic blocks of MC. Thus, MC tends to undergo the hydrophobic association at an earlier stage (i.e. at lower temperature).

The critical association concentration (CAC) of SDS is another important parameter in a polymer-SDS aqueous solution [25,26]. The CAC of a surfactant is generally smaller than its CMC. Our results in Fig. 6 may also suggest that 6 mM is the CAC of SDS in the presence of MC. Before 6 mM, SDS molecules are present as free unimers or some of them are bound to some MC chains. Beyond 6 mM, on the other hand, the SDS molecules begin to form the micelles to surround the hydrophobic groups or hydrophobic blocks of MC. This micellization is called 'polymer-induced micellization,' which is different from the micellization of SDS in pure water. In the presence of MC, the free micelles of SDS are considered not to exist when the binding of SDS to the polymer chains has not reached the saturation.

Table 1
Clouding points and clear points for 0.03 mM MC solutions with various SDS concentrations

	SDS (mM)						
	0	2	4	6	8	12	15
Clouding point (°C)	60.2	59.2	54.6	49.0	53.0	62.0	68.4
Clear point (°C)	32.3	31.3	30.1	28.4	29.2	33.7	38.7

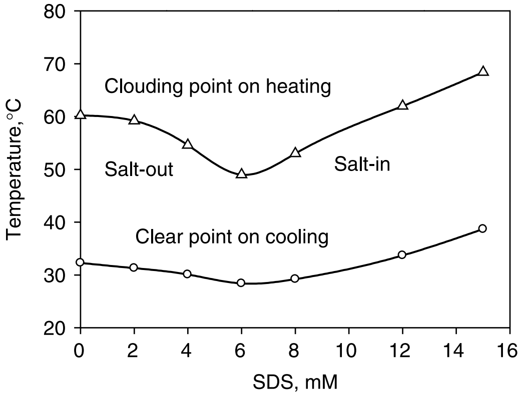


Fig. 6. Clouding points and clear points as a function of SDS concentration.

When the SDS concentration is higher than the CAC (6 mM), the polymer-induced SDS micelles are formed and their hydrophobic cores can act as the comfortable 'cages' for the hydrophobic groups of MC to reside. Since the shells of the SDS micelles are highly hydrophilic, the formation of the SDS cages is able to stabilize (or in other words, solubilize) 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 SDS cages must be removed. A higher temperature has to be applied to destroy the SDS cages, and as a result the so-called salt-in effect is observed.

3.4.2. Two-step gelation

From the thermal and rheological results shown in Figs. 2 and 3, we believe that at the high concentrations of SDS (especially SDS ≥ 10 mM), the gelation of MC occurs by two steps, which are clearly indicated by the bimodal peak of endotherm. Our discussion here about the two-step gelation of MC can be made by referring to Fig. 5(b). From Fig. 5(b), we have known that the gelation of MC begins from the onset of the first peak of endotherm at each SDS concentration but ends at the offset of the second peak of endotherm. The MC solutions with 12 and 15 mM of SDS show that G' grows with temperature by a two-step pattern, which is consistent with the corresponding C_p curve.

It is interesting to know the mechanism for the two-step gelation of MC under the influence of SDS. The possible mechanism that we propose here is that the basic mechanism for the gelation of MC is not changed by SDS, which still occurs through the hydrophobic association of MC but the gelation of MC is delayed by SDS due to the molecular binding of SDS to MC. After the water cages have been broken up by heating, MC begins to gel through the association of the hydrophobic groups or blocks of MC that have not been bound by SDS molecules or caged by SDS micelles. This is the first step of gelation. For the hydrophobic groups or blocks of MC that have been caged by SDS micelles to associate with each other, the SDS cages must be removed. The removal or destruction of the SDS cages needs a higher energy. This is why the secondary peak of endotherm is observed in the higher temperature region. As the SDS cages are broken up, more hydrophobic groups or blocks of MC are exposed and they associate to form new junctions for the gel network. As a result, the second-step of gelation is observed.

4. Conclusions

In this work, the optical (i.e. turbidity), microthermal, and rheological properties of methylcellulose (MC, $M_w = 310,000$) aqueous solutions with various concentrations of sodium dodecyl sulphate (SDS) have been measured and the effects of SDS on the sol–gel transition of MC have been investigated systematically. It is found that the effects of SDS on the turbidity of a MC solution are different, depending on the SDS concentration. The salt-out and salt-in effects are observed at the low (≤ 6 mM) and high (> 6 mM) concentrations of SDS, respectively. For example, when SDS > 6 mM, a significant delay of gelation is observed, which is the so-called salt-in effect. A critical concentration of SDS for the transition from the salt-out to the salt-in effects is found to be about 6 mM, which is a critical association concentration (CAC) of SDS. For the salt-out and salt-in effects of SDS, the consistency among the optical, thermal and rheological results has been verified.

Addition of SDS to a MC solution changes the pattern of MC gelation and a two-step gelation of MC is observed especially at the high concentrations (> 8 mM) of SDS. A bimodal peak of endotherm is observed for the two-step gelation of MC. The two-step gelation has been explained using the mechanism based on the SDS cages. The SDS cages are formed to surround the hydrophobic units of MC and these SDS cages have to be broken up at high temperatures. The first-step gelation occurs through the association of the hydrophobic units of MC, which are not caged at low temperatures by SDS, whereas the second-step gelation does through the association of the hydrophobic units of MC that are exposed at high temperatures from the SDS cages.

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